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Electrokinetic treatment of environmental matrices. Contaminants removal and phosphorus recovery.

Dissertação para obtenção do Grau de Doutor em Ambiente

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“No profit grows where is no pleasure ta'en.
In brief, sir, study what you most affect.”

William Shakespeare
The Taming of the shrew (1590)

PREFACE

This dissertation is submitted as partial fulfilment of the requirements for the Doctoral Degree in Environment and includes the results of my Ph.D. study carried out from March 2012 to July 2015 in the Faculty of Sciences and Technology, Universidade NOVA de Lisboa, with stays abroad as visiting researcher in the Department of Civil Engineering, Technical University of Denmark (DTU), Lyngby, Denmark (June-September 2012), in the Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China (October 2012-February 2013) and in the Department of Chemical Engineering, Málaga University, Málaga, Spain (May-September 2014).

The dissertation is organized as follows:

Part I includes:

Section I - provides all the summarized information regarding the problem statement, motivation and the objectives of the work.

Section II - includes the description of material as methods used during this Ph.D.

Section III - compiles the major findings of the experimental work and examines some limitations.

Section IV - outlines the main conclusions and identifies future areas of research.

Appendices

Part II includes all the papers (organized by matrix) published or submitted during this Ph.D. study:

- Couto N, Guedes P, Zhou D-M, Ribeiro AB (2015) Integrated perspectives of a greenhouse study to upgrade an antimony and arsenic mine soil – potential of enhanced phytotechnologies, Chemical Engineering Journal, 262, pp. 563-570, DOI: 10.1016/j.cej.2014.09.021.
- Guedes P, Mateus EP, Couto N, Rodríguez Y, Ribeiro AB (2014) Electrokinetic remediation of six emerging organic contaminants from soil, Chemosphere, pp. 117, pp. 124–131, DOI: 10.1016/j.chemosphere.2014.06.017.
- Couto N, Guedes P, Mateus EP, Santos C, Teixeira MR, Nunes LM, Hansen HK, Gutierrez C, Ottosen LM, Ribeiro AB (2013) Phosphorus recovery from a water reservoir - potential of nanofiltration coupled to electrodialytic process, Waste and Biomass Valorization, 4(3), pp. 675-681, DOI: 10.1007/s12649-012-9194-7.

- Couto N, Guedes P, Ferreira AR, Teixeira MR, Mateus EP, Ribeiro AB (2015) Electrodialytic process of nanofiltration concentrates - phosphorus recovery and microcystins removal, Electrochimica Acta, 181, pp. 200-207, DOI: 10.1016/j.electacta.2015.04.081.
- Guedes P, Couto N, Ottosen LM, Ribeiro AB (2014) Phosphorus recovery from sewage sludge ash through an electrodialytic process, Waste Management, 34(5), pp. 886-892, DOI: 10.1016/j.wasman.2014.02.021.
- Guedes P, Couto N, Ottosen LM, Kirkelund GM, Ribeiro AB (*submitted*) Valorization of ferric sewage sludge ashes: potential as a phosphorus source.
- Guedes P, Magro C, Couto N, Mosca A, Mateus EP, Ribeiro AB (2015) Potential of the electrodialytic process for emerging organic contaminants remediation and phosphorus separation from sewage sludge, Electrochimica Acta, 181, pp. 109-117, DOI: 10.1016/j.electacta.2015.03.167.
- Guedes P, Mateus EP, Almeida J, Ferreira AR, Couto N, Ribeiro AB (*submitted*) Electrodialytic treatment of fresh sewage sludge: current intensity influence on phosphorus recovery and organic contaminants removal.

I hereby declare that, as the first or second author of the above mentioned manuscripts, I provided the major contribution to the research and experimental work developed, to the results interpretation and the preparation of these publications submitted during the Ph.D. project. The copyright of the publications was transferred to the editors, and these articles are reproduced with permission of the original publishers and subject to copy restrictions imposed by them.

The following papers are under preparation for submission:

- Couto N, Guedes P, Fan G, Zhou D-M, Ribeiro AB, Enhanced-electrokinetic remediation of arsenic-antimony co-contaminated soil – suitability of phosphate amendment and pH control
- Guedes P, Rodrigues A, Almeida J, Couto N, Mateus EP, Ribeiro AB, Electrodialytic treatment of sewage sludge: influence on microbiological community.

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ABSTRACT

There is a need to develop viable techniques for removal and recovery organic and inorganic compounds from environmental matrices, due to their ecotoxicity, regulatory obligations or potential supplies as secondary materials.

In this dissertation, electro –removal and –recovery techniques were applied to five different contaminated environmental matrices aiming phosphorus (P) recovery and/or contaminants removal. In a first phase, the electrokinetic process (EK) was carried out in soils for (i) metalloids and (ii) organic contaminants (OCs) removal. In the case of As and Sb mine contaminated soil, the EK process was additionally coupled with phytotechnologies. In a second phase, the electrodialytic process (ED) was applied to wastes aiming P recovery and simultaneous removal of (iii) toxins from membrane concentrate, (iv) heavy metals from sewage sludge ash (SSA), and (v) OCs from sewage sludge (SS).

EK enhanced phytoremediation showed to be viable for the remediation of soils contaminated with metalloids, as although remediation was low, it combines advantages of both technologies while allowing site management. EK also proved to be an effective remediation technology for the removal and degradation of emerging OCs from two types of soil.

Aiming P recovery and contaminants removal, different ED cell set-ups were tested. For the membrane concentrates, the best P recovery was achieved in a three compartment (3c) cell, but the highest toxin removal was obtained in a two compartment (2c) cell, placing the matrix in the cathode end. In the case of SSA the best approach for simultaneous P recovery and heavy metals removal was to use a 2c-cell placing the matrix in the anode end. However, for simultaneous P recovery and OCs removal, SS should be placed in the cathode end, in a 2c-cell.

Overall, the data support that the selection of the cell design should be done case-by-case.

Keywords: Electro-processes, cell design, environmental contaminated matrices, phosphorus recovery, heavy metals separation, emerging organic contaminants removal

RESUMO

Há uma necessidade de desenvolver técnicas viáveis para a remoção e recuperação de compostos orgânicos e inorgânicos de matrizes ambientais, devido à sua ecotoxicidade, às obrigações regulamentares ou ao seu potencial como recurso secundário.

Nesta dissertação foram aplicadas técnicas de electro -remoção e -recuperação em cinco matrizes ambientais contaminadas, visando a recuperação de fósforo e/ou remoção de contaminantes. Numa primeira fase, o processo eletrocinético (EK) foi aplicado a solos contaminados com (i) metaloides e (ii) compostos orgânicos (COs). No caso do solo contaminado com metaloides, o processo EK foi acoplado a fitotecnologias. Numa segunda fase, o processo eletrodialítico (ED) foi aplicado a resíduos para recuperação de fósforo (P) e remoção simultânea de: (iii) toxinas de concentrados de membrana; (iv) metais pesados de cinzas de lamas (CL) e (v) COs de lamas de estações de tratamento de águas residuais.

Demonstrou-se que o processo EK acoplado a fitorremediação é viável para a remediação de solos contaminados com metaloides pois, apesar de baixas remoções, a técnica combina as vantagens de ambas as tecnologias permitido ainda uma gestão sustentável do local. O processo EK também se demonstrou uma tecnologia de remediação eficiente, uma vez que promoveu a remoção e degradação de COs emergentes em dois tipos de solo.

Com o objetivo de recuperação de P e remoção de contaminantes foram testados diferentes modelos de célula ED. Para o concentrado de membrana, a melhor recuperação de P foi obtida numa célula de três compartimentos (3c), mas a maior remoção de toxinas foi obtida na célula de dois compartimentos (2c), com a matriz no compartimento do cátodo. No caso das CL a melhor abordagem para a recuperação simultânea de P e remoção de metais pesados foi a utilização de uma célula 2c com a matriz no compartimento do ânodo. No entanto, para a recuperação de P e remoção simultânea de COs as lamas devem ser colocadas no compartimento do cátodo, na célula 2c.

No geral, os dados confirmam que a seleção do desenho da célula deve ser definida caso-a-caso.

Termos chave: Eletro-processos, *design* da célula, matrizes ambientais contaminadas, recuperação de fósforo, de separação de metais pesados, remoção de contaminantes orgânicos emergentes

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ABBREVIATIONS

AC	alternate current
ACN	acetonitrile
AEM	anion exchange membrane
AES	atomic emission spectrometer
ALVT	*Águas de Lisboa e Vale do Tejo*
AFS	atomic fluorescence spectroscopy
A_S	asymmetry factor
BOD_5	biochemical oxygen demand
BPA	bisphenol A
Caf	caffeine
CEC	cation exchange capacity
C18E	C18 endcapped sorbent
CEM	cation exchange membrane
DAD	diode array detector
DC	direct current
DEHP	di(2-ethylhexyl)phthalate
DM	dry matter
dSPE	dispersive solid-phase extraction
DTU	Technical University of Denmark
EC	electric conductivity
EC-JRC	European Commission Joint Research Centre
ED	electrodialytic
EDR	electrodialytic remediation
EDS	electrodialytic separation
EDX	energy dispersive spectrometry
EK	electrokinetic
EOF	electroosmotic flux
EU	European Union
E2	17β-estradiol
EE2	17α-ethinylestradiol
F	flow rate
GCB	graphitized carbon black
h	peak height
HPLC	high-performance liquid chromatography
Ibu	Ibuprofen
IEC	ion exchange chromatography

INV	invertase
ICP	inductively coupled plasma
k	retention factor or capacity factor
K_{ow}	octanol-water partition coefficient
LAS	linear alkylbenzene sulphonates
LC	liquid chromatography
LD	limit of detection
LLE	liquid-liquid extraction
LOI	loss on ignition
LQ	limit of quantification
MAE	microwave-assisted extraction
MAAD	microwave-assisted acid digestion
MBPh	oxybenzone
MC-LR	microcystin-LR
MLD	method limit of detection
MLQ	method limit of quantification
MS	mass spectrometer
NF	nanofiltration
NP	4-nonylphenol
NPC	normal phase chromatography
NPH	neutral phosphatase
PVC	polyvinyl chloride
OCs	organic contaminants
OES	optical emission spectrometer
OP	4-octylphenol
P	phosphorus
PAH	polycyclic aromatic hydrocarbons
PBDEs	polybrominated diphenyl ethers
PCB	polychlorinated biphenyls
PCDD/F	polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans
PDA	photo-diode array detector
PFCs	perfluorochemicals
PM	passive membranes
PSA	primary and secondary amine
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
QuEChERS	quick easy cheap effective rugged safe
RPC	reversed-phase chromatography
R_S	resolution
SEC	size-exclusion chromatography

SEM	scanning electron microscopy
SOC	soil organic content
SPE	solid-phase extraction
SS	sewage sludge
SSA	sewage sludge ash
SVI	sludge volumetric index
TCC	triclocarban
TCS	triclosan
TOCs	trace organic contaminants
t_R	retention time
t_M	void time
UAE	ultrasound-assisted extraction
URE	urease
USA	United States of America
USEPA	United States Environmental Protection Agency
UV	ultraviolet
Vis	visible
V_R	retention volume
V_M	void volume
w	peak width
w_b	peak width measured at the base
$w_{½}$	peak half-height
WWTP	wastewater treatment plant
XRD	X-ray diffraction
2c	two compartment
3c	three compartment

PART I

“Everything is theoretically impossible, until it is done.”
Robert A. Heinlein
(1907-1978)

Section I

1. INTRODUCTION

1.1. Soil pollution

1.1.1. Background

Soil is a complex and dynamic system that should be regarded as a non-renewable resource at a human scale. Besides contributing to the maintenance of all forms of life that occur in the terrestrial surface, soil has several others functions as providing biomass and raw materials; storing, filtering and transforming substances; and acting as a carbon and biodiversity pool, as a platform for human activities and the landscape, and heritage archive [1].

There are many threats to soil - erosion, sealing, compaction, landslides, loss of organic matter, salinization, contamination and all these promote loss of biodiversity [1]. These have proven difficult to tackle and continue to be a challenge, in line with expected future developments in urbanization, intensive agriculture and industrialization. The long-awaited binding European Union (EU) Soil Directive is still at the proposal level [2] (MEMO/13/833, 02/10/2013).

Soil contamination is defined by the European Commission Joint Research Centre (EC-JRC) as "*the occurrence of pollutants in soil above a certain level causing a deterioration or loss of one or more soil functions*" [3]. There are more than 3 000 000 potentially contaminated sites worldwide that represent a lost economic opportunity and threaten the health and ecosystem [4]. Only in Europe, there are 2.5 million potentially contaminated sites in 39 countries member of European Environment Agency of which about 45% have been identified to date [5]. In the United States of America (USA), in 2014 there were 1 739 Superfund sites [6] and more than 450 000 brownfields [7]. Developing countries like China and India have also to deal with this environmental problem, due to rapid industrialization and economic growth [8-13].

Soil contamination is a result of anthropogenic activities. In Europe the production sectors contribute more to local soil contamination than the service sectors (an average of 60% compared to 32%) [14] with waste disposal/treatment and industrial/commercial activities accounting for an average of 38 and 34%, respectively (Figure 1.1). The main sources of soil contaminants are mining and smelting, fossil fuel combustion, process and manufacturing industries (specifically metallurgical, electronics and chemical), waste disposal, land spreading of fertilizers, fungicides and other agricultural materials, atmospheric deposition from traffic and waste incineration, the spillage of liquids such as solvents or oil and practices of irrigation with contaminated waters [15].

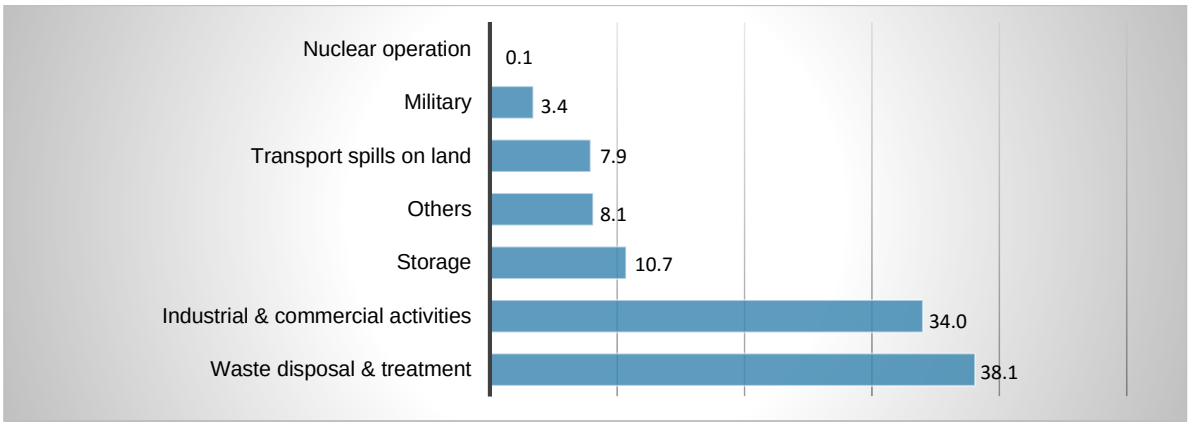


Figure 1.1. Average of key sources of soil contamination, based on 22 countries/regions [5].

The most frequent contaminants in EU affecting the solid matrix are heavy metals and mineral oils (total of 59%) (Figure 1.2). Contaminated soils can be simultaneously source and sink for pollution where, once introduced, may accumulate for a long time. Although soil contamination has been recognized as a worldwide problem, less than a tenth of the potentially contaminated sites have been remediated. This is due to the complex and challenging nature of both surface and subsurface contamination, as well as the cost and technical difficulty of dealing with contaminant mixtures, recalcitrant and persistent pollutants [16].

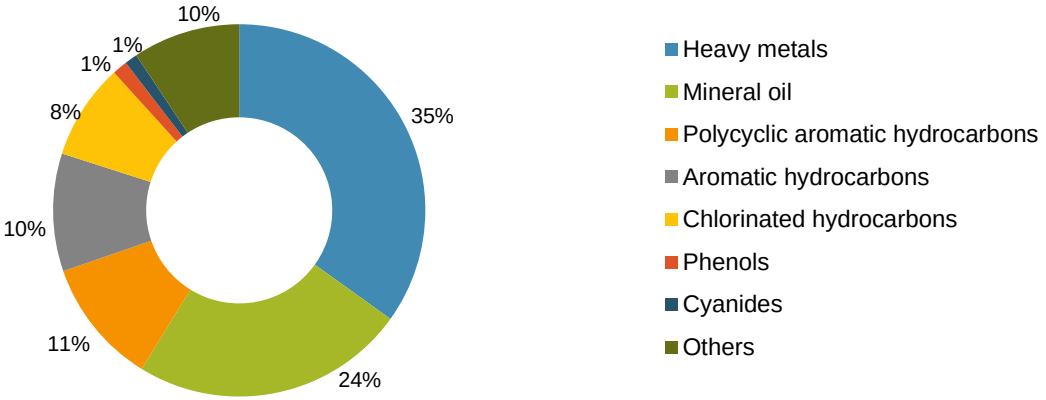


Figure 1.2. Contaminants affecting the solid matrix (soil, sludge, sediment) reported in 2011 [5].

For China, for example, a survey conducted by the Ministry of Environmental Protection and the Ministry of Land and Resources found that 16% of China's soil was polluted beyond acceptable standards, and 19.4% of China's total arable land was highly contaminated by heavy metals (2005-2013). The Environmental Protection Ministry of China reported Cd, Ni and As as the top pollutants [17, 18].

Contaminated soil continues to be commonly managed using "traditional" techniques (e.g. excavation and off-site disposal) which accounts for about one third of management practices [14]. The most common remediation technique has been the excavation of contaminated soil and its disposal in landfill (sometimes referred to as 'dig and dump'). However, increasing regulatory control of landfill operations

and associated rising costs, combined with the development of improved *ex-situ* and *in-situ* remediation techniques, is altering the pattern of remediation practices [14].

1.1.2. Mining areas

As a consequence of the technological development and global population growth, agriculture and industrial activities have intensified, leading to a considerable increase of metals in the different compartments of the environment. Open-pit mining involves the excavation of large quantities of waste rock (material not containing the target mineral) in order to extract the desired mineral ore. The ore is then crushed into finely ground tailings for processing with various chemicals and separating processes to extract the final product. In Canada on average for every ton of Cu extracted 99 t of waste material are produced (made up of soil, waste rock and the finely ground “tailings”) and must also be removed [19].

Mining industries produces tons of wastes and tailings that needs to be disposed of until further possible economically viable recovery of elements or, alternatively, gets deposited at the surface. This represents pollution sources that may directly affect loss of cultivated land, forest or grazing land, and the overall loss of production [20] and indirectly promote water pollution and siltation of rivers that will eventually lead to the loss of biodiversity, amenity and economic wealth [21]. One intrinsic problem of mining contamination is that pollution may persist for hundreds of years after the cessation of mining operations [22]. Abandoned mines are one of the most serious environmental issues faced by many European countries and Portugal is not an exception [23, 24]. In Portugal, pyrite extraction has a long tradition and represents an important industry, which has given rise to several pollution problems. Large volume of mine wastes occurs in Iberian Pyrite Belt as a result of ore extracted from metalliferous mining works during the last 100 years [25].

Soil heavy metal pollution has become a severe problem in many parts of the world [26, 27]. Unlike organic pollutants, the toxicity of metals is intrinsic to their atomic structure and they cannot be transmuted/mineralized to a total innocuous form [28]. This pollution not only degrades the quality of the atmosphere, water bodies, and food crops, but also threatens the health and well-being of other animals and human beings through the food chain [29-31]. High concentrations of heavy metal(loid)s, such as As, Cd, Cu, Pb, and Zn in soils have often been reported in a number of countries. For example, significant adverse impacts of As on human health have been recorded in Bangladesh, India, and China and it is claimed that millions of people are potentially at risk from As poisoning [32].

The geochemical baseline concentration and background level of different heavy metals in soils have been studied in various countries [33-36], being widely accepted that they represent the best approaches to establish the levels of non-contaminated soils. Different approaches have also been taken by establishing the geochemical baseline concentration of trace elements in Mediterranean soils [34, 35, 37, 38]. Most have focused on the total heavy metal content without considering the bioavailability of the different elements involved [39], even though, bioavailability constitutes the best indicator of the potential impact of these contaminants and should be taken into account [40].

The establishment of heavy metals limit or guidance values upon the existing data base for the European soils has been heavily discussed by the EC-JRC where pros and cons have been raised, which include not only sheer scientific arguments, but also economic or political aspects. At the end, the EC-JRC proposed values according to soil pH or soil texture (Table 1.1) as a starting point for further discussion [41].

Table 1.1. Ranges of heavy metal contents (*aqua regia* basis) within the soil texture classes [41]. Concentrations are expressed in mg/kg DM.

Element	Percentile*	Course	Medium	Medium Fine	Fine	Very Fine
Cd	50 P.	0.2 – 0.8	0.2 - 0.8	0.1 - 0.8	0.2 - 0.8	0.2 - 1.1
	90 P.	0.4 – 2.1	0.4 - 2.1	0.3 - 1.2	0.4 - 1.7	0.4 - 0.6
Cr	50 P.	7 - 30	17 – 35	17 - 39	19 - 58	21 - 60
	90 P.	13 - 73	26 - 124	28 - 66	27 - 85	31 - 59
Cu	50 P.	5 - 21	9 - 30	9 - 50	9 - 55	12 - 60
	90 P.	13 - 50	20 - 78	18 - 10	22 - 119	26 - 44
Hg	50 P.	0.02 - 0.10	0.04 - 0.13	0.03 - 0.17	0.04 - 0.14	0.03 - 0.13
	90 P.	0.05 - 0.40	0.06 - 0.43	0.05 - 0.35	0.07 - 0.34	0.08 - 0.27
Ni	50 P.	4 - 22	12 - 32	11 - 25	10 - 43	22 - 50
	90 P.	11 - 68	26 - 67	34 - 53	18 - 68	31 - 54
Pb	50 P.	8 - 24	10 - 42	12 - 48	14 - 45	12 - 61
	90 P.	17 - 77	19 - 124	21 - 121	21 - 116	25 - 53
Zn	50 P.	21 - 57	25 - 75	40 - 77	36 - 98	33 - 127
	90 P.	47 - 141	65 - 159	62 - 135	58 - 191	68 - 144

* stablished based on the observed 50 and 90 percentiles presented in Annex 1 of Part 2 of the report.

The significance of the chosen bases of reference has to be valued differently. It seems little target-orientated to draw conclusions about usual contents of heavy metals solely by means of pH or soil texture. Whereas the evaluation approach regarding parent material and land use points the right way [41].

1.1.3. Agricultural Areas

Sludge is the residue originated from the wastewater treatment. The EU encourages the use of sewage sludge (SS) in agriculture through the Directive 86/278/EEC as they are rich in organic matter and present other essential elements such as nitrogen and phosphorus (P) [42]. Although the nutrients in the treated sludge can improve soil fertility in the short term where nutrients are in short supply, there is a risk on the heavy metals accumulation, potentially damaging long-term fertility of the soil, as well as the risk associated with other types of contaminants e.g. organics and prions, that can endanger public health. Less than 5% of EU farmland is currently treated with SS. However, the requirements of EU legislation such as the urban waste water treatment directive and the landfill directive, which limit other disposal options for SS, may tend to increase their application to land [43].

The SS directive requires the pre-treatment of sludge before its discharge to agricultural soil to provide protection to potential receptors (soil, vegetation, animal and human) against pathogens. Without any other specifications, the directive requires biological, chemical or thermal pre-treatment. The pre-treatment must be efficient enough to prevent the application of sludge to soil from being hazardous. It requires concentration limits for certain heavy metals (Cd, Cu, Hg, Ni, Pb and Zn), and also limits the rates and longevity of application of treated sludge in areas where fruit and vegetable crops are grown and where animals are grazing.

When the sewage directive was adopted, it was based on the existing knowledge of that time. Currently, the EU recognizes the need for its revision in light of new scientific evidence about potential risks to human health, the environment and soil quality. The proposal for the revision of the directive in the "3rd draft of the working document on sludge" sets stricter limits on heavy metals depending on the pH of the soil (Table 1.2) and includes chromium in the analysis [44]. The draft suggests that each treatment plant carry out a minimum number of chemical and biological analyses regarding the quantity of sludge produced per year. The proposal also includes an analysis of some organic contaminants (OCs) that were not included in the original directive [44]. Moreover, the EU is currently reviewing the possibility of analysing halogenated organic compounds (AOX), nonylphenol (NP), linear alkylbenzene sulphonates (LAS), di(2-ethylhexyl)phthalate (DEHP), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans (PCDD/F) in sludge applied to agricultural land (Table 1.2). It should be stated that Portugal has tight legislation (Decreto Lei 276/2009, October 2) as well as several other Member States.

Table 1.2. Limit values proposed for concentration of organic compounds and heavy metals in sludge for use on land (European Commission, 2000).

Heavy metals	Limit values (mg/kg DM)	Organic compounds & Dioxins	Limit values (mg/kg DM)
Cd	10	AOX[1]	500
Cr	1 000	LAS[2]	2 600
Cu	1 000	DEHP[3]	100
Hg	10	NP/NPE[4]	50
Ni	300	PAH[5]	6
Pb	750	PCB[6]	0.8
Zn	2 500	PCDD/F[7]	100 (ng TE/kgDM)

[1] Sum of halogenated organic compounds; [2] Linear alkylbenzene sulphonates; [3] Di(2-ethylhexyl)phthalate; [4] It comprises the substances nonylphenol and nonylphenol ethoxylates with 1 or 2 ethoxy groups; [5] Sum of the following polycyclic aromatic hydrocarbons: acenapthene, phenanthrene, fluorene, flouranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1, 2, 3-c,d)pyren; [6] Sum of the polychlorinated byphenils components number 28, 52, 101, 118, 138, 153, 180; [7] Polychlorinated dibenzodioxins/ dibenzofuranes.

Regardless of the debate on the type of organic compounds and their limits in different countries, no current European guidelines exist for these compounds. Similarly, no regulation takes into account an analysis of new emerging contaminants in SS. Degradation and attenuation during wastewater and sludge treatment remove significant amounts of OCs, but many are transferred to the sludge and may

be present in residual concentrations in the dry solids depending on the initial amounts, their lipophilicity and the extent of destruction during wastewater and sludge treatment [45]. Despite increasing concerns related to potential human toxicity, evidence of adverse effects to the environment and endocrine-disrupting properties, more knowledge is required about the occurrence and detection of emerging contaminants in sludge as well as their degradability and actual risk.

During the last decades, many research projects have focused on the presence of these trace organic contaminants (TOCs) in raw sewage, treated water, and various environmental matrices [46, 47]; and in the evaluation of conventional wastewater and upgraded processes to remove some priority and emerging TOCs [48, 49]. These contaminants can be found in low concentrations in the environment, TOCs, and they often accumulate by biomagnification and bioaccumulation into biological organisms [50]. Increasing evidence indicates possible adverse impacts to the target organisms due to long-term and low-dosed exposures to pharmaceuticals in the environment, including chronic toxicity, endocrine disruption, antibiotic resistance, as well as toxic effects on reproduction of terrestrial and aquatic organisms [51, 52]. For example, it was reported that the removal of triclosan (TCS; 5-chloro-2-(2,4-dichlorophenoxy)-phenol) and triclocarban (TCC; 3,4,4′-trichlorocarbanilide) in wastewater treatment plant (WWTP) is incomplete (through mass balance studies) [53]. Consequently, TCS and TCC can be released into the environment in WWTP effluents and by land application of biosolids being regularly detected in surface waters receiving WWTP inputs [54-56], and also found in vegetables tissues (pumpkin and zucchini) [57].

The most common endocrine disrupters found in groundwater, surface water, wastewater effluents and SS are TCS; tributyltin; 17β-estradiol (E2); bisphenol A (BPA); nonylphenol (NP); the synthetic musks galaxolide and tonalide; the pharmaceuticals paracetamol, ibuprofen (Ibu), naproxen, diclofenac and fluoxetine; polybrominated diphenyl ethers (PBDEs); and perfluorinated compounds (PFCs) [45, 58-60]. Other compounds like the estrogens E2 and 17-α-ethynylestradiol (EE2) and the central nervous system active compound caffeine (Caf), have also frequently been detected at the effluents of the WWTPs [61, 62].

1.2. Phosphorus

Current population growth rates require an increased supply of staple foods and to guarantee it, a sufficient nutrient level of agricultural soils needs to be maintained by application of soil fertilizers. One indispensable nutrient for plant growth is P and phosphate rock, its primary source, is becoming progressively limited [63]. Independently of the “P peak” occurring in 50 years or in 250 years, there is general consensus that the quality of remaining reserves is in decline (both in terms of P_2O_5 content and the presence of heavy metals and other contaminants). Additionally, the phosphate layers are becoming more physically difficult to access meaning that more waste is being generated and that exploration costs are increasing [64]. For all these reasons, phosphate rock is included in the EU list of 20 Critical Raw Materials (2014).

The EU is almost entirely dependent upon phosphate imports, with China, Jordan, Morocco, South Africa and USA controlling 85% of global phosphate reserves [65]. As a consequence, EU is vulnerable to geopolitical tensions in the countries that export phosphate and to its volatile prices (as demonstrated during the 800% spike in the price of phosphate rock in 2008) [64]

Currently, 178.5 Mt of phosphate rock, equivalent to 23 Mt of P, is being mined every year [66], 90% of which is used for food production as fertilizer (approx. 82%) and feed additives (approx. 7%) [63]. Within the whole process, there are substantial losses at all stages: mining and fertilizer processing, transport and storage, application, harvest, food processing and retailing, and food consumption that can cause diverse problems such as toxic algal blooms which reduces the suitability of aquatic systems for drinking water, and recreation and thus requiring expensive treatment processes [67]. A schematic representation of the problem is presented in Figure 1.3.

Figure 1.3. Phosphorus problem scheme (adapted from [68]).

The use of P must be sustainable as it "*must ensure that all the world's farmers have sufficient access to phosphorus in the long run to produce enough food to feed humanity, whilst minimizing adverse environmental and social impacts*" [64]. This will make the full recycling of P a condition *sine qua non* for global and European food security [64].

1.2.1. Wastewater treatment plants as phosphorus sources

The water and sewage industry is at a transformation point. There is a challenge to develop and extend conventional centralized water and sewage systems on the existing planning parameters [69]. Factors including climate change impacts, changing of hydrological conditions, population growth, resource scarcity, aging infrastructure, energy constraints, economic limitations in financing large scale systems, and changing expectations for water quality (e.g. EU water directives) contribute for the need of the plants to adapt to these uncertainties. This approach is based on the idea that an environmentally, economically and socially sustainable sanitation system requires sewage to be viewed as a set of resources to be recovered, recycled and reused (water, energy, nutrients) rather than a waste product to be treated to successively higher standards before released to the environment [69].

It has been estimated that humans consume approximately 3 million t P globally [70]. So, every year, the global population excretes around 3 million t of P in urine and faeces. It has been estimated that in

Australia 8 000 t of P are discharged annually with human excreta, and 40–50% of the P that reach a treatment plant is applied to agricultural soils as biosolids [71]. In Europe, the potential production of P from urine has been estimated in 0.3 kg P *per* person *per* year [72]. The available P from human excreta is reported to also be split near equally between rural and urban areas (i.e., 1.6 million t excreted in urban environments, 1.7 million t excreted in rural environments) [73]. This split is likely to become more urban in the future because an estimated 70% of the world's population is expected to live in cities by the year 2050 [74]. If collected, the P available from human excreta could account for 22% of the global P fertilizer demand [75]. In EU, the P-content in SS from WWTP is estimated to be 400 000 tP/y from which 240 000 tP/y are not used in land spreading. If P-recycling was enforced by law the market may potentially generate 1 200 M€/y [76].

Nowadays, concepts to recover P within the wastewater treatment scheme are particularly attractive, if they promise to obtain a product which is free from contaminants and with a high quality as fertilizer [77].

The effluent of WWTPs has a large quantity of phosphate [67] and, to limit eutrophication potential of wastewaters, P removal has been in the toolbox of wastewater-treatment engineers for several decades [78], e.g. chemical or biological P precipitation. But these approaches do not recycle it as a truly sustainable product, as it is removed from the liquid phase together with various other waste products like organic chemicals [45, 79], metals [80] or even pathogens [81-83].

In a common WWTP there are several potential locations for P recovery from the liquid phase: the effluent, the supernatant liquor from side-stream treatment and the sludge liquor [84]. The theoretical recovery potential from liquid phase in common activated sludge plants is limited to <55% (Figure 1.4).

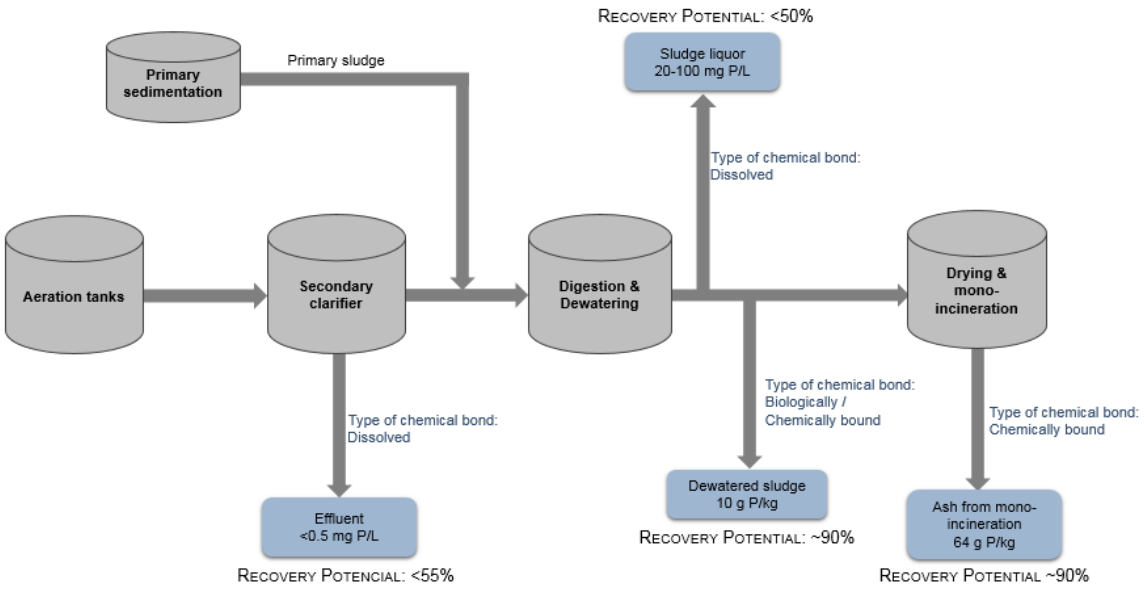


Figure 1.4. Different recovery possibilities, the recovery potential and typical concentrations of P in a wastewater treatment plant of P (related to the concentration present in the influent).

In WWTPs without P removal, 90–95% of the incoming P load is contained in the SS [77, 84]. However, direct application of treated SS is difficult not only due to the presence of heavy metals and OCs but also to the risk associated with the presence of pathogens [85], public perception, odours and/or difficulties of transport and storage. To avoid direct use of treated SS as fertilizer, a side recovery technology may be the answer and there are several potential applications aiming P recovery from SS, i.e. primary, excess and raw sludge, stabilized sludge before and after dewatering [84]. In these cases the theoretical recovery potential is significantly higher than with separation processes from the aqueous phase, approx. more 40% (Figure 1.4).

Another option is P recovery from sewage sludge ashes (SSA). These ashes are generally considered a waste material to be disposed into landfill [86] but they can also be reused as adsorbents [87], in geotechnical applications or in construction materials [88-90]. However, none of the above applications make use of the valuable P present in the SSA. The application of SSA in soils is still a controversial subject as it raises questions of toxicity that must be carefully addressed, prior to its application, due to the high levels of contaminants. Major concerns are generally about the heavy metals, which can accumulate in the soil over time, and enter the food chain or groundwater systems. These occurrences depend primarily on metal concentrations in SSA, their antecedent concentrations in the soil, their mobility from the SSA and subsequently from the soil, and their uptake by plants.

Phosphorus recovery from SSA first involves the re-dissolution of the bound P followed by its separation. The advantage of treating SSA is their high inorganic formation, which, in contrast to SS facilitates P recovery. Furthermore, the incineration of organic matter causes the enrichment of P in the ashes [84]. In this case, P recovery potential from the SSA is the same as from the SS, approx. 90% (Figure 1.4).

Taking into consideration that the increased utilization of secondary resources is an important issue, e.g. in the EU waste strategies, it makes sense to search for the upgrade of these waste matrices while recycling P. This offers the immediate advantage of avoiding the environmental impacts associated with primary production from phosphate rock, complemented with the re-use of an essential nutrient that is being wasted. For these reasons, the technologies that promote P re-use within the wastewater treatment scheme are particularly attractive.

There are already different approaches (see reviews [63, 78, 91]) which vary on the origin of the used matter (e.g. wastewater, SS and its ashes) and the type of process (e.g. precipitation, wet chemical extraction, and thermal treatment). The electrokinetic (EK) process can also be an effective technique for P recovery from these waste streams.

1.2.2. Phosphorus as a contaminant

Contaminations resultant of the inputs of P from point sources (e.g. sewage outfalls) and diffuse sources (e.g. leaching from agricultural fields) into aquatic ecosystems, cause diverse problems such as toxic algal blooms which reduces the suitability of aquatic systems for drinking water and recreation may have a negative impact on public health demanding expensive treatment processes [67]. One fundamental cause of P loading is the inefficient P use in crop production. When P fertilization exceeds its removal

by the crop, most of the surplus will remain in the soil being added to its P reserve [92]. Soils with excessive P reserves in turn pose the highest risk to the environment [93], mainly linked to the hydrological cycle, where rain events can erode the soil enriched with this element into water bodies.

The P balance (inputs and outputs) in Portugal [94] is presented in Figure 1.5 where the difference between the total annual quantity of P entering the soil and the quantity of P leaving it, based on the cycle, is showed.

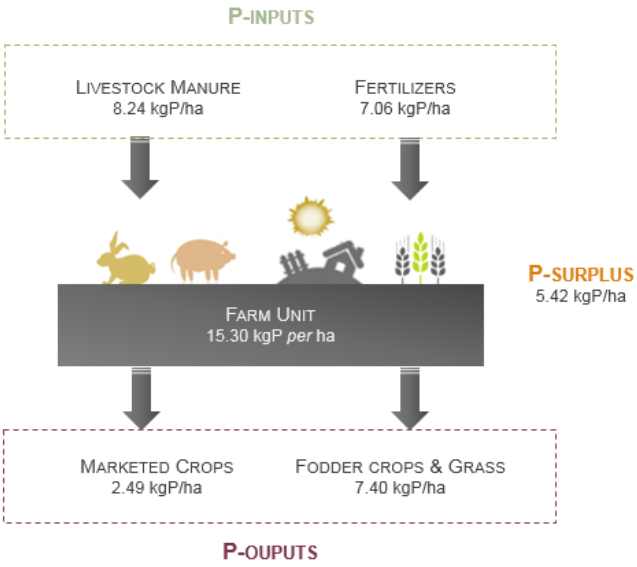


Figure 1.5. Average of total P inputs and outputs in agriculture in Portugal (2005-2008).

The analysis of the P balance in Portugal for the years between 2005 and 2008 shows a surplus of 5.42 kg P/ha. Part of this P-surplus is lost into groundwater due to leaching process or into surface water by run-off. The resultant of P-inputs from these non-point sources in the freshwater bodies may lead into an excessive algal growth in dams, lakes and rivers, reducing their suitability for drinking water, recreation use, requiring expensive treatment processes [67].

Already in 2001, it was determined that, although the trophic status is only known to 55% of the larger reservoirs in Portugal, 4% proved to be oligotrophic (total P < 10 mg P/m^3), 28% mesotrophic (10 mg P/m^3 < total P < 35 mgP/m^3) and 23% eutrophic (total P > 35 mgP/m^3) [95]. In the case of Portuguese Azores islands, from their 24 lakes, almost 50% are eutrophic, nine mesotrophic and four oligotrophic [96]. Considering that most lakes indicate a consistent increase in the level of the trophic state, the ability to succeed in combating lake eutrophication by the involvement and cooperation of local inhabitants, small factories, and farmers in reducing P discharges is very important. Also, to deal with the future economic and environmental problem of the lack of P sources, it is important to access the possibility to also recover it from surface waters.

1.3. Electrokinetic process

1.3.1. Principles overview

The electrokinetic (EK) process is based on the application of a low level current (direct or alternate; DC or AC) density, in the order of a few mA/cm and low potential gradient, in the order of V/cm [97], between suitably located electrodes (Figure 1.6). The contaminants are moved out of the matrix towards one of the electrode compartments by three main transport processes: electromigration, electroosmosis and electrophoresis. Other types of mass transport, like diffusion and fluid advection, are also present to some extent.

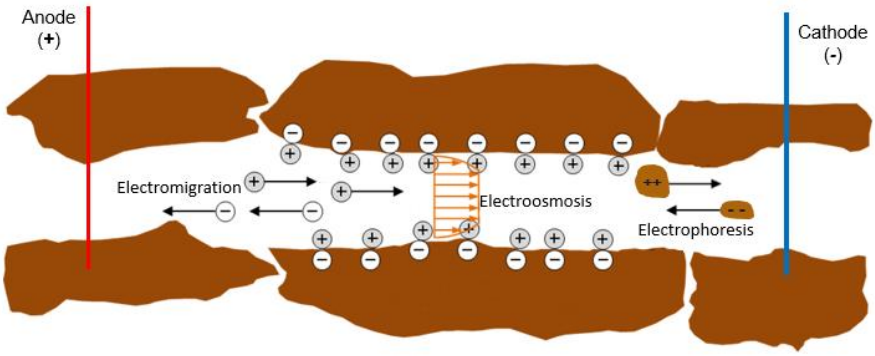


Figure 1.6. Schematic representation of the electrokinetic process (adapted from [98]).

Electromigration is the movement of ions under an applied electric field and is the main transport mechanism for soluble charged species where zeta potential may be small or even absent [99, 100]. Negative ions will move towards the anode whereas positive ions move towards the cathode, from where ions can be separated by ion exchange or chemical and electrochemical precipitation. The current efficiency of electromigration of specific ionic species is expressed as the proportion of electrical charge carried by the species of interest, relative to the amount of charge carried by all charged species in solution [100].

Electroosmosis is the mass flux of pore fluid relative to soil particles. The electroosmotic flux (EOF) normally goes from the anode to cathode because the species in the diffusive double layer are often positively charged [99]. It can be from cathode to anode when electrolyte concentration is high and the pH of pore fluid is low reversing the polarity of the surface charge [97, 101, 102]. Electroosmosis is the main mechanism for the removal of uncharged or weakly dissociated OCs [103]. The EOF component will be almost negligent in coarse sands and high plasticity clays at low water contents (electromigration will dominate). In fine sands, silts and low activity clays, at high water contents and low conductivities, electroosmotic transport would be as significant as electromigration.

Electrophoresis is the movement of charged colloids that are attracted electrostatically to one of the electrodes and repelled from the other [104]. This movement can be neglected in systems where the

solid phase is stationary (soil systems) [105] but it is very important in unconsolidated soils. If the electric current is applied to slurry, the role of electrophoresis is significant [106].

Diffusion is the movement of species under a chemical concentration gradient. In general, this is a secondary transport being only significant in some areas of soil where gradients are especially high (like areas where acid and basic fronts, or metal cations and hydroxyl ions are met).

Generally, *fluid advection*, the transport mechanism of a substance or conserved property by a fluid due to the fluid's bulk motion, resulting from head hydraulic gradients is an important contribution to global transport. In some cases, for example, when EK is applied to act as a barrier in order to avoid groundwater contamination. In this case, hydraulic gradient is an important driving force to the movement of water and, consequently, of the solved contaminants across the electrical barriers.

Electrokinetic treatment relies on several interacting mechanisms but the dominant and most important electron transfer reactions that occur at electrodes during the process is the electrolysis of water (equations 1.1 and 1.2):

$$H_2O \rightarrow 2\,H^+ + \tfrac{1}{2}\,O_2\,(g) + 2\,e^- \quad \text{(anode)} \qquad (1.1)$$

$$2\,H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2\,(g) \quad \text{(cathode)} \qquad (1.2)$$

Due to the formation of hydrogen ions in the anode an acid front is carried towards the cathode by electrical migration, diffusion, advection and pore fluid flow / hydraulic potential difference [97, 107]. Consequently there is a pH decrease near the anode and, at the same time, an increase in the pH near the cathode due to the formation of hydroxide ions [108]. The hydroxide ions are mobilized towards the anode by electromigration and diffusion. However, the transport of hydroxide ions is overshadowed by electroosmotic, advection and neutralization by the hydrogen ions (water is generated at the meeting point) [97, 101]. The development of an acid and basic front can have significant effects on the magnitude of electroosmosis as well as on contaminants solubility, ionic state and charge, and level of adsorption [104].

When the concentration of ions in the electrolytes is increased, other electrode processes may occur at the surface of the inert electrodes. For example, in the case were Me^{n+} is a metal ion with *n* positive charges, it may get deposited at the cathode surface (equation 1.3) or precipitate as oxide, carbonate and phosphates, depending pH, chemical constituents of the pore water and current flow (equation 1.4) [104].

$$Me^{n+} + ne^- \rightarrow Me \quad \text{(cathode)} \qquad (1.3)$$

$$Me(OH)_n + ne^- \rightarrow Me + nOH^- \quad \text{(cathode)} \qquad (1.4)$$

If chlorides occur in the solution, chlorine gas can be produced (equation 1.5):

$$2Cl^- \rightarrow Cl_2 \uparrow + 2e^- \quad \text{(anode)} \qquad (1.5)$$

1.3.2. Electrodialytic process

The electrodialytic (ED) process is based on the combination of the electrokinetic movement of ions and electrodialysis [109]. The general principal is very similar to EK but instead of using passive membranes (PM), ion exchange membranes are used (Figure 1.7).The anion exchange membrane (AEM) allows only passage of anions and is placed between the central compartment and the electrolyte solution at the anode end and between the central compartment and the electrolyte solution at the cathode end a cation exchange membrane (CEM) is placed, that allows only the passage of cations.

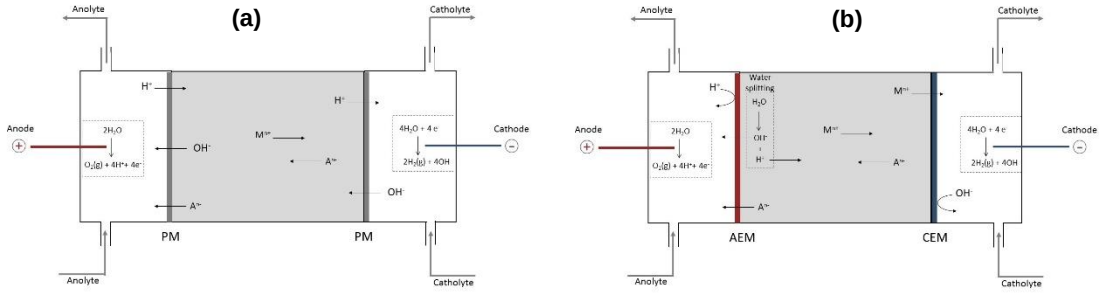


Figure 1.7. Principles of the EK (a) and ED (b) process in a 3c-cell.

The ion exchange membranes prevent the waste of current in transporting ions from one electrode compartment through the matrix into the second electrode compartment. Furthermore, the ion exchange membranes make the conditions in the central compartment less dependent on the choice of electrolyte solution than if passive membranes were used. This is beneficial especially when further concentration of the removed compounds for reuse is planned. EK enhanced remediation, namely electrodialytic remediation (EDR) presents several advantages [110]:

- application of a low-level direct current to move the charged species;
- use of ion exchange membranes allowing to regulate the direction and magnitude of the ion fluxes;
- possibility to control the degree of elements removal by adjusting the flow rates of the solutions contacting with membranes;
- the elements removed might be recycled;
- the “cleaned” matrix might be further used.

The remediation of solid waste products by the ED process started in 1992 at the Technical University of Denmark (DTU) and was patented in 1995 (PCT/DK95/00209) (Figure 1.7). EDR was originally applied to moist and consolidated soil for *in situ* treatment. Later, a faster and continuous process was developed [111-113] in which the solid matrix is suspended in a solution (most often water) and stirred, primarily to use *ex situ*. This method was used successfully for the remediation of heavy metals contaminated soils, both in soil mass containing fluid [114] or a high fluid content slurry/suspension [111-113], for the clean-up of different contaminated matrices like mine tailings, treated wood waste, different

types of ashes, SS, freshwater sediments and harbour sediments [115-122]. Recently, the new development in EDR is the two compartment (2c) electrodialytic setup, also developed at DTU and patented in 2015 (PCT/EP2014/068956), in which the anode is placed directly in the compartment in which the soil or the contaminated matrix is suspended and stirred simultaneously.

1.3.3. Application of electrokinetic processes

1.3.3.1. EK process alone and coupled with phytoremediation

The EK process has already been demonstrated to be successful and cost-effective in removing a wide variety of heavy metals in many bench- and field-scale studies [97, 108]. According to the experiments and pilot-scale studies conducted, metals such as lead, chromium, cadmium, copper, uranium, mercury and zinc, as well as PCBs, phenols, chlorophenols, toluene, trichlorethane and acetic acid, are suitable for EK remediation [108].The process has also been applied to different matrices for the remediation of both organic and inorganic contamination [110, 118, 122-128], being particularly suitable for permeability media.

Regardless of promising results, this method has its own drawbacks (Table 1.3).

Table 1.3. Advantages and limitations of electrokinetic remediation (adapted from [108]).

Advantages	**Limitations**
In situ and *ex situ* technology	Limited by the solubility of the contaminant and the desorption of contaminants from the soil matrix
Simultaneously treats inorganic and organic compounds in porous media	Acidic conditions and corrosion of the anode may create difficulties in *in situ* remediation
Use of the pH shift produced by the electrolysis of the water to effectively desorb contaminating ions	Precipitation of species close to the electrode
Potentially effective in both saturated and unsaturated soils	Necessity to apply enhancing solution
Effective method for inducing movement of water, ions, and colloids through fine-grained materials	The application of higher voltages to the soil, process efficiency decreases due to the increased temperature
Competitive in cost and remediation effectiveness compared	Removal efficiency is significantly reduced if soil contains carbonates and hematite, as well as large rocks or grave

For heavy metals removal, the EK process is highly dependent on acidic conditions as it favours the release of the heavy metal contaminants into the fluid phase. However, acidification of soils may not be an environmentally acceptable method [108]. Also, the remediation process is very time-consuming, varying from several days to a few years [108]. There are some other limitations of the proposed technique that need to be overcome like the solubility of the contaminant and its desorption from the matrix; low target ion concentration and high non-target ion concentration; requirement of a conducting

pore fluid to mobilise contaminants; and heterogeneity or anomalies found at sites, e.g. large quantities of iron or iron oxides [108].

In order to overcome the difficulties in removing some contaminants, several chemicals can be used to enhance the contaminants dissolution and transport. Another option is to develop combined remediation technologies which synergetic effect improves the mobilization and the transport of the contaminants out of the matrix. One possible solution is to combine EK with phytoremediation that is a cost effective natural option to upgrade contaminated lands by different mechanisms [129].

In phytoremedtiation, the time to perform a remediation scheme, geological and climatic determinants or toxicity may be a constraint to the success of this technique (Table 1.4). Metals may be removed by phytoextraction. In this process, plants uptake the contaminant by roots followed by its translocation and accumulation in the aboveground biomass. This biomass may be further harvested and further disposed of or reused for environmental applications (e.g. biomass production, phytomining). The level of accumulation depends on plant tissue (shoot or root) [130] and can be season dependent [131]. The accumulation levels are also related with soil type, bioavailability and plant species [130]. The mechanism of metal tolerance and detoxification enable some plant species to survive, grow and reproduce in contaminated sites [132]. In the specific case, mining areas can be rehabilitated by plants with potential to accumulate metals and/or metalloids. For example, plant species spontaneously growing in mining areas contaminated with As naturally accumulate this metalloid, mainly when in its available form [133-136].

Table 1.4. Advantages and limitations of phytoremediation (adapted from [137, 138]).

Advantages	**Limitations**
In situ and passive technique	Limited to shallow soils or where contamination is localized to the surface (<5 m) and plants are selective in metal remediation
Solar-driven and low cost	Limited practical experience and therefore not accepted by many regulatory agencies
High acceptance by the public	There is little knowledge of farming, genetics, reproduction and diseases of phytoremediating plants
Reduced environmental impact, contributes to the landscape improvement, provides wildlife for animal life	Dependent of heavy metals concentrations in the soil (can be toxic and lethal to plants) and plants may not adapt to climatic and environmental conditions at contaminated sites
Reduction of soil erosion, dispersal of dust and contaminants by wind	Toxicity and bioavailability of degradation products remain largely unknown
Reduction of surface runoff, leaching and mobilization of contaminants in soil	Treatment slower than the traditional physico-chemical techniques
Easy harvesting of the plants	Contamination may spread through the food chain if accumulator plants are ingested by animals
The harvested biomass can be economically valuable	If the plants release compounds to increase the mobility of the metals, these can be leached into groundwater
Plant process more easily controlled than those of microorganisms	The area to be decontaminated must be large enough to allow application of cultivation techniques

Besides remediation, methods for stabilizing the contaminant (phytostabilization) can also be applied for long-term remediation of As. This method limits uptake and excludes mobilization of As. The major benefit of phytostabilization is that the vegetative biomass above ground is not contaminated with As, thus reduces the risk of As transfer through food chains [139].

The coupling of EK process with phytoremediation also known as EK-assisted phytoremediation (Figure 1.8), aims at:

- use the EK field to enhance the removal of the contaminants by the plants through increasing their bioavailability (through enhancement of solubilization and/or selective mobilization) thus facilitating phytoextraction process;
- use the plant to simultaneously rehabilitate soil properties that are being changed by the presence of EK.

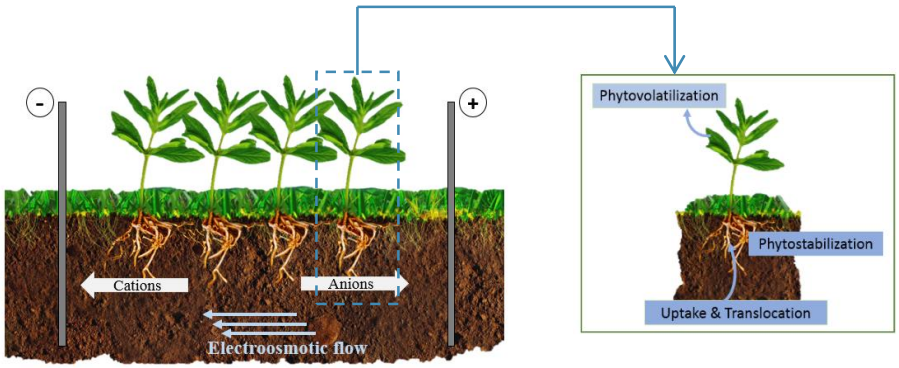


Figure 1.8. Schematic representation of *in situ* electrokinetic enhanced phytoremediation.

Phytoremediation coupled with EK process was reported to evaluate metals uptake by different plant species [140-142]. With the coupled technique a re-distribution of soil metals between electrode compartments, changes (normally increase) plant uptake compared with the absence of an electric field. Soil pH also changes, normally, decreasing in the anode compartment [140, 141] which may lead to the activation of soil heavy metals in the anode region [141]. The applied voltage may also be determinant in the efficiency of the process [141]. Literature [143, 144] reports the use of DC and AC in EK assisted phytoremediation and, in general, concludes that AC field do not promote considerable pH variation or metal redistribution, as happens with DC field. The root and shoot development may change as a reflex of the application of electric field from a slightly inhibition in the anode compartment due to soil acidification and movement of nutrient cations (e.g. Ca^{2+}) [140] to positive or negative effect depending on the applied voltage [141].

In one hand, EK process affects soil chemistry, most commonly the acidification of the soil (when a DC field is applied), and possible disappearance of most of the natural microflora due to the toxic effect of the acidic pH but, on the other hand, plant growth favours increased enzymatic and microbial activity [145]. In a study [146] carried out with the purpose of understanding the effect of electric field on physico-chemical soil properties and enzymatic and microbial activity the differences among the three soil

compartments (anode, central compartment and cathode) were reported. NO_3^-, NH_4^+, available K and P increased compared with their initial soil concentration. Basal soil respiration and microbial biomass carbon significantly increased near the anode and cathode. All tested enzymatic parameters were inhibited by DC field. DC field was the main factor affecting the soil properties but plant growth counteracted to same extent its impact on soil properties.

The efficiency and extent of phytoextraction is dependent on contaminant bioavailability for uptake, speciation and efficiency of each plant species regarding metal uptake (ability to intercept, absorb and accumulate contaminants) [129, 147-149] as plants have specific responses to metal/metalloid tolerance, accumulation mechanisms and genetic and environmental factors, e.g. as light and temperature in greenhouse conditions [150].

Phytoremediation of recalcitrant OCs in the shallow subsurface (soil and root zone) requires a symbiotic relationship between the plant and the soil microbial community [151]. Most EK-phytoremediation studies focus on treatment of heavy metal-polluted soils [145] where the electric field accumulates contaminants around the plant roots increasing bioavailability [141]. Therefore further research should focus on using EK in combination with phytoremediation to treat OCs.

1.3.3.2. Nutrient recovery from WWTP

Electrodialysis is an extraction technology which selectively separates anions and cations across an ion exchange membrane, driven by an applied electrical field between electrodes. Anions (e.g. PO_4^{3-}) move towards the anode, passing through the AEM which allows only negatively charged species to pass through while rejecting positively charged species. Through this process, cations and anions are obtained separately in concentrated solutions [152].

Contrary to most heavy metals, phosphate in the pore water exists as anionic species unless the pH is strongly acidic. Four speciation states need to be considered for P, namely H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. The corresponding acid dissociation constant (pKa at 298 K) are 2.12, 7.2, and 12. At pH below 2, phosphate dominantly exists as phosphoric acid and has no electric charge. Thus, it is unaffected by the electric field. Under alkaline conditions (pH 7), the bi- and trivalent species prevail, which implies a double or triple amount of energy to move one phosphate ion [153].

Aiming at P recovery from the SSA, it is expected that the dissolution of phosphate minerals is increased under acidic conditions due to the pH-dependent solubility of P compounds. The pH will also determine the affinity of dissolved phosphate towards variable charge surfaces and if the transport velocity in an electric field is influenced by ionic charge and thereby dependent on the chemical speciation (as referred above).

Phosphorus extraction from SSA using a EK process in a packed bed has been tested and the investigation showed that it was possible to concentrate a small part of the P in processing solutions at the anode, but also that the setup used was not feasible from the point of energy demand [153]. One option to improve the efficiency is to combine ED process with acid extraction by suspending the SSA in acid just prior to the treatment. Ideally during the process, P is concentrated in the processing solution

in the anode compartment (anolyte) and the heavy metals in the processing solution in the cathode compartment (catholyte).

Experiments conducted in an ED cell with 3 compartments (3c) showed that it was possible to separate P into one processing solution, heavy metals (Cu, Zn, Ni, Pb) into another, keeping the ash suspended in a third solution (that still contained P after 1 week of electrodialytic separation, EDS) [154]. The combination of ED in the 2c-cell setup and initial acidification of the stirred suspension with H_2SO_4 was more effective in dissolving P and separating the heavy metals [155]. This new approach uses the acid produced by electrolysis at the anode combined with initial acidification of the suspension by H_2SO_4 to promote a faster mobilization of the P and heavy metals. Mobilized heavy metals will then electromigrate from the suspension liquid and concentrate into the cathode compartment. In this setup, up to 96% of the P in the ash was dissolved after 7 days. Using the 3c-cell setup and initially suspending the ash in distilled water, resulted in 53% dissolution of the total recovered P after 7 days [155]. This shows that the 2c-cell setup is a good approach to avoid the use of mineral acids as it also avoids the precipitation of secondary minerals such as gypsum [155].

Ashes characteristics can highly influence P recovery. Comparing P recovery, in a 3c-cell, of Fe or Al rich SSA, showed that with the most Al rich SSA only a minor part of P was transported into the anolyte and the major part stayed in solution of the SSA suspension [154]. This was mostly attributed to the formation of uncharged species between P and Al. At a high acid addition (11.4 mole H^+/kg SSA) P was transported equally into the anolyte and catholyte and thus no separation was obtained in the Al rich SSA. At lower acid additions the separation was better, but here the major part of P was in the SSA suspension (in the SSA or dissolved) and separation was not obtained during the week the experiments lasted. In the Fe rich SSA the separation was better, as Fe was mainly present in insoluble particles speciation between Fe and P in the SSA suspension.

In SSA from gasification of SS where P was precipitated with Fe and Al salts, it was possible to extract up to 26% of the P. Another SSA from co-gasification of a mixture of biologically precipitated SS and wheat straw pellets showed more promising results with recoveries up to 90% using a 2c-cell.

Recovery of P from wastewater or raw sludge using 3c-cell was more effective at a low pH using anaerobically digested sludge [156]. This may be due to the hydrolysis of organic matter during anaerobic digestion and the anaerobic conditions which improved P availability and extractability. Extraction of P from highly concentrated streams was less effective in the 2c-cell setup, cathode in direct contact with the wastewater, due to a rise in pH and subsequent precipitation of P.

1.4. Analytical methodologies

The analytical process starts with the analytical question on the subject of investigation and forms a close chain to answer the question (Figure 1.9). Using a proper sampling technique a test sample is taken, adequately prepared and then measured. The measured data is evaluated on the basis of a correct calibration and then interpreted with regard to the object under study [157].

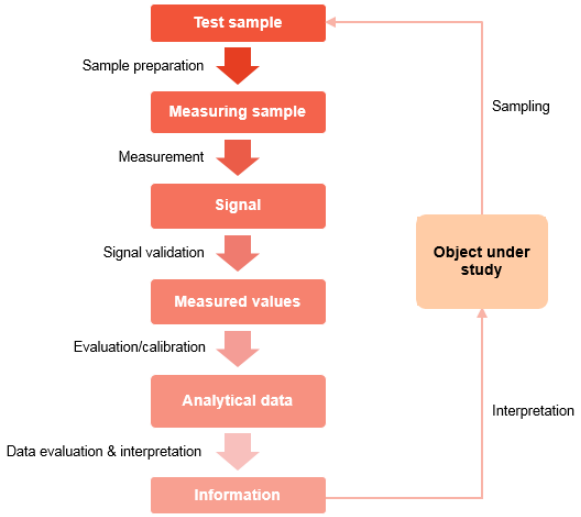


Figure 1.9. The analytical process (adapted from [157]).

In order to obtain reliable data on the concentration of the compound of interest in the samples, robust and sensitive analytical methods are thus necessary. According to various estimates, sample preparation typically accounts for 70–90% of the analysis time. Thus, a great effort is going into the development of reliable sample preparation procedures characterized by the simplicity of both operations and devices involved in the process [158]. In this section, an overview of the main analytical techniques used for the extraction and analysis of samples will be presented.

1.4.1. Microwave-assisted acid extraction

Microwave-assisted extraction (MAE) uses microwave energy to heat the sample–solvent mixture. The extraction solvents available for MAE are limited to those solvents that absorb microwaves (solvents with permanent dipole leading), although the use of solvent mixtures with and without dipoles opens up a variety of potential solvent mixtures.

The main advantages of MAE, from the green chemistry point of view are [159]:

- significantly reduced required solvent (which reduces waste generation) and decreased extraction time when compared with other extraction techniques such as Soxhlet;
- reducing the required amount of sample;
- consequent reduction of costs and the energy costs;
- the ability to process many samples simultaneously.

MAE can be conducted with open vessels or closed vessels. In the latter devices, up to 12 extraction vessels can be irradiated simultaneously. A schematic representation can be seen in Figure 1.10.

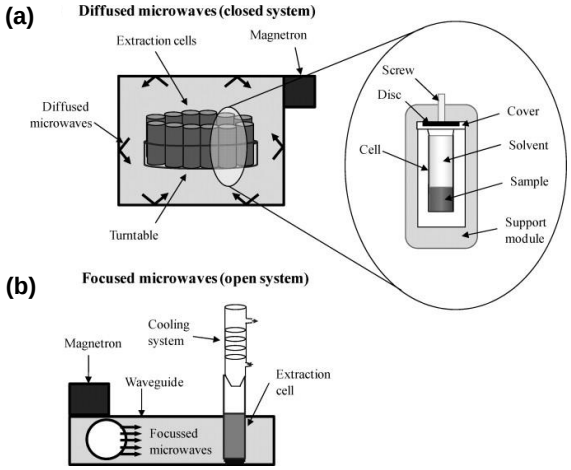


Figure 1.10. Schematic view of devices for (a) pressurized and (b) focused MAE [159].

In the specific case of heavy metals, microwave-assisted acid digestion (MAAD) using various mineral acids (e.g. HCl, HNO_3, HF) can be carried out based on some reference methods. For example, the United States Environmental Protection Agency (USEPA), in its method 3051, proposes the use of MAE for the extraction of heavy metals from solid matrices such as sediments, sludges, soils and oils [160].

1.4.2. Ultrasound-assisted extraction

Ultrasound-assisted extraction (UAE) is an advantageous alternative to conventional methods such as Soxhlet extraction as it is inexpensive, simple, and an efficient extraction technique. Ultrasound energy has been widely used for the leaching of organic and inorganic compounds from solid matrices. The enhancement in extraction is mainly attributed to the effect of acoustic cavitations produced in the solvent by the passage of an ultrasound wave [161]. Cavitation is the formation of microbubbles in a liquid when a large negative pressure is applied to it. These bubbles grow to an unstable size collapsing violently which releases an intense local energy with important chemical and mechanical effects. During bubble collapse instantaneous temperatures of several thousand degrees and pressures in excess of 1000 atm is generated [162]. Ultrasound also exerts a mechanical effect, allowing greater penetration of solvent into the matrix, increasing the contact surface area between the solid and liquid phase. As a result, the solute quickly diffuses from the solid phase to the solvent [161].

In the specific case of organic compounds extraction some reference methods are also based on the power of ultrasound. For example, the USEPA, in its method 3550, proposes the use of UAE for the extraction of organic compounds at low concentration levels from solids such as soils, sludge and wastes [163]. UAE has the potential to fulfil the requirements of a sensitive and reliable method as it [164]:

i. provides an efficient contact between the solid matrix and the solvent, usually resulting in a greater extraction of analyte;

ii. reduces the extraction time and the volume of organic solvent required for an efficient extraction when compared with other extraction techniques such as Soxhlet or liquid-liquid extraction (LLE);
iii. it is possible to select the solvent or solvent mixture that allows the maximum extraction efficiency and selectivity;
iv. a wide range of sample sizes can be used;
v. several extractions can be performed simultaneously;
vi. it is a highly reproducible and effective technique, and no specialized laboratory equipment is required;
vii. the equipment for ultrasonication is very simple, easy to operate and relatively cheap.

The principal drawback associated with the use of UAE for organic compounds extraction, is sonochemical degradation. As a result of cavitation, extreme temperatures and pressures can be developed locally within the bubbles during their collapse and theses bubbles operate as hot spot microreactors [162]. It has been suggested that, during UAE, the solvent can dissociate and the resulting radicals can react with the analytes [165]. For example, water may dissociate within the cavitation bubble to produce $HO^{\bullet}$ and $H^{\bullet}$ radicals that migrate towards the interface with the bulk solution [164] being very important to optimize the water content of the extraction solvent.

1.4.3. Solid phase extraction

Solid Phase Extraction (SPE) is a very “popular” technique currently available for fast and selective sample preparation. Due to its high versatility, the SPE procedure is used for many purposes, such as purification, trace enrichment, desalting, derivatization and class fractionation. The principle of SPE is similar to that of LLE. It involves partitioning between a liquid (sample matrix or solvent with analytes) and a solid sorbent phase. However, instead of two immiscible liquid phases (LLE) SPE involves partitioning between a liquid (sample matrix with analyte or solvent) and a (absorbent) solid phase. The general procedure is based on 5 steps:

i. Choosing the adsorbent;
ii. Conditioning and re-equilibration;
iii. Addition of the sample (enrichment);
iv. Remove interference (washing step);
v. Eluting the compound of interest.

There are several SPE phases commercially available. Reverse-phase, normal phase or mixed-sorbent SPE have been reported in column or cartridge format for clean-up purposes. In reverse phase SPE (C18, C8 and polymeric such as OASIS) the retention mechanism is the interaction of non-polar groups of the analytes of interest and non-polar functional groups of the adsorbent through the Van der Waals force. This interaction is interrupted by solvents having non-polar character which therefore are used as eluents of analytes. More polar adsorbents are used for normal phase silica $(SiO_2)_x$, alumina (Al_2O_3), magnesium silicate $(MgSiO_3)$ or Florisil. Polar adsorbents are used to remove matrix interferences from

organic extracts of solid matrices. A mixed-sorbent is chemically designed to have multiple sites on a single particle retention. These sites exploit different retention mechanisms by incorporating chemically different ligands in the same sorbent. For example, adsorbents containing hydrophobic alkyl chains and the cation or anion exchange sites on the same adsorbent particle. Mixed-sorbents exploit the interaction with different functional groups in a single analyte or different analytes in multiple functional groups.

After selecting the sorbent, the cartridge is conditioned. Conditioning involves the addition of a solvent in order to remove impurities and activate the solid phase (Figure 1.11). Usually, this step is performed with the eluting solvent. After, the matrix solvent is passed through the cartridge to promote re-equilibrium. This step helps to put the cartridge with the solvent composition and pH environment compatible with that of the sample solution thus avoiding undesirable chemical changes when the sample is applied [166].

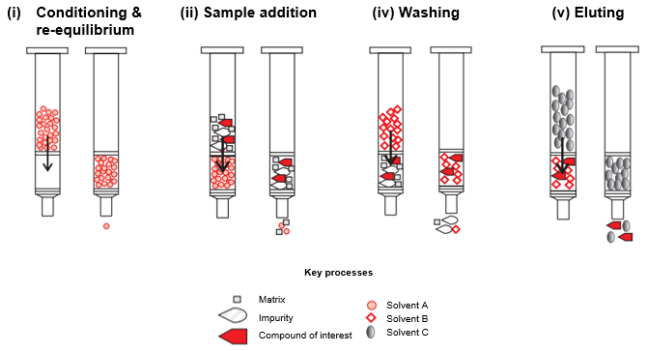


Figure 1.11. Schematic representation of SPE method (adapted from [167]).

The sample solution is then passed through the cartridge with the object of retaining the analytes of interest. The sample size must be selected so as to be well within the capacity of the sorbent bed for whichever components are to be retained (breakthrough volume) and the flow rate of the solvent should not be excessive (normally no more than 10 mL/min) otherwise retention efficiency will be impaired or separations incomplete [166]. After, the cartridge is washed. This step is necessary to remove all of those components not retained by the sorbent during the retention step and which may remain trapped in the interstitial solvent. Finally, elution is carried out to recover the retained analytes [166].

1.4.4. QuEChERS method

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method was firstly introduced by Anastassiades *et al.* [168]. QuEChERS was developed using a method of extraction of pesticides in fruits and vegetables, along with the cleaning method that eliminates sugars, lipids, organic acids, sterols, proteins, pigments, and excess water. This technique offers a user-friendly alternative to traditional LLE and SPE. The QuEChERS method is a two-step process: extraction and clean-up (Figure 1.12). In the first stage, the homogenized samples are extracted and distributed using an organic solvent

and the salt solution. Then, the supernatant is removed and cleaned again using dispersive solid-phase extraction (dSPE). The dSPE is based on the addition of the sorbent material into an extract aliquot to remove the matrix interferences, which is then separated from the extract bulk by centrifugation. In this way, dSPE avoids passing the extract through a SPE column, using a much smaller quantity of sorbent and solvent, saving time and labor [169].

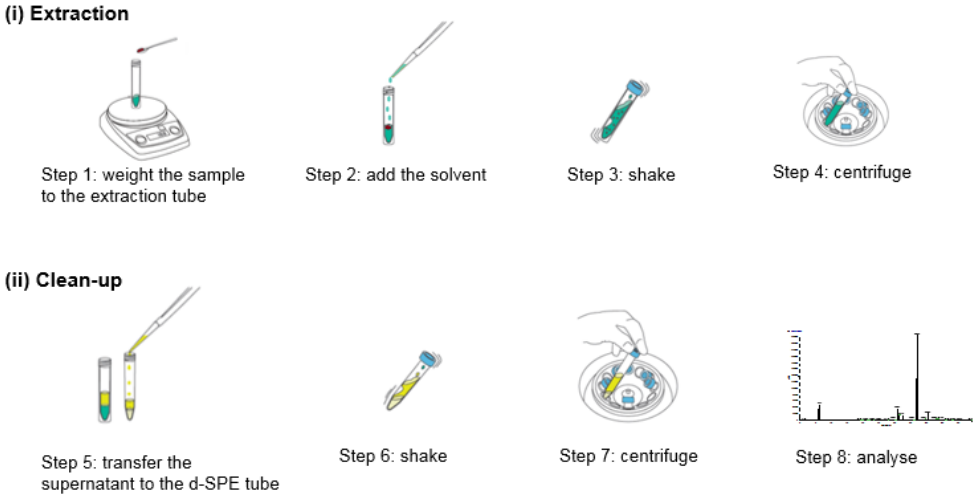


Figure 1.12. QuEChERS procedure (adapted from [170]).

Its effectiveness depends on the properties of the analyte, composition of the matrix (interferents), equipment, and analytical technique available in the laboratory [171]. Two differing standard exist with regard to the buffer type: the American standard AOAC [172], which involves the use of an acetate buffer; and European Standard EN15662 [173], which involves the use of a citrate buffer. The salts and adsorbents used in the dSPE kits are:

- Magnesium sulfate ($MgSO_4$) - removes excess water from the sample;
- Primary secondary amine (PSA) - removes organic acids, fatty acids, sugars and anthocyanin pigments from the sample;
- C18 endcapped sorbent (C18E) - removes fats, sterols, and other non-polar interference from the sample;
- Graphitized carbon black (GCB) - removes the pigment of the sample, but not for use with planar pesticides.

The QuEChERS method is popular especially for the determination of a wide range of compounds, mainly pesticides in different food matrices, due to its simplicity, low cost, susceptibility to high performance and high efficiency with a minimum number of steps [168, 174, 175]. The method is also applicable to the analysis of other class of compounds, including pharmaceuticals, mycotoxins, and polycyclic aromatic hydrocarbons, in a wide variety of complex environmental matrices [175].

The choice of solvent(s) is one of the most important decisions in any extraction. There are many aspects that have to be considered. Which, including: the ability to cover the desired analytical range

(from polar to nonpolar compounds); selectivity during removal; partition and cleaning; Achieving water separation; susceptibility to chromatographic separation techniques; cost; safety; environmental impact; and management issues (e.g., ease of evaporation). Acetonitrile (ACN) is the most commonly used in QuEChERS due to its ability to easily separate the water after the addition of a suitable mixture of salts ($MgSO_4$ and NaCl).

1.4.5. Chromatography

Chromatography has been defined as a separation process that is achieved by the distribution of substances between two phases, a stationary phase and a mobile phase. Those solutes that are preferentially distributed in the mobile phase will move more rapidly through the system than those preferentially distributed in the stationary phase. Thus, the solutes will elute in order of their increasing distribution coefficients with respect to the stationary phase [176].

1.4.5.1. Basic terms and concepts

a) *Retention and void time*

Retention time (t_R) is the time between the sample injection and the peak maximum. The retention time of an un-retained component or the first baseline disturbance by the sample solvent is called the void time (t_M, or hold-up time).The adjusted retention time, t_R' is equal to ($t_R - t_M$), i.e., the time the solute resides in the stationary phase stationary phase [166, 177].

b) Peak height and width

The solute peak has both a peak width (w) and a peak height (h) (Figure 1.13). The peak width is usually measured at the base (w_b) or at the peak half-height ($w_{½}$) [166, 177]. Two tangent lines are drawn from the steepest inflection points of the peak. The distance between the two points at which the two tangents intercept with the baseline is w_b [177].

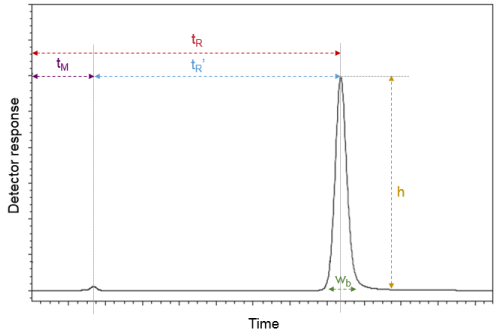


Figure 1.13. A chromatogram showing retention time (t_R), void time (t_M), peak width (w_b), and peak height (h) (adapted from [177]).

c) Retention, void volume

The retention volume (V_R) is the volume of mobile phase needed to elute the analyte at given flow rate (F), and is calculated by equation 1.6. The void volume (V_M) is the total volume of the liquid mobile phase contained in the column (also called hold-up volume), being calculated by equation 1.7. It is the volume of the empty column minus the volume of the solid packing. Note that V_M is the sum of the intra-particle volume and the interstitial volumes inside the pores of the solid support [166, 177].

$$V_R = t_R \times F \quad (1.6)$$

$$V_M = t_M \times F \quad (1.7)$$

d) Retention factor

The retention factor or capacity factor (k) is the degree of retention of the sample component in the column [166, 177]. k is defined as the time the solute resides in the stationary phase (t_R') relative to the time it resides in the mobile phase (t_M). Basically in can be calculated by equation 1.8.

$$k = \frac{t_R - t_M}{t_M} \quad (1.8)$$

e) Asymmetry factor

Very few peaks are perfectly Gaussian. For that reason the asymmetry of a peak must be quantified by the asymmetry factor (A_s) (Figure 1.14).The A_s is used to measure the degree of peak symmetry and is defined at peak width of 10% of peak height [166, 177]. The two areas A and B allow the calculation of the asymmetry factor (equation 1.9).

$$A_s = \frac{B}{A} \quad (1.9)$$

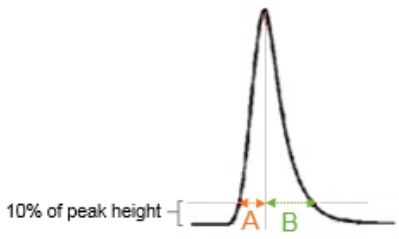


Figure 1.14. A diagram showing the calculation of peak asymmetry (A_s).

f) Resolution

Resolution (R_s) is a measure of the degree of separation of two adjacent analytes (Figure 1.15). R_s is defined as the difference in retention times of the two peaks divided by the average peak width (equation

1.10). Since peak widths of adjacent peaks tend to be similar, the average peak width is approximated by one of the peaks weights.

$$R_s = \frac{t_{R2} - t_{R1}}{\left(\frac{w_{b1} + w_{b2}}{2}\right)} = \frac{\Delta t_R}{w_b} \quad (1.10)$$

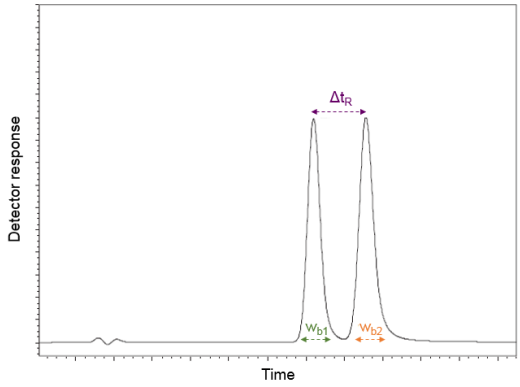


Figure 1.15. Representation of chromatographic resolution (adapted from [177]).

It should be noted that R_s = 0 indicates complete co-elution or no separation; R_s = 0.6 indicates that a shoulder is discernible or a slight partial separation; R_s = 1 indicates that a partial separation and is the minimum separation required for quantitation; R_s = 1.5 indicates baseline separation [177].

1.4.5.2. High-performance liquid chromatography (HPLC)

The aim of liquid chromatography (LC) is to separate compounds in a liquid sample using a liquid phase [177]. The main components of this system, represented in Figure 1.16 are the solvent reservoir, pump, loop injector as injection port, guard column and analytical column, detector and the computer that records the chromatogram and in which the integration is performed [166].

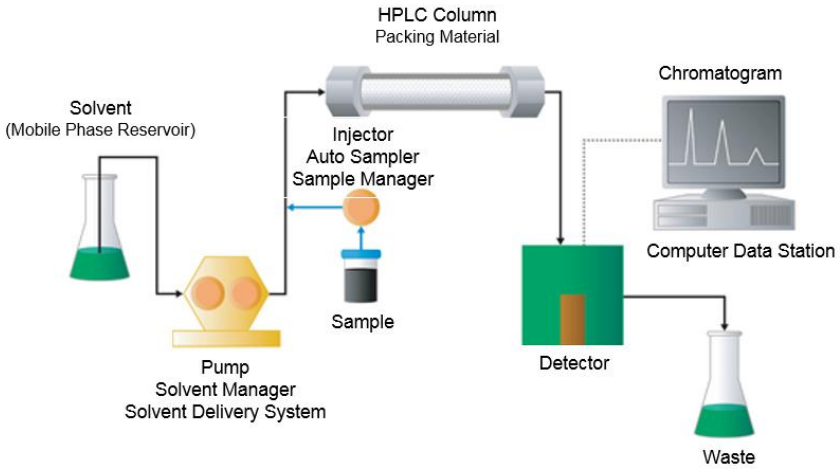


Figure 1.16. Schematic view of the different components of a HPLC system (from Waters [178]).

There are the four major separation modes of HPLC: size-exclusion chromatography (SEC), ion exchange chromatography (IEC), normal phase chromatography (NPC) and reversed-phase chromatography (RPC). The SEC separation mode is solely based on the analyte molecular size. The IEC separation mode is based on the exchange of ionic analytes with the counter-ions of the ionic groups attached to the solid support. The other two modes are based on polarity. In the NPC the polar compounds in the mixture will be more retained by the polar column (typically silica or alumina) phase than non-polar compounds will. The RPC is the most common separation mode. In this mode, the silica is modified to make it non-polar by attaching long hydrocarbon chains to its surface, typically with either 8 or 18 carbon atoms in them, and a polar solvent is used, e.g. water (Figure 1.17). In this case, the non-polar compounds in the mixture will be more retained to the stationary phase (due to attractions with the hydrocarbon groups, van der Waals dispersion forces) than the polar compounds. The polar ones will therefore pass more quickly through the column [166].

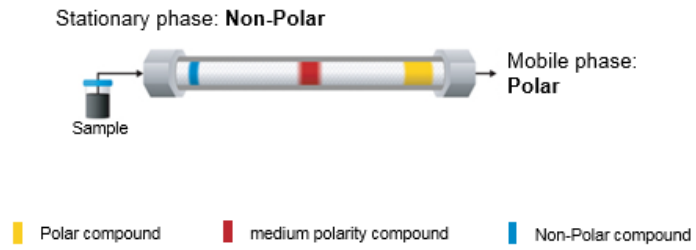


Figure 1.17. Scheme of the principles of the reversed-phase chromatography (adapted from [179]).

After passing the column, an HPLC detector measures the concentration (or mass) of eluting analytes by monitoring one of their inherent properties. There are several HPLC detectors being the most common the Ultraviolet-Visible (UV-Vis) absorbance detector since most analytes of interest (e.g. pharmaceuticals) have UV absorbance [177]. Absorbing species in the range 190–800 nm and their response is linear with concentration, obeying the Beer-Lambert law (equation 1.11):

$$A = \varepsilon \times b \times c \qquad (1.11)$$

where, A is absorbance, ε the molar absorptivity, b the path length and c the concentration.

An UV-Vis detector consists of a deuterium lamp (UV region) and a tungsten lamp (visible region), a monochromator and a small flow cell. A monochromator consists of a movable grating or prism that allows the selection of a specific wavelength to pass through the exit slit. A dual-beam optical design is common. Here the light source is split into a sample and a reference beam, and the intensity of each beam is monitored by a separate photodiode. Only the sample beam passes through the sample flow cell. They are not appreciably flow or temperature sensitive, have a wide linear range and good but variable sensitivity [166].

1.5. Motivation and Objectives

There is a need to develop new solutions for the remediation of both organic and inorganic pollutants in contaminated environmental matrices, both due to their ecotoxicity and regulatory obligations to soundly dispose or eliminate these contaminants.

The main research objective of this Ph.D. study was to *dig the process* and find out the applicability of the EK process as remediation and/or separation technique. For that, the process was applied to matrices based on soil and water (Figure 1.18), according to the undergoing projects.

The electro –removal and –recovery, by means of EK and ED processes, were applied as main treatment techniques to five different contaminated matrices (Figure 1.18). In a first phase, the EK process was carried out in soils for (I) metalloids and (II) OCs removal. In the case of metalloids, the EK process was additionally coupled with phytotechnologies. In a second phase, the ED process was applied to wastes aiming P recovery and simultaneous removal of (III) toxins from membrane concentrate, (IV) heavy metals from SSA, and (V) organic compounds from SS.

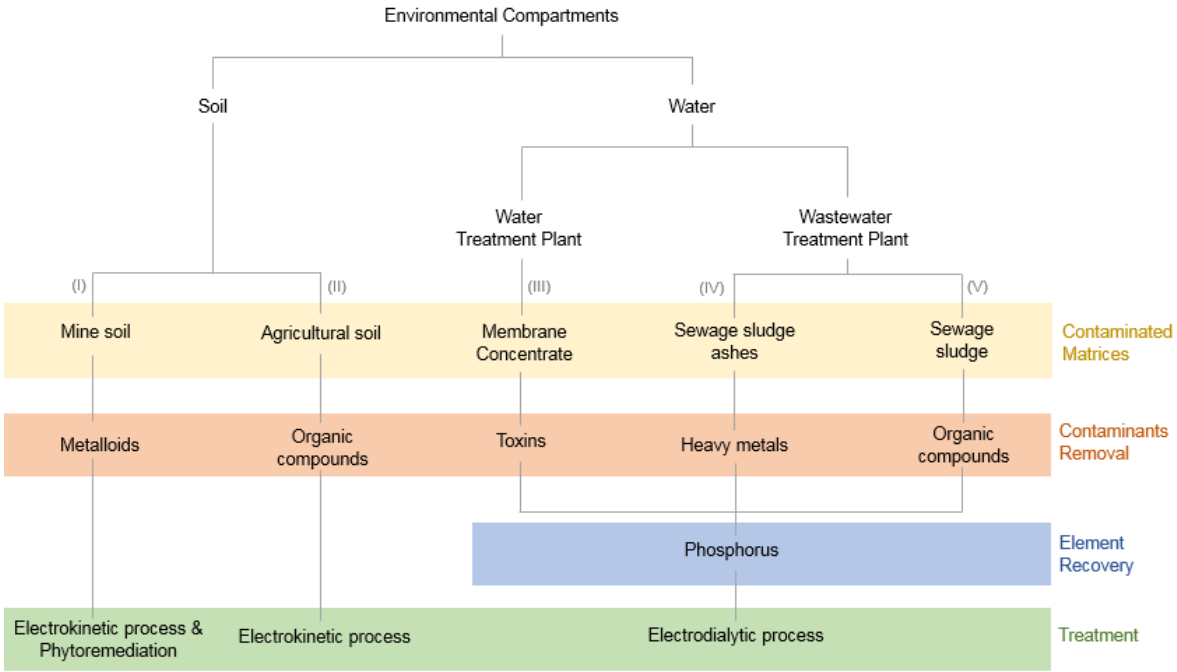


Figure 1.18. Experimental work flow diagram.

In order to pursue the main objective, other goals were appointed and pursued, namely:

- develop and test methodological and analytical approaches for determining the studied OCs in solid (soil and sewage sludge) and liquid (electrolyte and effluent) matrices;
- analyse and understand the degradation mechanism of the OCs during the EK process;
- identify the major biological changes that occur in the sewage sludge after the application of EK.

1.5.1. Study objects background

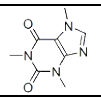
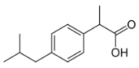
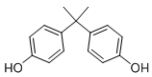
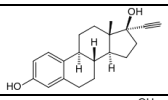
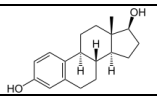
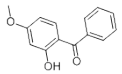
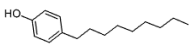
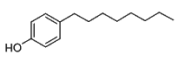
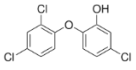
In order to fulfil the Ph.D. objectives the following studies were conducted:

a) Development of analytical methods for organic contaminants determination

The aim of this work was to develop analytical methods for the determination of the selected OCs under study.All analytes were selected after literature survey among the compounds most frequently detected in WWTP (Appendix 1, page 145). Three criterions were followed (i) compounds considered as emerging; (ii) that present different physico-chemical characteristic (e.g. solubility, octanol-water partition coefficient); and (ii) that could be analysed by multi analytical method.

Nine different compounds were selected: caffeine (Caff), ibuprofen (Ibu), bisphenol A (BPA), 17α-ethinyloestradiol (EE2), 17β-oestradiol (E2), oxybenzone (2-hydroxy-4-methoxybenzophenone, MBPh), *p*-nonylphenol (NP), *p*-octylphenol (OP) and triclosan (TCS). All compounds characteristics can be seen in Table 1.5. Methods for the extraction of the compounds were developed for liquid samples (SPE) soil (UAE) and sludge (QuEChERS). All samples were qualitatively and quantitatively analysed by HPLC-DAD. The method validation was conducted following RELACRE guidelines [180].

Table 1.5. Chemical structure and properties of the emerging organic contaminants.

Compound	Chemical structure	Formula	MW (g/mol)	log K_{OW}[a]	pKa[b]	Sol. in water (mg/L)	UV abs. (nm)	CAS-No
Caffeine (Caf)		$C_8H_{10}N_4O_2$	194.19	-0.07	14.0 [c]	2.16×10^4 [d]	273	58-08-2
Ibuprofen (Ibu)		$C_{13}H_{18}O_2$	206.19	3.97	4.91	21 [d]	220	15687-27-1
Bisphenol A (BPA)		$C_{15}H_{16}O_2$	228.29	3.32	9.6-11.3	120 [d]	277.1	80-05-7
17α-ethinylestradiol (EE2)		$C_{20}H_{24}O_2$	296.40	3.67	10.3	11.3 [e]	280	57-63-6
17β-oestradiol (E2)		$C_{18}H_{24}O_2$	272.38	4.01	10.7	3.90 [e]	280	50-28-2
Oxybenzone (MBPh)		$C_{14}H_{12}O_3$	228.25	3.82	7.56	69 [d]	288/329	131-57-7
p-nonylphenol (NP)		$C_{15}H_{24}O$	220.35	5.76	10.7	7 [d]	277	104-40-5
p-octylphenol (OP)		$C_{14}H_{22}O$	206.32	5.30	10.4	19 [f]	277	1806-26-4
Triclosan (TCS)		$C_{12}H_7Cl_3O_2$	289.54	4.76	7.9	10 [g]	282	3380-34-5

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, www.SigmaAldrich.com. Notes: [a] logarithm of the octanol-water partition coefficient; [b] logarithm of acid dissociation constant: [c] 40 °C; [d] 25 °C; [e] 27 °C; [f] 22 °C; [g] 20 °C.

b) Metalloids removal from a mine soil

The aim of this work was to assess the potential of EK process alone or coupled with phytoremediation to rehabilitate mine areas. This work was carried out at the Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China. The soil was collected from a mine area contaminated with As and Sb. Two plants were selected for the study: Indian mustard and ryegrass. Phosphate amendment was also applied aiming to improve As and Sb desorption. The impact of the applied technologies on biomass, metalloid uptake, available soil nutrients and enzymatic activities were also assessed.

c) Organic contaminants removal from soil

The aim of this work was to assess the potential of EK for the remediation of soils contaminated with organic compounds and how they are mobilized. The study was conducted with: two estrogenic steroid hormones, three industrial reagents and one antimicrobial agent. The target compounds (selected from Table 1.5) were E2, EE2, BPA, NP, OP and TCS. For the EK process two different agricultural soils were used in the experiments (collected from a rice field), aiming to understand how their properties would affect the remediation process. The effect of different current intensities and pH control in the anolyte (to increase soil flushing) was also assessed.

d) Microcystins removal and phosphorus recovery from membrane concentrate

Toxic cyanobacteria blooms are associated with nutrient enrichment of surface waters. Nanofiltration (NF) is a pressure-driven process used in water treatment plants to guarantee safe levels of contaminants in drinking water. The process results in the production of a slurry enriched with P and cyanotoxins (microcystin-LR, MC-LR), as well as natural organic matter. This slurry is considered a toxic residue being disposed of.

The aim of this work was to assess the potential of ED for the recovery of P as well as MC-LR removal from membrane concentrates (designated concentrates) resulting from the NF of natural waters (Figure 1.19).

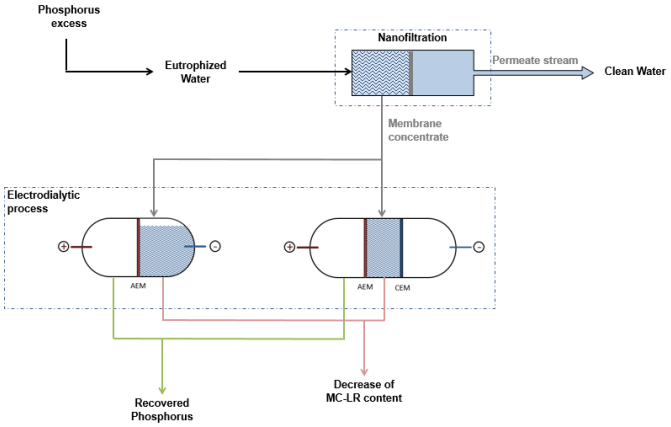


Figure 1.19. Schematic representation of the concept for electrodialytical phosphorus recovery and MC-LR removal from NF membrane concentrates.

e) Phosphorus recovery and heavy metals removal from sewage sludge ashes

These works aimed to evaluate the simultaneous P recovery and removal of heavy metals from the combination of acid extraction and ED separation. This work was carried out at DTU, Lyngby, Denmark. Initially, due to sewage sludge heterogeneity, a characterization of ashes collected from two incinerators (Lynetten and Avedøre) located in Copenhagen was done. Samples were collected in different dates and from different points, immediately after incineration and/or from the deposit where they stay until final destination.

The selected ashes were then subjected to acid washing and ED treatment aiming P recovery. ED process was tested by suspending the ashes in mineral acid and using 3c and 2c-cell set-ups. The influence of acid concentration (pH) on ED process was also evaluated.

f) Phosphorus recovery and organic contaminants removal from sewage sludge

These works aims to evaluate the simultaneous P recovery and OCs removal (Caf, BPA, E2, EE2, Ibu and MBPh) from sewage sludge using the electrodialytic separation.

Initially, due to the sewage sludge complexity and heterogeneity (physico-chemical parameters and microbiological community), the initial experiments were carried out with a sample collected and frozen. This aimed at assessing the best ED 2c-cell design aiming simultaneous P recovery and OCs removal.

After defining the best cell design, new experiments were carried out with sludge collected in the day of the experiments and different applied currents were studied. Simultaneous to the study of P recovery and OCs removal, the microbiological community (namely protozoa and metazoa) was also studied.

1.6. Original contribution

This dissertation presents several contributions targeting the aforementioned objectives and including some existing knowledge gaps. Regarding the application of the EK and ED process to the different matrices, it specifically considered the following:

- The EK enhanced phytoremediation had never been tested on a mine soil contaminated with As and Sb.
- Previous studies have not considered the electrokinetic removal of emerging OCs.
- The application of the ED process for P recovery from SSA was one of the first trials.
- The ED process was applied for the first time to:
    - membrane concentrates resulting from the nanofiltration of waters from a Water Treatment Plant aiming P recovery and toxins removal;
    - SS aiming simultaneous P recovery and emerging OCs removal;

- The evaluation of the effect of the direct current on the microbial community of the SS had never been assessed.

1.7. Dissertation outline and content

After this introductory chapter, Section II presents a synthesis of the experimental approaches implemented to reach the objectives. Section III shows the major findings from the experimental work presented in detail in the Section II of the dissertation. Finally, the summary of the overall conclusion and future developments are presented in Section IV.

Part II of the dissertation includes all the publications in peer-reviewed journals (published and submitted) that were developed during the Ph.D. study. As Part I is a summary of the publications presented in Part II, some overlap and repetition are inevitable.

Section II

2. MATERIALS AND METHODS

2.1. Contaminated Matrices

2.1.1. Mine Soil

A contaminated soil with As and Sb was sampled from a mine area located in Lengshuijiang city, Hunan Province, People's Republic of China. The soil was air-dried and passed through a 10 mm sieve for the experiments.

2.1.2. Agricultural Soil

Three soils were used in this study, soils SO1, SO2 and SO3.

The SO1 was sampled at Valadares, Vale de Milhaços, Portugal, at 0 – 15 cm depth, and corresponds to an Eutric Regossol (World Reference Base for Soil). It was used in the EK experiments only as a support medium, further on explained (section 2.2.2.2, page 45). Soils SO2 and SO3 were sampled at Paul de Magos, Salvaterra de Magos, Portugal, at 0 – 20 cm depth, and correspond to Fluvisols (World Reference Base for Soil). Both soils were used in the EK experiments as spiked matrices.

2.1.3. Membrane concentrates

The concentrates were collected after the nanofiltration process, kindly produced and supplied by Margarida Ribau Teixeira´s research team at University of Algarve, Portugal. The production of concentrates was carried out using a plate-and-frame unit (Lab-unit M20) described in detail elsewhere [181]. A thin film composite nanofiltration membrane with a hydraulic permeability of 82.2 kg/h.m^2.bar at 21 °C. The linear regression of the deionized water flux with pressure (between 5 and 30 bar) had a regression coefficient of r^2=0.997, and a membrane molecular weight cut-off of *ca.* 114 Da, NF90 (DowFilmtec) was used. The experiments consisted of concentration runs, mimetizing industrial NF operation at different water recovery rates (defined between permeate and initial feed volumes).

The NF feed water was a surface water from two Portuguese Dam reservoirs: Amoreiras (101.2 km^2 and 11 hm^3, Alentejo, Portugal) and Funcho (200 km^2 and 42.8 hm^3, Algarve, Portugal). Since no occurrence of cyanobacterial blooms was reported in both reservoirs during the experimental period,

2.2 mg/L of KH_2PO_4 and 10 μg/L of microcystins, extracted from cultures of *Microcystis aeruginosa* grown in laboratory (supplied by Pasteur Culture Collection), were added to the surface water.

The concentrate product was frozen and transported to the FCT-UNL where the ED experiments were performed.

2.1.4. Sewage sludge ash

The SSA samples were collected after incineration by fluidized bed combustion at Avedøre and Lynetten WWTPs, located in Copenhagen, Denmark. No major industries discharge wastewater to the studied plant facilities, prevailing non-industrial wastewater. The plants treat annually 345,000 and 500,000 population equivalents, respectively. At both plants P in the wastewater is precipitated in a Bio-P tank followed by addition of iron salt. After incineration of the sewage sludge, the ash is collected in electrofilters and the ferric ash is disposed of. In total, eight samples of ash were collected. From Avedøre, two samplings (2012 and 2014) were made directly after the electrofilters (fresh). From Lynetten, six samples (twice in 2012 and once in 2013) were collected from the electrofilters (fresh) and from the disposal site (deposited). The deposited ash was collected from the top part of the ash pile, existing in an open air warehouse (without door or windows). The storage time for the deposited ash was unknown. The SSA samples were stored in closed plastic containers at room temperature until the experimental work was carried out.

2.1.5. Sewage sludge

The sewage sludge (SS) samples were collected at a wastewater treatment plant located in Quinta do Conde, Sesimbra, Portugal (38°34'13" N, 9°2'7" W). The plant has the capacity to treat in the project horizon 19,300 m^3/day of urban wastewater, corresponding to about 94,000 population equivalents. The level of treatment installed is tertiary. The secondary tank is an aerobic reactor, of suspended biomass, where appropriate conditions are secured to promote the development of a population of microorganisms which ensure biological purification of *Águas de Lisboa e Vale do Tejo* (ALVT) wastewater conditions. The effluent of the reactor is then routed to the secondary settling tank for phase separation, where the samples were collected. Sampling of the SS was carried out following the recommendations of the norm NF EN ISO 5667-15 (October 2009) on the conservation and treatment of sludge and sediment samples.

The first set of experiments was carried out with SS (SS1) collected in January 2014 (Table 2.1). An initial screening of the studied contaminants was carried out in the SS1 and none of the compounds was detected in the sample. The sample was then packed in wide-mouth bottles of polytetrafluoroethylene (PTFE) and frozen until use.

The second set of experiments was carried out with SS sampled in different days between May and July 2015 (samples SS2-SS7, Table 2.1). These samples were collected, transported to the laboratory and immediately used in the experiments.

Initial sample characterization was carried out at the wastewater treatment laboratory of ALVT, Quinta do Conde.

Table 2.1. Sewage sludge samples used in the experiments.

Sample	Date	Type of sample	Experiments set
SS1	15-01-2014	Frozen	Set-1
SS2	13-05-2015	Fresh	Set-2
SS3	21-05-2015	Fresh	Set-2
SS4	04-06-2015	Fresh	Set-2
SS5	18-06-2015	Fresh	Set-2
SS6	02-07-2015	Fresh	Set-2
SS7	09-07-2015	Fresh	Set-2

2.2. Experimental design

2.2.1. Metalloids removal from mine soil

2.2.1.1. pH desorption tests

To determine the pH dependent extraction of As and Sb, 5 g of air-dried soil were suspended in 25 mL of HNO_3 and NaOH solutions with different concentrations (from 0.01 to 1.0 M). The suspensions were placed in a horizontal agitating table at room temperature, for 7 days, after which they were filtered by 0.45 µm filters using syringes, and As and Sb were determined by inductively coupled plasma - atomic emission spectrometer (ICP-AES). The same procedure was applied to the soil previously incubated with phosphate (0.5 M PO_4^{3-}) for 48 h. Control extractions were performed only with water, as well as without soil.

2.2.1.2. Electrokinetic experiments

Each experiment was performed with a lab-made EK set-up (Figure 2.1), which included an electric power supply, a soil column, a four channel peristaltic pump, two electrode chambers and two solution reservoirs.

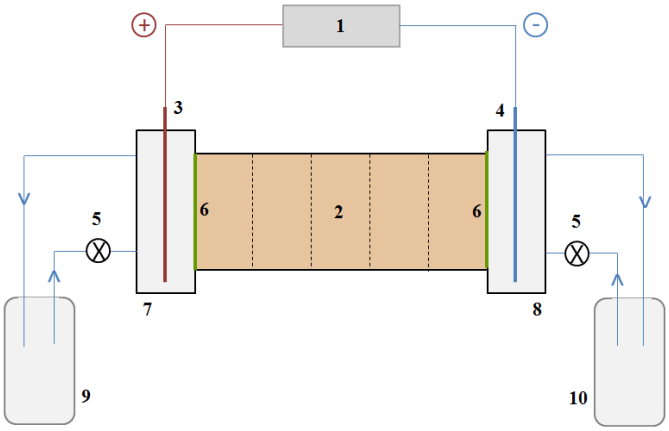


Figure 2.1. Schematic view of the electrokinetic cell set-up used with the mine soil: (1) DC power supply; (2) soil cell; (3) anode; (4) cathode; (5) peristaltic pump; (6) fritted glass membrane; (7) anode chamber; (8) cathode chamber; (9) anolyte reservoir; (10) catholyte reservoir.

The peristaltic pump was cycled to refresh the electrolytes in their chambers at a rate of 40 rpm. Two square titanium alloy electrodes (length of 4 cm) were used as the working electrodes. The soil column was a polyvinyl chloride (PVC) cylinder (length of 12.5 cm, internal diameter of 6.6 cm). Two porous fritted glasses were used as passive membranes to prevent soil leakage from the soil column to the electrode chambers. About 500 g of soil, with and without phosphate amendment was compacted in the soil columns. The EK set-up was assembled and deionized water was cycled for 24 h to allow soil water saturation in the central compartment. A DC potential gradient was applied to the cell (20 V), for 90 days, and four EK experiments performed (Table 2.2). For the experiments with pH control, the anolyte was daily adjusted with NaOH to keep its value above 12.

Table 2.2. Experimental design of electrokinetic treatments alone and coupled to phytoremediation for metalloids removal from the mine soil.

	Experiment	P-amendment (0.5 M PO_4^{3-})	pH anolyte adjustment (>12)	Voltage (20 V)	Plant (*I. mustard or ryegrass*)	Duration (day)
EK cell	E-1	-	-	Yes	-	90
	E-2	-	Yes	Yes	-	90
	E-3	Yes	-	Yes	-	90
	E-4	Yes	Yes	Yes	-	90
EK- phyto.	T-1	-	-	-	Yes	15
	T-2	Yes	-	-	Yes	15
	T-3	-	-	Yes *	Yes	15
	T-4	Yes	-	Yes *	Yes	15

*8 h *per* day.

After each experiment, the soil was removed from the column, divided into five equal sections, labelled as S1 to S5 from the anode to the cathode end. The pH and soil electric conductivity (EC) were

determined in the soil and electrolyte samples. Soil was then extracted for As, Sb and P analysis (section 2.3.2.2, page 55) and electrolyte solutions were filtered by 0.45 µm filters using syringes and analysed by inductively coupled plasma - optical emission spectrometer (ICP-OES). Soil section S1, S3 and S5 were also analysed for mobile and mobilizable fractions (section 2.3.2.3, page 55).

2.2.1.3. Electrokinetic-assisted phytoremediation

Rectangular plastic boxes (26.5 cm × 17.5 cm × 8 cm) were filled with a total of 3000 g of mine soil and fertilized with a solution of 0.99 g of urea and 0.96 g of monopotassium phosphate. Experimental boxes were divided into three compartments (cathode:central:anode) using a vertical nylon mesh (Figure 2.2). In the cathode and anode regions, 900 g of soil were used whereas 1200 g were in the central compartment. Graphite rods (diameter of 6 mm, length of 15 cm) were used as working electrodes as they are low cost and inert. Four rods (2 plus 2) were vertically inserted into the soil in opposite sides. Before the experiment, soil was incubated with 70% of its water holding capacity for 7 days. Pregerminated seedlings of Indian mustard (*Brassica juncea*) and ryegrass (*Lolium perenne*) were transplanted to experimental boxes and grew for 10 days. After this period a proportion of 12:16:12 exemplars were left in each box and the remaining sacrified and grown for more 35 days.

Eight treatments were done in this trial (Table 2.2): plant alone (ryegrass or Indian mustard) (T1); plant (ryegrass or Indian mustard) and phosphate amendment (T2); plant (ryegrass or Indian mustard) and EK process – 20 V (T3); plant (ryegrass or Indian mustard), phosphate amendment and EK process – 20 V (T4). Phosphate amendment was applied in a concentration of 0.5 M of PO_4^{2-} (as KH_2PO_4). Each treatment was carried out in triplicate.

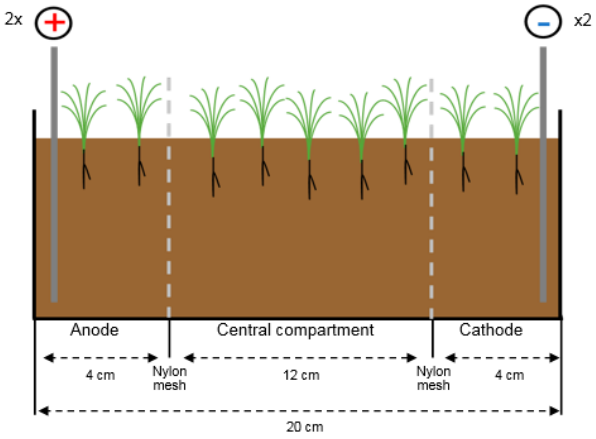


Figure 2.2. Experimental scheme of the electrokinetic-assisted phytoremediation set-up used with the mine soil.

Pot experiments were performed in a glass greenhouse. Moisture content was kept at 70% of soil water holding capacity throughout the study. A DC current was applied 8 h *per* day for 15 days, being its values monitored throughout the experiment.

At the end of the experimental period, soils were collected for the determination of As and Sb concentration (section 2.3.2, page 55), available nutrients and enzymatic activities (section 2.3.2.4, page 55), pH and EC were carried out. Plants were divided in roots and shoots, and As and Sb determined in both tissues (section 2.3.2, page 55).

2.2.2. Organic contaminants removal from agricultural soil

In order to assess the contaminants mobilization and remediation/degradation by EK (the objective of this study), the soil was spiked with a mixture of the selected compounds, approximately 500 ppm of each analyte in acetone. This was done to assure that all the contaminants would be detected in all cell compartments (anolyte, catholyte, membranes and soil sections), even in cases of high degradation efficiencies and to test the limits of the technique by using a highly contaminated matrix.

2.2.2.1. Electrokinetic laboratory cell

The EK experiments were carried out in a laboratorial cell. The cell is divided into three compartments (3c), consisting of two electrode compartments (length of 7.46 cm, internal diameter of 8 cm) and a central one (length of 3 cm, internal diameter of 8 cm), in which the soil, saturated with deionised water, is placed (schematic representation shown in Figure 2.3).

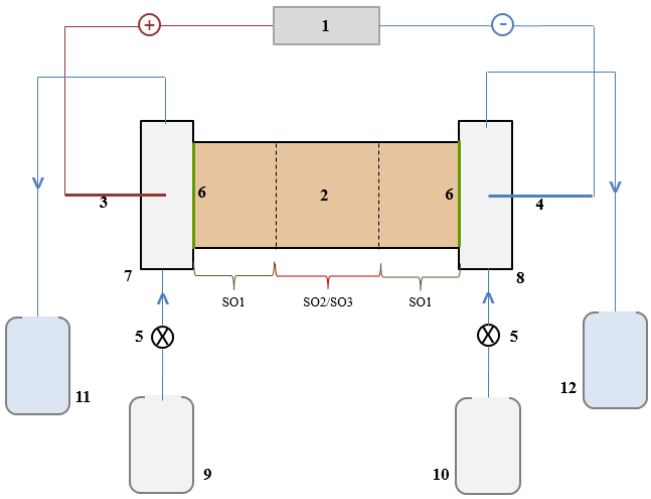


Figure 2.3. Schematic view of the electrokinetic cell set-up used with the agricultural soil: (1) DC power supply; (2) soil cell; (3) anode; (4) cathode; (5) peristaltic pump; (6) cellulose filters; (7) anode chamber; (8) cathode chamber; (9) anolyte reservoir; (10) catholyte reservoir; (11) anolyte receiving reservoir; (12) catholyte receiving reservoir; (SO1) non-contaminated soil; (SO2/SO3) contaminated soils.

A set of five cellulose filters, previously tested and known to work as passive membranes (Whatman 42) were used to assure the separation between the electrode compartments and the central one. A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC and the voltage drop was monitored (Kiotto KT 1000H multimeter). The electrodes were platinized titanium bars (length

of 5 cm, diameter of 3 mm; Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 7, being circulated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions. In each of the electrode compartments, the electrolytes were removed to collecting flasks. The incoming flows to the electrode compartments were maintained constant (1 mL/min), but the outlet flows also depend on the value of the EOF.

2.2.2.2. Electrokinetic experimental conditions

Six different laboratory experiments (A–F) were carried out, according to the experimental conditions presented in Table 2.3. The central cell compartment of the EK cell was filled with three slices of soils, being the middle slice of soil 2 (SO2, silty loam) or soil 3 (SO3, loamy sand) spiked with the organic compounds under study. The outer two slices of soil 1 (SO1, sand) were used for minimizing the contaminants diffusion towards the electrode compartments (Figure 2.3). The detection and quantification of the contaminants in each soil was carried out before all experiments. Electrolyte samples (catholyte and anolyte) were collected on a daily base during the experiments, for further contaminants quantification, and their pH and volume registered. At the end of each experiment, the total soil in the cell was sectioned in three sections ($SO1_{anode}$, SO2 or SO3, $SO1_{cathode}$) and each SO1 and SO2/SO3 sample into three and five subsamples, respectively. Smaller subsamples were also collected for pH and water content measurements. The contaminants contents in the soils, electrolyte solutions and in the passive membranes were analysed, following the procedures described in section 2.3.8 (page 59). A control experiment for each soil, without applied current, was also carried out (exp. A and E)

Table 2.3. Experimental conditions used in the experiments with agricultural soil.

Experiment	Soil (central compartment)	Current (mA) *	pH adjustment	Time (h)
A	SO2	0	-	96
B	SO2	10	-	96
C	SO2	20	-	52
D	SO2	10	Anolyte pH ≈ 13[a]	96
E	SO3	0	-	96
F	SO3	10	-	96

[a] pH adjustment was carried out in the anolyte reservoir (number 9 in Figure 2.3). * 10 mA=0.03 mA/cm^2 and 20 mA=0.06 mA/cm^2.

2.2.2.3. Photo and electrodegradation experiments

Contaminants photo and electrodegradation were also assessed. Degradation experiments were conducted for 6 h (electrolytes estimated residence time in the EK cell) at a constant current of 10 mA. Two containers (not completely closed), one for the cathode and other for the anode, containing 400 mL of electrolyte solution were spiked with the studied organic compounds (1 mg/L). A filter paper was used as a saline bridge. The filter paper was submersed in a 1 M KNO_3 solution for 3 s, and then left drying

for 30 s in order to remove the excess solution. One end of the filter paper was placed in the cathode end and the other in the anode end. The power supply, electrodes and the filter paper used were similar to the ones used for the EK experiments. Electrolytes pH was not controlled during treatment. The initial and final electrolyte samples and filter paper were collected and analysed following the procedures described in section 2.3.8 (page 59). Hydrogen peroxide formation was also controlled using semi-quantitative test strips Quantofix Peroxide 25 (Macherey-Nagel, Germany).

2.2.3. Microcystins removal and phosphorus recovery from membrane concentrate

2.2.3.1. Electrodialytic laboratory cell

Two cell designs were used for the ED experiments, Figure 2.4a and 2.4b. The design in Figure 2a is divided into 3c (adapted from [182]), consisting of two electrode compartments (each one with an electrode) and a central one (length of 1.5 cm, internal diameter of 8 cm), in which the membrane concentrate was placed. The 3c were separated by ion exchange membranes (CEM, IC1-61CZL386; AEM, IA1-204SXZL386, both from Ionics Inc., Massachusetts, USA). The design in Figure 2b (adapted from [183]), is divided into two (electrode) compartments, separated by an AEM (similar to the previous one). Membrane concentrate was placed in the cathode compartment.

The electrodes were platinized titanium bars (length of 5 cm and diameter of 3 mm, Bergsøe Anti Corrosion A/S, Denmark). A power supply (Hewlett Packard E3612A) was used to maintain a constant direct current and the voltage was monitored by a multimeter (Kiotto KT1000H). The electrolyte was a 10^{-2} M $NaNO_3$ with pH 7 being circulated using a multichannel peristaltic pump (Watson-Marlow 503 U/R, UK) in a closed circulation system.

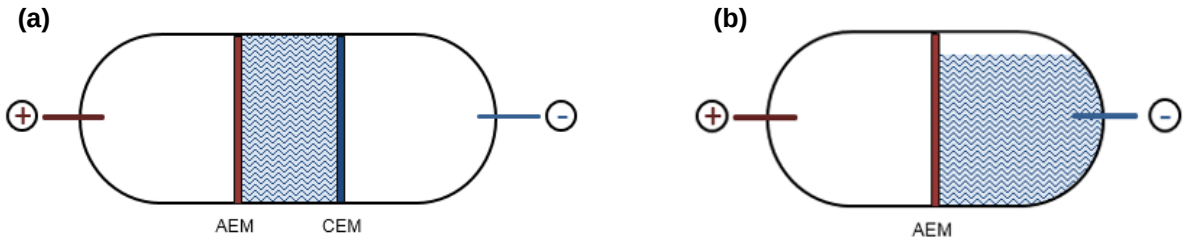


Figure 2.4. Electrodialytic cell designs used with the membrane concentrates: (a) 3 compartments (experiments C1, A-E, G and T) and (b) 2 compartments (experiments C2, F and H).

The conditions of the experiments carried out with the membrane concentrates are presented in Table 2.4. Experiments are divided in two sets. Set-1 experiments were conducted with a "standard" 3c-cell in 2012. Set-2 experiments, were conducted after the development of the 2c-cell and performed across 2014 and 2015 with both cell set-ups.

Table 2.4. Experimental conditions of the electrodialytic process applied to membrane concentrates.

	Experiment code	Membrane concentrate	Current intensity (mA)	Cell design	Duration (h)
Set-1	T1	1	10	3C	48.5
	T2	1	20	3C	21.0
	T3	2	10	3C	6.5
Set-2	C1	6	0	3C	12.0
	C2	6	0	2C	12.0
	C3*	7	10		12.0
	A	3	10	3C	7.0
	B	3	20	3C	5.0
	C	4	10	3C	7.0
	D	5	10	3C	8.0
	E	8	10	3C	12.0
	F	8	10	3C	12.0
	G	8	10	2C	12.0
	H	8	10	2C	12.0
	I	7	10	3C	12.0
	J	7	10	2C	12.0
	K	6	10	3C	12.0

Legend: experiment code C: control experiments; A-D: experiments to study P migration; E-H: experiments to study P migration and MC-LR degradation.
***** experiment performed with beakers (detailed information in text).

Initially three experiments (set-1, T1 to T3) were carried out aiming at assessing if P recovery from concentrate was possible. After, the second set of experiments were designed and carried out. Summing-up, the set-2 is divided in control experiments (C1 to C3), experiments to study P migration (A to H and T) and experiments to study simultaneous P migration and microcystin degradation (I-K). All the experiments were carried out in dark conditions. The cell design with 3c (Figure 2.4a) was used in the first set of experiments with concentrates #3 to #5 (experiments A to D). A 2c-cell (NF concentrate in cathode compartment and an AEM separating both compartments) was also used to assess if a different and simpler cell design would improve P recovery in the anode compartment. The comparison between cell designs for P removal was carried out in experiments G and H for 2c (Figure 2.4b) and in experiments E and F for 3c. Membrane concentrate #8 was used in both cases.

The cell design with 2c was also used in the second set of experiments with concentrate #6 (controls C1 and C2 and experiment K) and #7 (control C3 and experiments I and J). The controls C1 and C2 were used to mimetize, respectively, the 3c and 2c-cell designs, without the application of electric current. A control experiment to assess microcystin electrodegradation (C3; #7) was also carried out.

Experiments A-D run between 5 and 8 h (depending on concentrate characteristics) and were considered finished after the steeply voltage increase. The concentrates used for experiments E to H (#8; 3000 µS/cm), I and J (#7; 2980 µS/cm) and K (#6; 1635 µS/cm) presented higher conductivity than those previously tested. In this case, the criteria to stop the experiments was not the abrupt voltage increase but a fixed time interval (12 h) that would allow the monitoring of P migration.

In the experiments with a cell design with 3c, the application of 10 mA corresponded to a current density of 0.06 mA/cm^2, whereas 20 mA to 0.12 mA/cm^2. In the cell design with 2c the current density was also of 0.06 mA/cm^2 for 10 mA.

For the electrodegradation control (C3), three beakers (not completely closed) were used, where cathode and anode beakers contained 200 mL of electrolyte each, and the third beaker 100 mL of membrane concentrate (Figure 2.5). Two filter papers were used as a saline bridge. Papers were submersed in a 1 M KNO_3 solution for 3 s, and then left drying for 30 s in order to remove the excess solution. The power supply and the electrodes were similar to the ones used for the ED experiments. The initial and final electrolytes, concentrates and filter paper were collected and analysed according to the procedures described in section 2.3.4 (page 56).

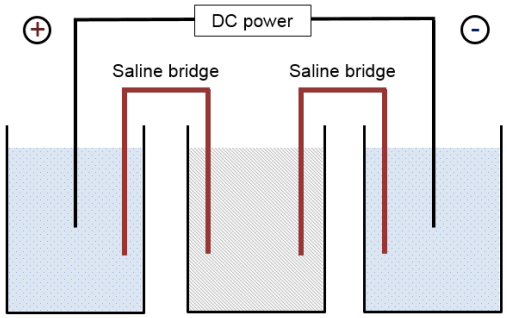


Figure 2.5. Scheme of the laboratory cell for the electrodegradation experiments.

The concentrates and electrolyte samples were collected at the beginning and at the end of each experiment and analysed for P and microcystin (section 2.3.4, page 56) content. Electrolyte samples were also hourly collected, to follow P recovery and stored at 4 ºC until analysis. Microcystin were analysed immediately after extraction.

2.2.4. Heavy metals removal and phosphorus recovery from sewage sludge ashes

2.2.4.1. Electrodialytic experiments

The experiments were carried out in two ED laboratory cells (Figure 2.6) divided in 3c [182] or 2c [183], with a stirrer in the ash compartment to maintain the matrix suspended. The cell was made of Plexiglas with an internal diameter of 8 cm. The ion exchange membranes separating the central compartment from the electrode compartments were commercial membranes from Ionics (AEM, AR204 SZRA B02249C; CEM, CR67 HUY N12116B). Platinum coated electrodes from Permascand were used as working electrodes, and a power supply (Hewlett Packard E3612A) maintained a constant current. The length of the ash compartment was 10 cm. Through a hole, the stirrer made of flexible plastic flap fastened to an insulated wire (total length of the flap *ca*. 5 cm and width of 6 mm) was placed approximately in the middle of the compartment, coupled to a HETO motor, with a rotation velocity of

1300 rpm. The sewage sludge ash was suspended in different concentrations of H_2SO_4 (0.08 and 0.19 M) in the ratio of 1:10 (mass:volume), and 500 mL of 10^{-2} M $NaNO_3$ was used as anolyte and as catholyte, with pH adjusted to 2 with 1:1 HNO_3.

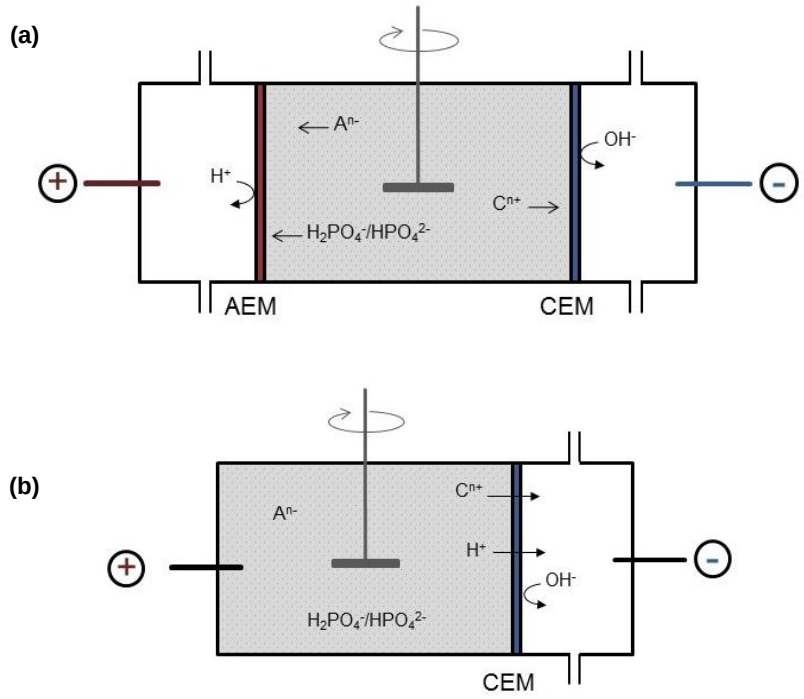


Figure 2. Schematic view of a 3c (a) and a 2c (b) electrodialytic cell used with the sewage sludge ashes.

During the experiments voltage drop, current density, pH in the electrolytes and pH and conductivity in the SSA suspension were measured. The pH of the electrolytes was manually adjusted to pH between 1 and 2 with 1:1 HNO_3 when necessary.

A total of twelve ED experiments (six experiments for each SSA sample) were carried out, all run at 50 mA, for different periods of time (Table 2.5). In the experiments with a 3-cell the application of 50 mA corresponded to a current density of 0.08 mA/cm^2, whereas in the 2c-cell was of 0.10 mA/cm^2.

At the beginning and at the end of each experiment, samples were taken from catholyte and anolyte and from the suspension, for P and heavy metal analyses. At the end of the experiments the SSA suspensions were drained through filter paper before drying, to separate the solids from the liquid phase, and water content was measured. Membranes and cathode were soaked in HNO_3 (1 and 5 M, respectively) for 24 h, to release metals for further analysis. SSA (three replicates), aqueous phases, electrolytes, membranes and cathode were analysed for P and heavy metal contents, using the same ICP-OES. Anolyte final samples of experiments S3-F and S3-D were analysed by standard colorimetric methods.

Table 2.5. Design of the experiments with the sewage sludge ashes collected from Lynetten 2012 (F-fresh SSA; D-deposited SSA; electrolyte $NaNO_3$ 10^{-2} M with pH adjusted to <2).

Experiment	Cell design	Ash compartment	H_2SO_4 (M)	Duration (day)
S1-F	3c	central	0.08	3
S1-D	3c	central	0.08	3
S2-F	3c	central	0.08	7
S2-D	3c	central	0.08	7
S3-F	3c	central	0.08	14
S3-D	3c	central	0.08	14
S4-F	3c	central	0.19	7
S4-D	3c	central	0.19	7
S5-F	2c	anode	0.08	7
S5-D	2c	anode	0.08	7
S6-F	2c	anode	0.19	7
S6-D	2c	anode	0.19	7

Experiments from S1 to S3 were conducted in 2012 and a 3c-cell was used. Experiments from S4 to S6, were conducted after the development of the 2c-cell and performed across 2015 with both cell set-ups.

2.2.5. Organic contaminants removal and phosphorus recovery from sewage sludge

2.2.5.1. Electrodialytic laboratory cell

Three different ED cell designs were tested in accordance to Figure 2.7 (from a to c). The experiments were carried out in a 2c ED laboratorial cell [183]. The compartments had an internal diameter of 8 cm, an electrode each, and were separated by a commercial ion exchange membrane, from Ionics (CEM, CR67 HUY N12116B, or an AEM, AR204 SZRA B02249). The compartment where the sewage sludge was place had a length of 10 cm and was equipped with a stirrer, whereas the electrolyte compartment had a length of 5 cm. The electrodes were platinized titanium bars, (length of 5 cm and diameter of 3 mm, Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC and the voltage drop was monitored (Kiotto KT 1000H multimeter). The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution, being circulated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions.

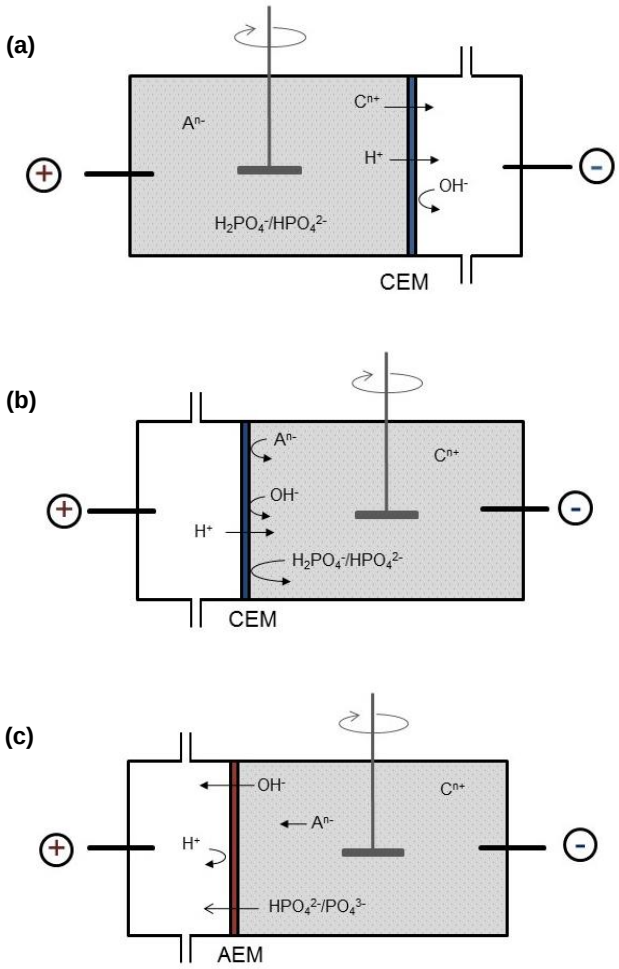


Figure 2.7. Schematic design of the three laboratory cell set-ups used with the sewage sludge. The sewage sludge was placed at the (a) anode with CEM (Exp-1 and Exp-2), (b) cathode with CEM (Exp-3 and Exp-4) and (c) cathode with AEM (Exp-5 to Exp-10).

2.2.5.2. Electrodialytic experimental conditions

The sludge cell compartment of the ED cell was filled with 350 g of sewage sludge (90-95% water). For this, a funnel was placed in the agitator hole and the sewage sludge was poured through it and, as the SS was too thick, 50 mL of deionized water were used to help the passage through the funnel. Prior to the beginning of the experiments, the SS was spiked with a mixture of the contaminants under study. In order to assess the contaminants mobilization and remediation/degradation under the influence of ED (one of the study goals), the SS was spiked with approximately 8 mg/L of each analyte in 1:1 MeOH:Acetone. This was done to assure that all the contaminants would be quantified or detected in all cell compartments at the end of the experiments (sewage sludge, effluent and electrolyte), even in cases of high degradation efficiencies, as well as to test the limits of the technique by using a highly contaminated matrix.

Experiments were carried out according to the experimental conditions presented in Table 2.6.

In the first set of experiments, conducted with the frozen sludge (SS1), two control experiments without the application of electric current were carried out, in Control-1 the sewage sludge was separated from the electrolyte by a CEM and in Control-2 the separation was done by an AEM. Two experiments with the application of 20 and 50 mA were then carried out using the cell schemes of Figure 2.7a. Another two experiments were carried out, also with the application of 20 and 50 mA, using the scheme of Figure 2.7b. In relation to the cell scheme of Figure 2.7c, taking into consideration the results obtained for 20 mA on the previous set-ups, only one experiment was carried out applying 50 mA. In total seven experiments were done in duplicate, in a fume hood protected from the sunlight, for 5 days.

Table 2.6. Experimental design of the sewage sludge experiments (electrolyte $NaNO_3$, 10^{-2}M).

Set	Experiment*	Sludge compartment	Membrane	Current (mA)	Duration (day)	Matrix [c]	Scheme (see figure)
Set-1 [a]	Control-1		CEM	0	5	SS1	
	Control-2		AEM	0	5	SS1	
	Exp-1	Anode	CEM	20	5	SS1	2.7a
	Exp-2	Anode	CEM	50	5	SS1	2.7a
	Exp-3	Cathode	CEM	20	5	SS1	2.7b
	Exp-4	Cathode	CEM	50	5	SS1	2.7b
	Exp-5	Cathode	AEM	50	5	SS1	2.7c
Set-2 [b]	Control-3		AEM	0	3	SS2	
	Exp-6	Cathode	AEM	50	3	SS3	2.7c
	Exp-7	Cathode	AEM	75	3	SS4	2.7c
	Exp-8	Cathode	AEM	100	3	SS5	2.7c
	Exp-9	Cathode	AEM	50-75-50	3	SS6	2.7c
	Exp-10	Cathode	AEM	100-75-50	3	SS7	2.7c

Legend: CEM - cation exchange membrane; AEM - anion exchange membrane. *Two replicates of each experiment were carried out. [a] Experiments conducted with frozen sewage sludge and initial electrolyte pH adjusted to ≤ 2.; [b] Experiments conducted with fresh sewage sludge and no initial electrolyte pH adjustment; [c] see Table 2.1.

In the second set of experiments only the design of Figure 2.7c was used and the experiments were conducted with fresh SS. A control experiment without the application of electric current was carried out (Control-3). Three experiments with the application of 50, 75 and 100 mA were then carried out. One experiment was carried increasing the current intensity every 24 h, 50-75-100 mA, and another decreasing, 100-75-50 mA. In total six experiments were done in duplicate, in a fume hood protected from the sunlight, for 3 days. In parallel to all experiments, two beakers containing only the sewage sludge and the other the spiked sewage sludge, both with agitation without electric current, were carried out as microbiological control.

In the experiments the application of 20 mA corresponded to a current density of 0.04 mA/cm^2, 50 mA to 0.10 mA/cm^2, 75 mA to 0.16 mA/cm^2 and 100 mA to 0.21 mA/cm^2.

During the experiments voltage drop, current density and pH were measured. To measure the pH, samples from the sewage sludge and electrolyte were collected to a small beaker, pH measured and the samples were returned to the cell. Electrolyte pH was manually adjusted to pH between 1 and 2 with 1:1 HNO_3 when necessary. In a second set of experiments, during the experiments anolyte samples were collected for total-P analysis every 24 hours.

At the end of the experiments anolyte samples were collected. The sewage sludge in the cell was collected, centrifuged and filtrated under vacuum to separate the solid (sludge) from the liquid phase (effluent). The filtrated sludge was then extracted (two replicates) for OCs determination (section 2.3.8, page 59). The remaining sewage sludge sample was then dried in an oven at 50 ºC till constant weight and the water content determined. Finally, for P, Fe, Al and Ca determination, the dried sewage sludge sample was extracted (section 2.3.7, page 58). The liquid samples, effluent and anolyte were then filtered through a 0.45 µm filter and extracted for OCs and for P colorimetric analysis (section 2.3.7, page 58) and for P, Fe, Al and Ca ICP-AES determination. Iron, Al and Ca analysis and colorimetric P determination were only carried out for the experiments of Set-2.

Membranes and electrodes were soaked in HNO_3 (1 and 5 M, respectively) for 24 h and the liquid used for further P analysis. Afterwards, membranes were again soaked in acetone and placed in an ultrasonic bath for 10 min to promote a better cleaning.

In the first set of experiments, samples before and after ED experiments were observed in a microscope for qualitative analysis of the microbiological community. In the second set of experiments, sewage sludge was analysed before, during and after the ED process for both qualitative and quantitative control of the microbiological community. During ED, the samples were collected at time 0, 6, 24, 48 and 72 h of experiment (t0, t⅓, t1, t2 and t3). All samples were collected and placed in capped plastic bottles, half of the vial volume. Sewage sludge from the ED cell was collected at half height and if there was the formation of foam at the top of the cell, it was collected separately. All samples were analysed following the procedure described in section 2.3.6 (page 57).

2.2.5.3. Electrodegradation experiments

Contaminants electrodegradation was also assessed in the setup scheme of Figure 2.8. Degradation experiments were conducted for 6 h at a constant current of 25 mA. Two containers, one for the cathode and another for the anode, were separated by a CEM placed in the middle of the bridge. Two experiments were carried out in duplicate. In one experiment the cathode end contained 200 mL of electrolyte solution spiked with the studied contaminants, and only electrolyte solution in the anode. In the second experiment, the opposite was carried out, with only the anode end being spiked with the studied contaminants. The spiked electrolytes contained approx. 8 mg/L of each contaminant.

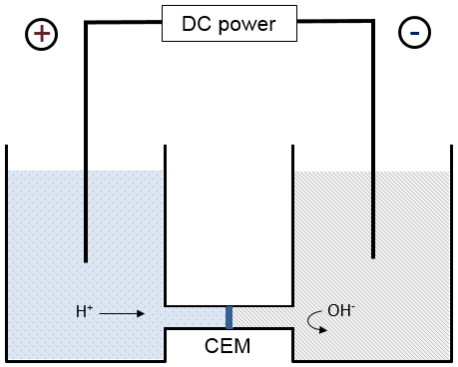


Figure 2.8. Scheme of the laboratory cell used for the electrodegradation experiments (CEM - cation exchange membrane).

The electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 2. The power supply, electrodes and CEM used were the same as the ones used for the ED experiments. The containers were protected from sunlight. Electrolytes pH was not controlled during treatment. The initial sample was collected and then sampling and pH measurements were carried out every 30 min during the experiments. At the end, the final samples were collected and pH and volume registered. Hydrogen peroxide formation was also controlled using semi-quantitative test strips Quantofix Peroxide 25 (Macherey-Nagel, Germany).

2.3. Analytical methodologies

2.3.1. Chemicals and solvents

The water used for analyte extractions and their analytical determinations was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). Acetonitrile (ACN), methanol (MeOH) and acetic acid were LC-MS grade purchased from Sigma–Aldrich. Formic acid was LC–MS grade from Fluka. Sodium nitrate ($NaNO_3$) was reagent grade from Panreac and sodium hydroxide (NaOH) from Sigma-Aldrich. All the other used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain), Merck (Darmstadt, Germany) and Fluka (U.S.A).

For the mine soil experiments, plant reference materials GBW10010 and GBW10015 were used for analytical control.

For the membrane concentrate experiments, P standard solution from Fluka TraceSelect (1000 mg/L ref. 51474) and the standard reference material EnviroMAT Drinking Water, (High, EP-H-3) and SCP Science (ref.140-025-032) were used.

Caffeine (≥ 90%), BPA (≥ 99%), E2 (≥ 97%), EE2 (≥ 98%) and OP (≥99%) were purchased from Aldrich (Steinheim, Germany), Ibu (≥ 98%) from Fluka (U.S.A.), TCS (Irgasan, ≥ 97%) from Sigma-Aldrich (Steinheim, Germany), MBPh (≥ 98%) from Alfa Aesar and NP (≥ 90%) from Riedel Haën.

2.3.2. Mine soil

2.3.2.1. Mine soil characterization

Soil was air dried and passed through a 10 mm sieve and pH, EC, cation exchange capacity (CEC), and soil organic content (SOC) were determined by conventional methods [184]. The soil pH and EC were determined by a pH meter (Shanghai REX Instrument, model pHS-3B, China) and an EC meter (Shanghai REX Instrument, model DDS-11A, China), respectively, with a soil to water ratio of 1:2.5. The CEC was analysed by ammonium acetate extraction method and soil SOC by dichromate oxidation method.

2.3.2.2. Determination of metalloids and phosphorus

For the measurement of As, Sb and P, all soil samples were air dried and sieved through a 100-mesh nylon sieve. Soil was digested with *aqua regia* (HNO_3:HCl, 1:3 (v/v)) followed by As, Sb and P analysis by ICP-AES. Vegetal material was digested in 1:5 (v/v) of $HClO_4$:HNO_3 followed by atomic fluorescence spectroscopy (AFS). Plant reference materials were used for analytical control.

2.3.2.3. Mobile and mobilizable metalloids fraction

The soil before and after EK experiments (soil sections 1, 3 and 5) was submitted to Cai's two-step sequential extraction procedure [185]. The mobile and mobilizable fractions were obtained according to the following procedure: (i) mobile fraction: 25 mL of 0.1 M $NaNO_3$ added to 0.5 g of soil and shaken for 24 h; the suspension was centrifuged and the supernatant collected for further analysis; (ii) mobilizable fraction: 25 mL of 0.1 M KH_2PO_4 added to the residue and shaken for 1 h; the suspension was centrifuged and the supernatant collected for further analysis. To both supernatants, 23 mL of deionized water and 2.5 mL of HNO_3 were added prior to analysis by ICP-AES.

2.3.2.4. Available nutrients and enzymatic activities

Available nutrients and enzymatic activities were carried out using the methodologies described elsewhere [184]. In brief, P was extracted with 0.5 mol/L $NaHCO_3$ and determined using the molybdenum blue method; K was extracted with 1 mol/L CH_3COONH_4 and determined by flame photometry (Shanghai FP 640 model, China) and inorganic N was extracted with 2.0 mol/L KCl in a 1:10 soil to solution ratio (1 h) followed by determination using an automatic procedure (Skalar San segmented flow analyser, Netherlands). For soil invertase (INV) activity, 5 g of soil were incubated (24 h; 37 ºC) with 15 mL of 8% sucrose as substrate, 0.5 mL of toluene and 5 mL of phosphate buffer (pH 5.5) and the produced glucose determined by 3, 5 – dinitrosalicylic acid colorimetric method (DNS method) at 508 nm. For urease (URE) activity, 5 g of soil were mixed with 0.5 mL of toluene, 20 mL of citrate buffer (pH 6.7), 10 mL of 10% urea followed by incubation (37 ºC; 24 h) and the released ammonium determined by Indophenol Blue Method (578 nm). For soil neutral phosphatase (NPH), 5.0

g of soil and 20 mL of 0.5% disodium phenyl phosphate of citrate buffer (neutral pH) were incubated (37 ºC; 2 h) and then the produced phenol was extracted and oxidized by potassium hexacyanoferrate in alkaline conditions. The oxidation products were determined by 4-aminoantipyrine colorimetric method (510 nm). Controls were performed whenever needed.

2.3.3. Agricultural soil characterization

Physico-chemical characterization of the soil was performed by the Research Unit of Environmental and Natural Resources (*Unidade de Investigação Ambiente e Recursos Naturais*, UIARN) at the National Institute for Agricultural Research located in Oeiras. Portugal.

2.3.4. Membrane concentrate

2.3.4.1. Membrane concentrate characterization

The surface waters and membrane concentrates were analysed for conductivity (Crison GLP32 conductimeter), pH (25 ºC, Whatman WTW pH340 meter), turbidity (HACH 2100N turbidity meter of high resolution, 0.001 NTU), dissolved organic carbon (DOC) (Shimadzu TOC 5000A analyser, 50 ppb–4000 ppm) and UV 245 nm absorbance (SpectronicUnicam UV300 UV–vis spectrophotometer), using standard methods of analysis. The total P present in the samples was determined by ICP-AES. Calibration was carried out by using a P standard solution. External calibration was carried out (using an aqueous 5% HNO_3 to prepare different concentrations), between 0-2 mg/L and the limit of quantification is 0.05 mg/L. Analytical control was pursuit by analysing a standard reference material and blank solutions. For all experiments, mass balances were between 80 and 120%.

2.3.4.2. Mycrocistins extraction and analysis

MC-LR extraction was carried out according to the method described elsewhere [181] and followed the operating procedure developed by Meriluoto and Spoof [186]. Analytes were analysed by liquid chromatography using a high pressure liquid chromatography equipped with a photo-diode array detector (HPLC-PDA; Dionex, ICS-3000). A C18 column was used (Atlantis dC18 3 µm, 4.6 x 30 mm; Waters). The mobile phase used a gradient of Mili-Q water and acetonitrile, both with 0.05% (v/v) of trifluoracetic acid. Chromatograms were analysed between 180 and 900 nm, with a main detection at 238 nm to the typical absorption spectra of MC-LR. Calibration was carried out by using a MC-LR standard solution (10 µg/mL in MeOH).

2.3.5. Sewage sludge ash

2.3.5.1. Sewage sludge ash characterization

Characterization of the SSA and heavy metals extraction were carried out with oven dried ash (105 ºC). For all characterization procedures five replicates of each type of ash were carried out. Water content was calculated as weight loss at 105 ºC for 24 h. Ash pH was measured in a 1:2.5 (mass:volume) suspension in deionized water using a Radiometer pH electrode. Loss on ignition (LOI) was determined in a muffle at 550 ºC for 30 min.

Morphology analysis was performed by scanning electron microscopy supported by energy dispersive spectrometry (SEM-EDX) without pre-treatment of the SSA samples. The accelerating voltage of the SEM was 20-25 kV with large field detector (and X-ray cone). Different areas of the samples were analysed by SEM and the element distribution was examined using EDX. Ash mineralogy was studied by X-ray diffraction (XRD) for the identification of the major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-70 2Θ.

2.3.5.2. Acid washing

To determine the pH dependent extraction of P and metals, 10 g dried SSA were suspended in 50 ml HNO3 of different concentrations (0.00; 0.01; 0.05; 0.08; 0.10; 0.30; 0.50; 0.70 and 1.0 M). The suspensions were placed at an agitating table for 7 days at room temperature. At the end of the experiment, pH was measured and suspensions were filtered by vacuum using 0.45 µm filters and the concentrations determined by ICP-OES. Each extraction was made in duplicate and reference samples were made using distilled water with the same procedure. pH dependent extractions was carried out for the Lynettefællesskabet SSA (2012, 1st sampling).

2.3.6. Sewage sludge

2.3.6.1. Sewage sludge biological characterization

For qualitative control of the microbiological community of the SS used in the first set of experiments, samples were analysed in the WWTP treatment facilities within 5 h after sampling, in an Olympus BX41 microscope (Olympus, Tokyo, Japan).

For the second set, sewage sludge was analysed before, during and after the ED for the identification and quantification of metazoa and protozoa community. Samples were collected at time 0, 24, 48 and 72 h of experiment (t0, t1, t2 and t3, respectively). An additional sample, after 8 h (t⅓) was collected for Exp-6, Exp-7 and Exp-8. Basically, 2 g of sludge was collected, 6 mL of deionized water were added and samples observed for qualitative control in a Leica ATC 2000 microscope with a Leica EC3 camera and LAS EZ software (version 2.1.0) used to photograph the species from the samples. After the qualitative analysis, 200 µl of the previous dilution were diluted to 50 mL and Lugol solution [187] was

added to preserve the samples. Accordingly to the density of the protozoa in the samples, 2 or 2.5 mL was analysed in a Leica DMIL immersion microscope for quantitative determination following the Utermöhl method [188] adapted to the sewage sludge protozoa community. Richness, Simpson diversity index and Evenness were calculated for the samples.

2.3.7. Phosphorus and heavy metals extraction and determination

2.3.7.1. Sewage sludge ashes

The concentration of Al, Cd, Cu, Cr, Fe, Ni, P, Pb, and Zn were determined after a pre-treatment of the SSA in accordance to DS259 standard [189]: 1.0 g dry ash and 20 mL of HNO_3 (1:1) was heated until 120 ºC and 200 kPa for 30 min. The samples were filtered through a 0.45 µm filter and the element contents measured in an ICP-OES, Varian 720-ES. All metal concentrations are given on a dry weight basis. Five replicates were made for the initial SSA determinations. In terms of Fe, the DS259 standard does not give its total concentration and the reason is that there is a small mineral residue that contains insoluble Fe compounds, which is removed before the ICP analysis [190].

2.3.7.2. Sewage sludge

The concentration of P, Al, Fe and Ca in the SS was determined after a pre-treatment of the sample in accordance to EPA3051: 0.5 g of dry SS and 10 mL of HNO_3 (65%) were placed in a vessel and extracted in a Microwave from Milestone Ethos (Bergamo, Italy). The microwave programme was set to reach 175 ºC in 15 min and then keep the temperature for another 15 min. The samples were then collected and filtered through a 0.45 µm filter and stored until analysis. Liquid samples (effluent and electrolyte) were filtered through a 0.45 µm filter and also stored until analysis. The total P, Al, Fe and Ca content was measured in an ICP–AES (Varian 720-ES).

2.3.7.3. Phosphorus colorimetric analysis

Some of the SSA and SS samples were also analysed by standard colorimetric methods [191] for total P, inorganic P and orthophosphate content. The used colorimetric reagent containing 50 mL of H_2SO_4 5N, 5 mL of potassium antimony tartrate, 15 mL ammonium molybdate and 30 mL of ascorbic acid was prepared in the day of the analysis. For orthophosphates determination, samples were diluted in deionized water (till 50 mL), and the colorimetric reagent was added. After, absorbance was measured in a time range of 10-30 min. For inorganic and total P, samples were diluted in deionized water (till 75 mL). For inorganic-P, 1 mL of H_2SO_4 and HNO_3 solution was added and for total-P, 1 mL of H_2SO_4 and 0.4g of $(NH_4)_2S_2O_8$ were added. Samples were then placed in an autoclave at a pressure between 98 and 137 kPa for 30 min. After, phenolphthalein was added to each solution, and the sample pH was neutralized with NaOH. Samples were then diluted to 100 mL and 8 mL of colorimetric reagent was added. Absorbance was read in a time range of 10-30 min.

Absorbance of the developed colour was measured in the spectrophotometer (Pharmacia LKB Ultrospec Plus Spectrophotometer) at 880 nm. Blanc solutions and standards were used for analytical control.

Polyphosphates were determined by indirect method (polyphosphates = inorganic P – orthophosphates), as well as organic P (organic P = total P – inorganic P).

2.3.8. Organic compounds extraction and analysis

The HPLC methods and extraction procedures were developed/adapted, optimized and validated during this Ph.D. (results will be shown in chapter 3).

2.3.8.1. HPLC-DAD conditions

The determination of the organic compounds was performed by high performance liquid chromatography with a diode array detector (HPLC–DAD).

The equipment consisted on a Finnigan MAT HPLC system (Thermo Scientific, USA) equipped with a SP P4000 Pump, an AS 3000 auto-sampler, an UV6000LP and a TSP SN 4000 Interface.

Separation of the analytes of the samples from the experiments conducted with agricultural soils were carried out using a Chromolith Performance RP-18e column with 100 mm × 4.6 mm from Merck (Darmstadt, Germany) and an Onyx SecurityGuard cartridges (4 mm × 3.0 mm) from Phenomenex (Torrance, CA, USA). In the case of the samples from the sewage sludge experiments, a Chromolith HighResolution RP-18e column with 100 mm × 4.6 mm from VWR (Darmstadt, Germany) and an Onyx SecurityGuard C18 cartridges (5 mm × 4.6 mm) from Phenomenex (Torrance, USA) were used.

The UV wavelength was set to full scan between 200 and 800 nm in all cases. Target compounds were measured at 274 nm for Caf, 220 for Ibu, 279 nm for BPA and OP, 280 nm for NP, 281 nm for E2 and EE2, 283 nm for TCS and 290/324 nm for MBPh.

All eluents were filtered before use by Nylon 66 membranes (pore size of 0.45 µm; Bellefonte, PA, USA). All operations and data analysis were processed by the Xcalibur software v.1.3. (Thermo Scientific, USA).

Individual stock solutions of the organic compounds for calibration purposes were prepared at 400 mg/L in MeOH and stored at −18 ºC. Working solutions were prepared by the adequate mixture and dilution of the stock solutions.

a) Agricultural Soil

All HPLC runs were performed at a constant flow rate of 1 mL/min, in gradient mode. The eluents used were ACN/MiliQ water solutions (solution A: 35/65; solution B: 90/10), adjusted to pH = 2.8 using a formic acid solution (50% in water). The gradient run was set at 100% A from 0 to 12 min, then to 75%

B until 13 min, where it held until 25 min, then to 100% B until 27 min, where it held until 30 min. The system re-equilibration was performed for 3 min with 100% A.

b) Sewage sludge

All HPLC runs were performed at a constant flow rate of 1 mL/min, in gradient mode, with the oven set to 38 ºC. The eluents used were a mixture of ACN / MiliQ water / Formic acid (solution A: 5 / 94.5 / 0.5%; solution B: 94.5 / 5 / 0.5%). Solution A pH was 3.2 and Solution B was 3.6. Formic acid solution (50% in water). The gradient run was set to: 5 min; 97% A from 0 to 15 min, then to 95% B until 50 min, where it was held until 53 min, then to 97% A until 55 min. The system re-equilibration was performed for 5 min with 97% A.

2.3.8.2. Extraction

Strata X cartridges (200 mg/6 mL) from Phenomenex (Torrance, CA, USA) and Oasis HLB (200 mg, 6 mL) from Waters (Saint-Quentin En Yvelines Cedex, France) were initially tested for the SPE extraction.

a) Aqueous samples

The extraction of the analytes present in the electrolytes and effluent (aqueous phase of the sewage sludge) was performed by solid phase extraction (SPE), using Oasis HLB (200 mg, 6 mL). The SPE cartridges were conditioned by washing with 3 × 6 mL of methanol, followed by re-equilibrium with 3 × 6 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2, using nitric acid, before extraction. The aqueous samples, 200 mL, were passed through the cartridge at a flow-rate of approx. 10 mL/min by applying a moderate vacuum. After that, the cartridges were dried for approx. 2 min by vacuum. The retained analytes were eluted sequentially with 2 × 2 mL of methanol in the agricultural soil experiments, and 2 × 3 mL of MeOH in the sewage sludge experiments. All the extracts were collected as one and concentrated under a gentle stream of nitrogen till 1 or 0.5 mL. Samples were transferred to a vial and kept at −18 ºC until analysis.

b) Agricultural soil

Solid samples (soils and passive membranes) were extracted three times by sonication (UAE). The extraction procedure was adapted from Ribeiro *et al.*, [192]. Basically, soil was extracted using 50 mL of acetone for 10 min. In order to remove the particulate matter, the extracts were filtered through MFV-5 glass microfiber filters (diameter of 47 mm, pore size of 0.5 µm) from Filter-Lab (Barcelona, Spain). All the extracts were collected, as one. Samples were then concentrated using 250 and 50 mL pear-shaped evaporating flasks on a rotavapor, Büchi RE 111 (40 ºC /moderate vacuum) at 45 ºC till approximately 4 mL and after under a gentle stream of nitrogen till 1 or 0.5 mL. Samples were transferred to a vial and kept at −18 ºC until analysis.

c) Sewage sludge

Sludge (solid phase of the sewage sludge) extraction was performed using QuEChERS extraction (adapted from [193]). Extract tubes were obtained from Waters (Dublin, Ireland). The acetate buffer contained 1.5 g NaOAc and 6 g $MgSO_4$. The dispersive phase contained 150 mg PSA (primary and secondary amine) and 900 mg $MgSO_4$. A 2 g aliquot of homogenized sludge was weighed in a 50 mL polypropylene centrifuge tube containing NaOAc and $MgSO_4$. Then, 20 mL ACN+acetic acid 1% (v/v) were immediately added and manually shaken for 15 s and then swirled on a vortex mixer for 45 s to homogenize the sample. The extract was centrifuged at 10,000 rpm for 5 min. A 9.5 mL aliquot of the supernatant (ACN phase) was transferred to a 15 mL centrifuge tube containing the PSA and $MgSO_4$ and was manually shaken for 10 s and swirled on a vortex mixer for 60 s. After this step, the extract was centrifuged again (10,000 rpm for 5 min) and 8 mL supernatant were transferred to a 12 mL glass tube. The extract was evaporated under a gentle stream of nitrogen till 0.5 mL. All samples were stored at −18 ºC until analysis.

2.4. Statistical analysis

Statistical analysis was carried out using the GraphPad software (one-Way ANOVA Tuckey test at 95% confidence level (p<0.05) for all experiments, when applicable. For the sewage sludge experiments, statistical differences were evaluated for P distribution within the: different samples in the same experiment; and between the different experiments for the same sample. In terms of organic compounds, degradation percentages of each compound in the control was, firstly, individually compared to the different experiments with current application and, secondly, different compounds in the same experiment. The distribution was analysed in three variables: (i) same compound, same experiment, different compartments; (ii) same compound, different experiments, same compartments, and (iii) different compounds, same experiments, same compartments.

2.5. Minteq calculations

MINTEQ was used to gain further insight into the formation of charged phosphorus complexes in the SSA which could be transported through the AEM and CEM. For the calculations the chemical composition of the solution in experiments after the 7 days, with elements present in SSA with Fe as Fe3+ or as Fe2+. The pH was fixed to the final experimental pH and temperature to 25 °C. The Ionic strength was calculated in the program.

SECTION III

3. RESULTS AND DISCUSSION

3.1. Analytical methods development for organic contaminants determination

3.1.1. HPLC method development

The aim of the study was to separate all analytes in one chromatographic run at the shortest time possible. The chromatographic parameters considered for method development were retention factor (k) resolution (R_S), peak symmetry (asymmetry factor, A_S). The operational parameters were mobile phase composition, pH, temperature and flow rate. The mobile phase composition and the pH were investigated first.

Due to the wide range of polarities from Caf that presents a octanol-water partition coefficient logarithm (log K_{OW}) of -0.07 to NP with a Log K_{OW} of 5.76, the separation of the compounds was only possible using a gradient elution. Since these Caf and NP are the first and the last they dictate the basic conditions for the elution.

Acetonitrile was chosen as organic phase as compared to MeOH, presents a cleaner baseline (noise reduction) and offers a faster reequilibration after a chromatographic run due its lower viscosity [194]. Additionally, MeOH gives a more turbulent fluid when mixed with water (bubble formation in the HPLC mixing vessel).

To define the eluent A and B composition in order to achieve the required R_S and A_S, several tests were performed using different mistures of water and ACN in isocratic mode, 80/20, 70/30, 65/35, 50/50, 35/65, 20/80 and 10/90 (v/v). After the tests, the eluent A was defined to be a misture of 65/35 (v/v) and B (10/90) of Water/ACN. The effect of the mobile phase pH were tested using TFA and formic acid as modifiers (buffers). Due to the negative influence of TFA in the UV spectra of all the compounds (Figure 3.1), the mobile phase buffering was performed with formic acid to pH 2.8.

Later the flow gradient was tested (from 0.5 to 2.0 mL/min) and defined to 1 mL/min as it ensured all compounds separation with the lowest eluent consumption. Temperature was not controled.

Final HPLC conditions are described in section 2.3.8.1 and enabled an efficient separation of the analytes, $R_S \geq 1.25$ and $A_S \approx 1$, in a single run of 30 min. Mixed aqueous standard solutions, covering the concentration interval from approximately 0.5 to 20 mg/L for each compound, were used to determine the validation parameters of the analytical method:

- working range;

- linearity;
- analytical thresholds (detection and quantification);
- precision (repeatability and intermediate precision).

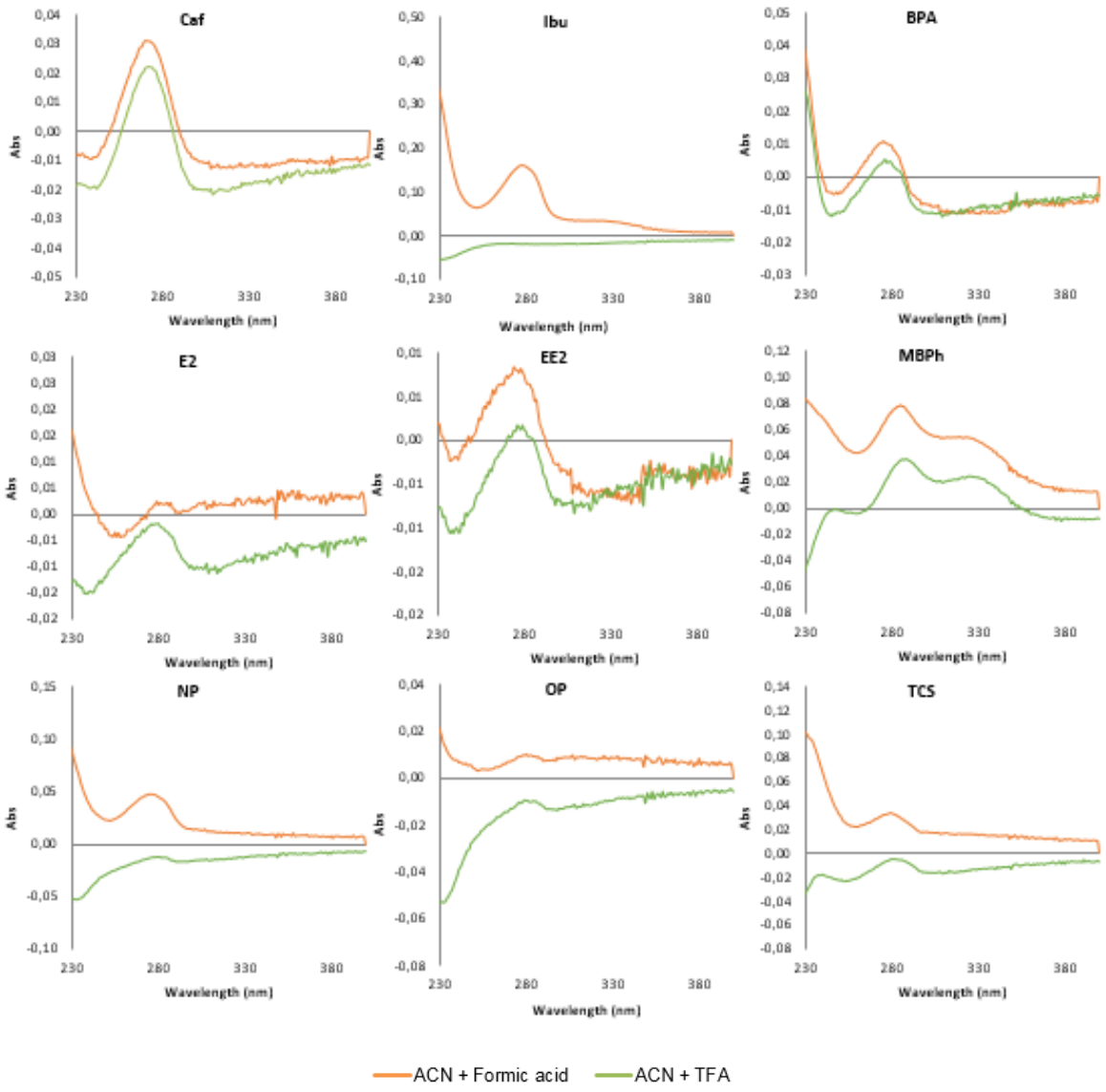


Figure 3.1. UV spectra of all compounds at 1 mg/L (measured in a UV spectrometer).

For the HPLC method used in the soil experiments (Table 3.1), the limit of detection (LD) and quantification (LQ) were determined after the injection of lowest standard, 0.5 mg/L, 10 times for the nine compounds in intermediate precision conditions (different operators and different days). The LD was estimated between 0.05 and 0.71 mg/L and LQ between 0.16 and 2.1 mg/L. The linear response range from 0.05 to 8.5 mg/L, with coefficient of determinations (r^2) higher than 0.98 (n = 5). The slope of the linear regression presented an overall variation lower than 10% for the different compounds. The precision of the HPLC-DAD method was determined by the intra-day and inter-day variation of one

mixed aqueous standard solution (5 mg/L) that was analysed in different days (n = 10). Repeatability was between 2.1 – 5.4% and intermediate precision was between 2.5 and 6.7% (n=10).

Table 3.1. HPLC method parameters for the soil experiments.

	Soil experiments				Sewage sludge experiments			
Compound	**LD (mg/L)**	**LQ (mg/L)**	**Working range (mg/L)**	**r^2**	**LD (mg/L)**	**LQ (mg/L)**	**Working range (mg/L)**	**r^2**
Caf	0.05	0.16	0.51 – 8.20	0.9985	0.11	0.34	0.49 – 8.24	0.9910
BPA	0.12	0.37	0.50 – 8.00	0.9916	0.14	0.42	0.48 – 8.00	0.9918
E2	0.62	1.9	2.14 – 8.54	0.9981	0.28	0.84	2.03 – 8.12	0.9815
EE2	0.48	1.5	2.06 – 8.22	0.9987	0.60	1.8	2.05 – 8.20	0.9859
Ibu	0.71	2.1	2.17 – 8.26	0.9976	0.67	2.0	2.02 – 8.08	0.9966
MBPh	0.17	0.51	0.53 – 8.42	0.9899	0.16	0.47	0.56 – 9.40	0.9894
TCS	0.65	1.95	2.06 – 8.22	0.9866	0.11	0.34	0.49 – 8.24	0.9910
NP	0.68	2.04	2.14 – 8.23	0.9877	0.14	0.42	0.48 – 8.00	0.9918
OP	0.32	0.96	2.05 – 8.11	0.9833	0.28	0.84	2.03 – 8.12	0.9815

Prior to the beginning of the experiments conducted with the SS and due to the high temperature variation in the laboratory between the months of April and May it was found that the compounds peaks showed fluctuations in the retention time (t_R) and peak deformation (peak asymmetry, A_S), making quantification difficult. To minimize the temperature fluctuations in the column a thermo-stabilized oven was acquired together with a monolithic HighResolution RP-18e column to increase separation efficiency.

Oven temperatures, between 35 and 40 °C, were tested using the HighResolution RP-18 column. The optimum temperature was defined to 38 ºC as it presented good A_S and R_S. In this run, the % ACN in eluent A was defined to 5% and in eluent B 94.5%, the remaining 0.5% was formic acid. The operational pH was 3.2 for eluent A and 3.6 for eluent B. It was also attempted to improve the separation and peak shape by diluting the standards in the mobile phase A, instead of 100% MeOH. The tests with the prepared standards in eluent A, together with the stabilized HighResolution RP-18e column temperature to 38 °C, led to an effective separation of all compounds, $R_S \geq 2.0$ and $A_S \approx 1$ (Figure 3.2).

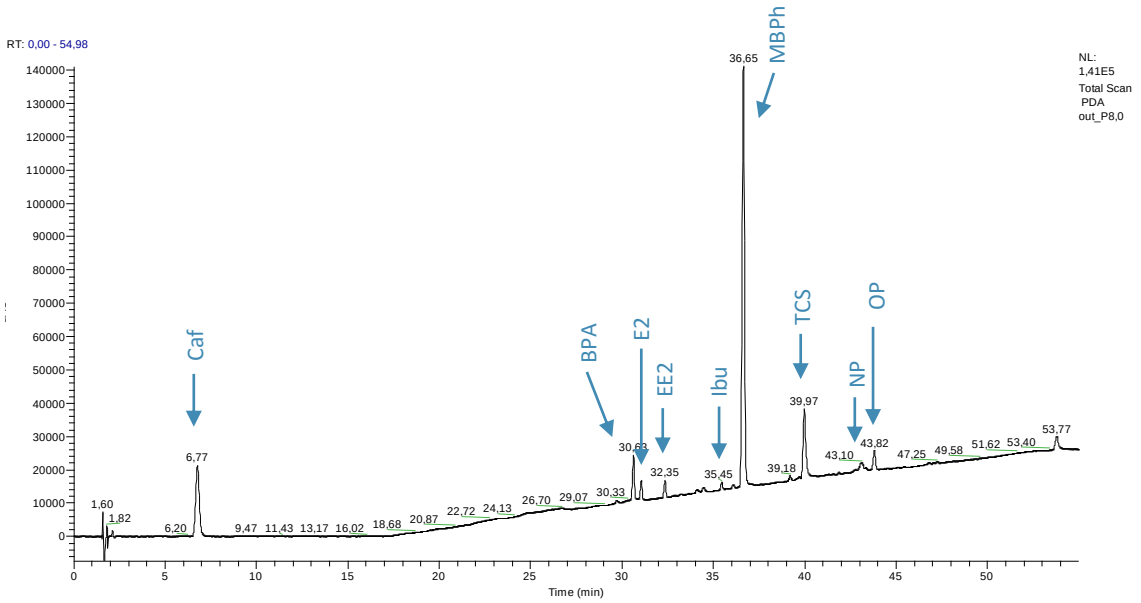


Figure 3.2. Stardard mix solution (8 mg/L) analysis with the column RP-18e (Chromolith ® HighResolution).

Based on the parameters described above, the validation studies of the analytical method were conducted according to following parameters:

- Working Range / Linearity;
- Analytical thresholds (detection and quantification);
- Sensitivity;
- Precision;
- Accuracy.

The LD and LQ for the HPLC method used in the SS experiments were determined after the injection of lowest standard, 0.5 mg/L, 15 times for the nine compounds in intermediate precision conditions (different operators and different days). The working range and linearity was also evaluated for a set of concentrations ranging from 0.5 to 8.5 mg/L for all compounds. Results can be seen in Table 3.1. The slope of the linear regression presented an overall variation (RSD) lower than 7% for the different compounds. The precision of the HPLC-DAD method was determined by the intra-day and inter-day variation of one mixed aqueous standard solution (2 mg/L) was analysed in different days (n=15). Repeatability was between 1.2 and 5.3% and intermediate precision was between 1.5 and 4.8% (n=15).

3.1.2. Solid Phase extraction (SPE)

To estimate the most suitable SPE phase an aqueous sample spiked with the OCs under study (0.5 mg/L) was extracted using cartridges filled with two different polymeric adsorbents, Strata-X and Oasis HLB. As general procedure protocol, the cartridges were conditioned:

1. conditioned using MeOH, 3x6 mL;
2. rinsed with water, 3x6 mL;
3. enriched at the flow rate of 10 mL/min;

4. dried for 2min under vacuum;
5. eluted with 2x2 mL of MeOH.

The obtained chromatograms showed that for the test conditions, the Strata-X resulted in the non-recovery of MBPh, which is not detected, and in low recoveries of TCS, NP and OP (between 40 and 55%) of (Figure 3.3).

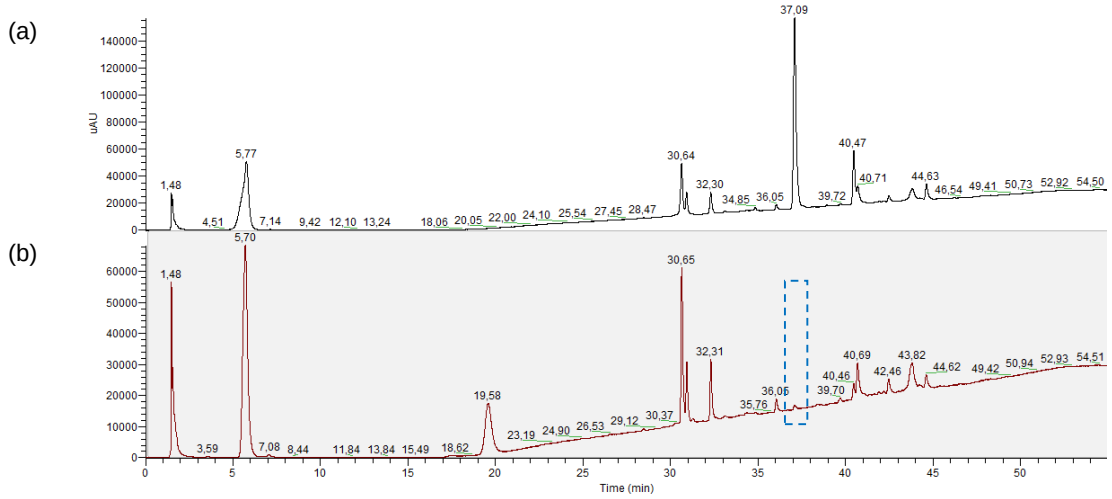


Figure 3.3. HPLC-DAD chromatogram of the organic compounds in aqueous solution using (a) Oasis HLB and (b) Strata-X.

Two hypotheses arise for the Strata-X results: (i) the compounds reached their breakthrough volumes or (ii) the compounds have high capacity factors and were strongly retained, preventing recovery for the experimental elution conditions. To assess the problem, another extraction procedure was performed with the Strata-X using the same method but, till point 5, elution 1, after which:

6. the rejected matrix was re-extracted using Oasis HLB (same procedure) and the sample analysed to verify if the compounds were not being retained in the cartridge (breakthrough volume)
7. the Strata X cartridge was re-eluted two more times with 2x2 mL of MeOH and the samples were analysed (elution 2 and elution 3). This aimed to verify if problem was poor recuperation and if by using higher volumes of MeOH the analytes would be eluted.

A basic scheme of the process can be seen in Figure 3.4.The obtained chromatograms showed that the compounds were not being detected after re-extraction of the matrix in the Oasis HLB (step 6). So, the low recuperation of compounds in the Strata-X was assumed, according to data, to be caused by a high retention in cartridge. MBPh started to be recovered after eluting the cartridge with 8 mL (elution 2, step 7). To promote an effective elution of the compounds from the Strata X cartridge, higher volume of eluent would be needed.

Oasis HLB probably presented better results due to the hydrophilic-lipophilic balance of the polymer phase [195], making it able to retain but also promoting the easier elution of both polar and non-polar compounds (log K_{OW} from -0.07 to 5.76).

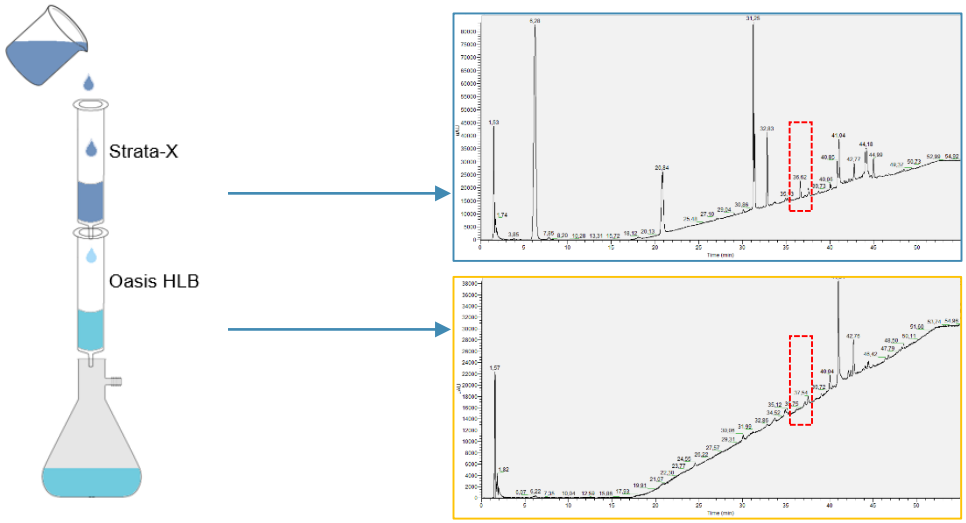


Figure 3.4. Scheme for Strata-X control experiments and chromatograms obtained by HPLC-DAD.

As the Oasis HLB require lower elution volume to achieve recoveries above 80% it was the phase of choice to perform the extraction of the analytes. The extraction was validated for the electrolyte samples concerning soil experiments, and for the electrolyte and effluent regarding the SS experiments. For optimization the following parameters were evaluated, analytical method thresholds (detection and quantification) and recoveries. The difference between the methods, is the amount of MeOH used in the elution step. For the soil experiments a total of 4 mL were used, whereas in the SS experiments 6 mL were used. This was due to matrix effects in the extraction. As SS is a highly complex matrix that contains higher organic content, a higher amount of MeOH was needed to achieve good recoveries**.** The washing step was not performed to avoid losses of Caf due to its low capacity factor. Method limits (MLD and MLQ) and recoveries can be seen in Table 3.2.

Recoveries were between 84 and 110% for the spiked electrolyte samples in both cases, and between 82 and 87% for the SS effluent. The lower recoveries achieved for the effluent are expected due to matrix effect.

Table 3.2. SPE extraction recoveries and method limits for the soil and sewage sludge experiments.

	Soil [a]			Sewage sludge [b]			
Compound	**Electrolyte Recovery (%)**	**MLD (µg/L)**	**MLQ (µg/L)**	**Electrolyte Recovery (%)**	**Effluent recovery (%)**	**MLD (µg/L)**	**MLQ (µg/L)**
Caf	99	0.25	0.8	97	86	0.55	1.7
BPA	95	0.60	1.9	96	85	0.70	2.1
E2	89	3.1	9.5	89	83	1.4	4.2
EE2	86	2.4	7.5	90	87	3.0	9.0
Ibu	84	3.6	11	87	87	3.4	10
MBPh	102	0.85	2.6	100	84	0.80	2.4
TCS	106	3.3	9.8	110	82	3.3	10
NP	88	3.4	10	91	85	3.3	10
OP	89	1.6	4.8	87	83	1.1	3.3

[a] Analysis performed with the HPLC method developed for the soil experiments.
[b] Analysis performed with the HPLC method developed for the SS experiments.

3.1.3. Ultrasonic assisted extraction (UAE)

The UAE extraction procedure was adapted from previous works [192] and validated for the compounds under study. The validation procedure of the entire method was carried out using spiked soil (1 mg/kg). Recoveries were determined as the average of 3 analyses of soil samples spiked with the OCs under study and extracted following the UAE procedure described in section 2.3.8.2 (page 60). All results can be seen in Table 3.3.

Table 3.3. UAE extraction recoveries and method limits for the agricultural soil samples.

Compound	**Recovery (%)**	**MLD (µg/kg d.w.)**	**MLQ (µg/kg d.w.)**
Caf	89	1.5	4.9
BPA	85	3.6	11
E2	84	19	58
EE2	87	15	46
Ibu	81	22	64
MBPh	99	5.2	15
TCS	110	20	59
NP	87	21	62
OP	88	9.7	29

Recoveries were between 81 and 110% for the spiked soil. This findings supports that potential sonochemical degradation was not significantly affecting extraction efficiency [162]. The MLD varied between 1.5 and 22 µg/kg d.w. whereas MLQ was between 4.9 and 28 µg/kg d.w..

3.1.4. Quick Easy Cheap Effective Rugged Safe extraction (QuEChERS)

QuEChERS extraction procedure was adapted from the method developed by Peysson *et al.*, [193]. The validation procedure of the entire method was carried out using spiked sludge. All SS samples were previously analysed and the signal corresponding to the traces of the target compounds was deleted. Recoveries were determined as the average of 11 analyses of spiked sludge samples. Sewage sludge samples (not spiked) were also extracted and the extract was spiked with the OCs under study (S_{sludge}) to evaluate the matrix effect. Matrix effect was calculated by comparing the response obtained for the standards directly injected in the mobile phase ($S_{solvent}$) and the response for the same amount of standard added to the already extracted sample (S_{sludge}). All results can be seen in Table 3.4.

Table 3.4. QuEChERS extraction recoveries and validation parameters for the sewage sludge samples.

Compound	Recovery SE (%) [a]	Matrix effect (%)	Recovery (%) [c]	Repeatability (CV %)	Intermediate Precision (CV %)	MLD (mg/kg d.w.)	MLQ (mg/kg d.w.)
Caf	102	+ 2	99	18	16	1.5	4.8
BPA	83	- 17	87	13	9.0	2.0	5.9
E2	93	- 7	98	29	5.4	3.9	12
EE2	89	- 11	84	28	7.3	8.4	26
Ibu	55	- 45	62	8.7	8.3	9.4	28
MBPh	91	- 9	94	14	8.5	2.2	6.6
TCS	83	- 17	91	29	6.4	9.2	28
NP	82	- 18	97	28	15	9.2	28
OP	83	- 17	95	8.3	15	3.1	9.2

[a] Recovery for the spiked extracts; [b] Recovery for the spiked SS;

Repeatability presented values between 8.3 and 29% whereas intermediate precision was between 5.4 and 16% for the spiked sludge. In some cases the matrix effect was very low (Caf, +2%). With the exception of Caf, all compounds presented suppression of the signal due to matrix effect, with Ibu presenting a decrease of 45%. Still, all compounds presented recoveries above 80%, except Ibu that presented a recovery of 62%.

Given the wide range of target analytes, MLD varied between 1.5 and 9.4 mg/kg d.w. whereas MLQ varied between 4.8 and 28 mg/kg d.w. Comparing to other methods, lower MLD and MLQ values can be obtained if other chromatographic methods are used. Peysson *et al.* [193] achieved a MLQ of 68 ng/g by using liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS).

3.2. Metalloids removal from mine soil

3.2.1. Soil characterization and pH desorption tests

The study was conducted using a soil collected from a mine area located in southern Hunan Province, China (Table 3.5). The soils texture presented 33% of clay, 9% of silt and 58% of sand being classified as Sandy clay loam soil. The concentration of As and Sb in the soil was 65.8 ± 0.8 mg/kg, 547 ± 0.8 mg/kg, respectively.

Table 3.5. Characterization of the soil (Lengshuijiang soil) used in the experiments.

Parameters	Content
Clay content (<2 µm) (%)	32.8
Silt content (%)	9.1
Sand content (%)	58.1
Textural classification	Sandy clay loam
pH_{H2O} (1:2.5)	6.3
Organic carbon (g/kg)	45.1
Cation exchange capacity ($cmol_{(+)}$/ kg)	14.5
Initial concentrations (mg/kg)	
As	65.8 ± 0.8
Sb	547 ± 0.8
P	668 ± 9.7

Desorption tests (Figure 3.5) showed that alkaline conditions promote both As and Sb desorption from the soil. Metalloids extraction was very low at pH below 7, after which desorption started to increase. As was extracted more 70% than Sb.

The soil amendment with P decreased both metalloids desorption (-58% for Sb and -35% for As).

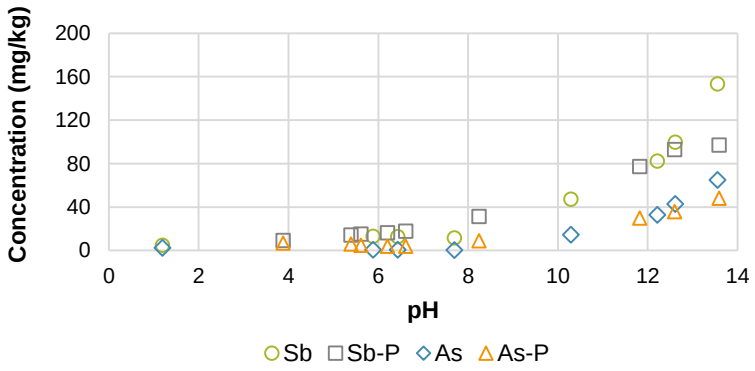


Figure 3.5. Concentration of as and sb extracted as a function of ph in batch extraction experiments for soil with P-ammedment: As-P, Sb-P; and soil without amendment: As, Sb.

3.2.2. Electrokinetic remediation

The feasibility of anolyte conditioning with NaOH and/or phosphate soil amendment on EK remediation of a mine soil contaminated with As and Sb was tested in a laboratory cell (Table 2.2, page 42). The electrolysis reaction at the anode caused a pH decrease in the anode compartment (Table 3.6) in the experiments without pH control (E1 and E3).

Table 3.6. Soil pH and EC and metalloids content after application of electrokinetic remediation.

Experiment	Electrolyte	pH	EC (mS/cm)	Concentration (mg/L)		Removal (%) [a]	
				As	Sb	As	Sb
E1	Anolyte	2.0	5.51	0.35	0.65	0.6	0.1
	Catholyte	10.8	0.41	0.02	0.13		
E2	Anolyte	12.4	11.5	3.63	3.28	6.1	1.0
	Catholyte	13.0	26.7	0.35	2.38		
E3	Anolyte	2.7	0.92	0.67	0.57	1.0	0.1
	Catholyte	9.9	0.89	0.00	0.01		
E4	Anolyte	12.5	10.6	11.01	7.03	17.3	1.9
	Catholyte	12.8	22.4	0.40	3.16		

[a] Sum of the concentration found in the anolyte and catholyte divided by the initial concentration.

In the experiment with P-amendment, E3, soil pH was less affected by the alkaline front, as OH^- electromigration may have been inhibited as the soil section near the (S5) presented a pH of 8.84 (Figure 3.6). The H^+ and OH^- ions may react during the EK process to form water [196] and, therefore, the neutralization of OH^- ions near the cathode often keeps the pH low or closer to neutral.

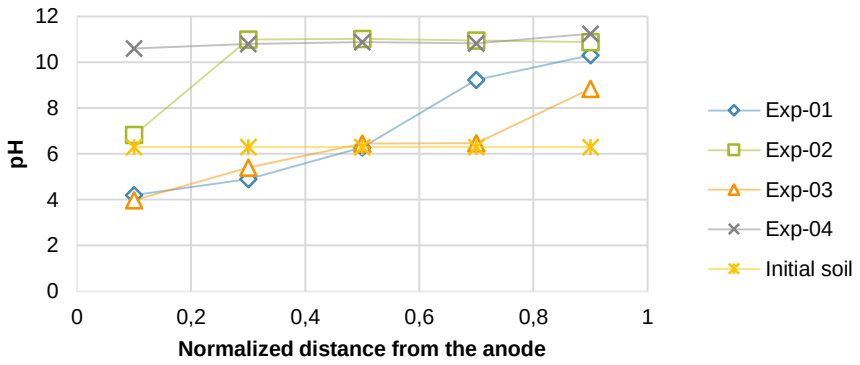


Figure 3.6. Soil sections pH after the electrokinetic process.

This was observed in E3, between soil sections near the cathode (S3 and S4), where the pH was 6.23. The pH of the anolyte buffered with NaOH was approximately 13.0 so, the soil pH near the anode (soil section S1) should have increased in the controlled experiments due to the neutralization of H^+. This was observed for E4 (S1 pH 10.59) but not for E2 (S1 pH 6.83). The low pH near the anode in E2 may be due to the dissociation of different species that released H^+ ions and may be responsible for this decrease.

Controlling soil pH during EK was beneficial for increasing contaminant solubilisation and their migration from the soil region adjacent to the anode. The highest removal rate was achieved after 90 days, for the experiment where both anolyte conditioning and phosphate amendment were performed, ca. 17% of As and 2% of Sb was removed from the soil (Table 3.6). The amount of both metalloids collected in the anode reservoir was higher than in the cathode reservoir for all EK experiments (e.g. for As in E4, 11.01 ppm in the anolyte *vs* 0.40 ppm in the catholyte). As the EOF was occurring to the cathode end, the results corroborating that As and Sb removal was directly related to electromigration rather than electroosmosis mechanism.

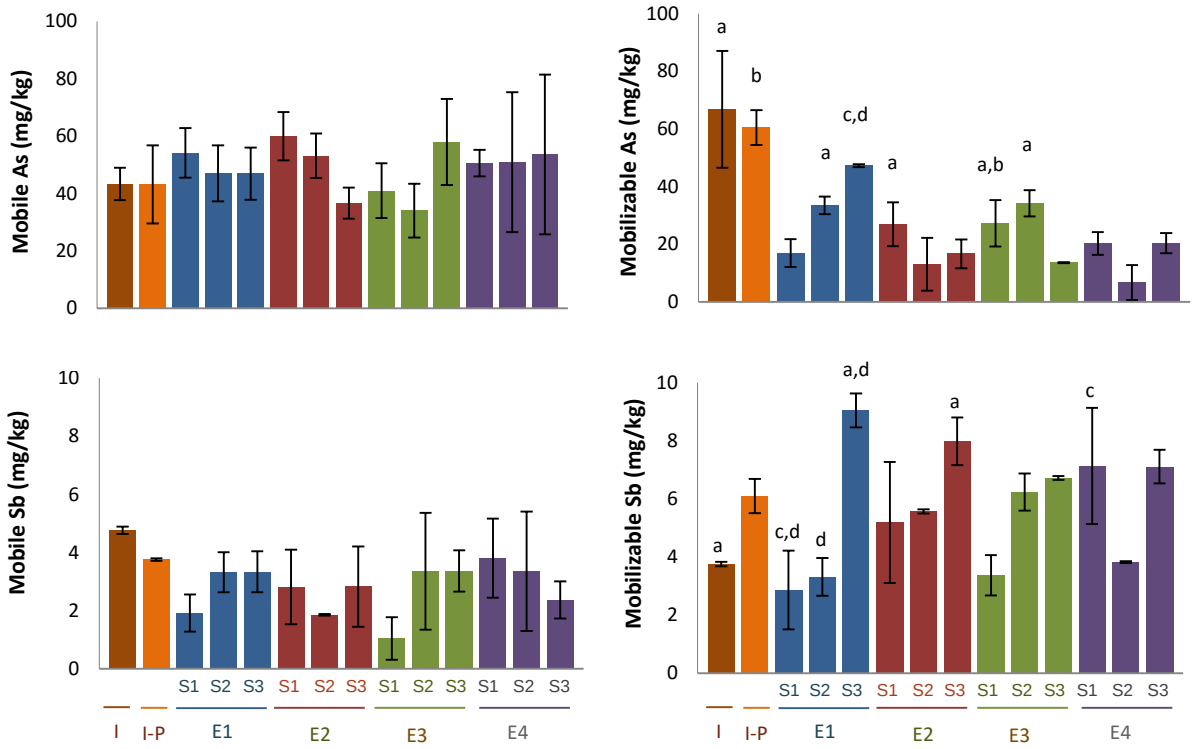
In this experiment lower remediation efficiencies were obtained comparing with literature. Better efficiencies for As removal were achieved for a contaminated soil through anolyte conditioning with NaOH [197], up to 43%, and with EDTA, 45% of As(V) for a spiked soil [198]. It must be noticed that when remediation schemes are applied to spiked matrices they usually present higher remediation although they are less “environmentally” reproducible. The electrolyte conditioning has the advantage of not only increasing the removal of As but also decreasing energy consumption [199]. Another option to improve remediation efficiencies is to couple EK with other technologies.

3.2.2.1. Mobile and mobilizable fractions

After a two-step extraction (Figure 3.7), to simulate the mobile (most available to biota and most easily leached to groundwater) and mobilizable fractions, the initial soil contained 43 ± 6% of the As in a mobile form and 67 ± 20% as mobilizable, with no statistical difference between fractions (p<0.05). For Sb, both fractions are low, 4.8 ± 0.1% and 3.8 ± 0.1%. When phosphate was added, no significant differences were found in the amounts of the fractions for both metalloids in relation to the initial soil. The high fraction of mobile As in the mine soil indicates that there is an environmental risk, as As can be potentially released to other environmental compartments. The obtained values reflect the fact that Sb is strongly bounded to the soil and thus less mobile in the environment. Still, 4% of mobile Sb represents a mean value of 26 mg of Sb *per* kg of soil that can be potentially released to the environment.

Comparing to the initial soil, the application of EK decreased the value of mobilizable As fraction, but no changes in the mobile form was observed. This means that the application of EK affected this fraction either by (i) changing this soil fraction characteristics and consequently decreasing the mobilizable As present or by (ii) making it mobile and removing it towards the electrode compartments. In E1, a difference (p<0.05) was found between the section near the anode (S1) and the section adjacent to the cathode (S5), with the highest mobilizable As being detected in S5. This was probably due to the pH

difference between both soil sections (Figure 3.7), with a higher pH resulting in a higher amount of mobilizable As (corroborating desorption results).



a – statisticaly different from I at p<0.05.
b – statisticaly different from I-P at p<0.05.
c – statisticaly different from E1-S1 at p<0.05
d – statisticaly different from E1-S5 at p<0.05

Figure 3.7. Fraction results for arsenic and antimony mobile and mobilizable fractions for the soil before and **a**fter EK (I - initial soil; i-p - initial soil with P- amendment).

For Sb, after applying EK to the soil, no statistically significant differences were found between the mobile fractions, comparing treatments and initial soil. Contrary to As, the mobilizable Sb fraction did not present significant changes after applying EK. This explains the low removal percentages achieved for this metalloid in the treatments tested in this work.

3.2.3. Electrokinetic enhanced phytoremediation

Phytoremediation alone and coupled with electrokinetic was also tested for the remediation of the contaminated soil (Table 2.2, page 42). Two plants were used, Indian mustard (*Brassica juncea*) and ryegrass (*Lolium perenne*). The experimental set-up can be seen (Figure 3.8)

In contrast to the experiments in the stationary EK cell, only a slight pH variation (less than 1) was found in the EK enhanced phytoremediation (Table 3.7), with no deleterious effect being observed in root biomass due to pH changes, e.g. acidification in anode compartment [140].

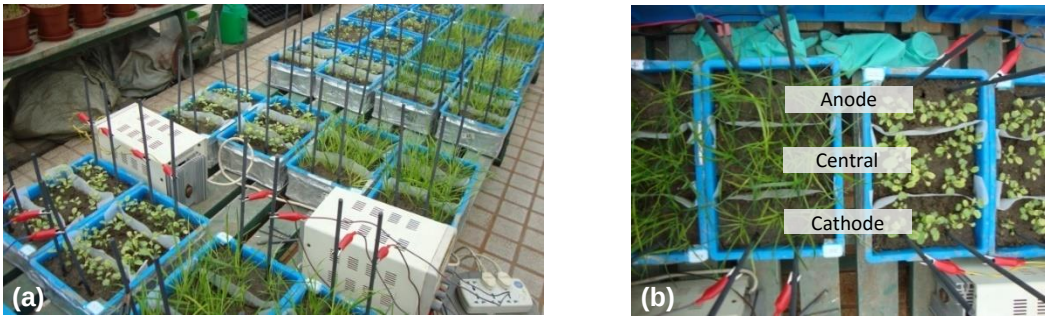


Figure 3.8. Boxes with contaminated soil and EK treatment: (a) experiment overview and (b) details of experimental boxes with ryegrass at left and Indian mustard at right.

Assuming that the presence of plant alone presented an average biomass of 100% a comparison was carried out between applied treatments. The P-amendment (T2) may act as fertilizer but its positive effect was only observed in Indian mustard root being statistically higher than the control in central compartment (301±108%). EK treatment (T3) enhanced Indian mustard belowground biomass, namely at central compartment (approx. more 124%) but lower effects were observed in ryegrass. Coupling P-amendment and EK (T4) resulted in an increase of shoot and root biomass in ryegrass (namely in central compartment) and a more pronounced increase in Indian mustard biomass comparing with plant alone (approx. more 263%). The increased concentration of elements in soil solution, due to the presence of DC field, makes them bioavailable to plants resulting in a positive effect on the growth of both species. Higher applied voltages (2 and 4 V/cm) had also been reported as decreasing plant biomass but a lower voltage (1 V/cm) had a positive effect on plant growth [141], as observed in this study.

Regarding soil nutrients, potassium electromigrated towards cathode compartment in the treatment with combined technologies and available nitrate was redistributed between soil compartments in the presence of EK, with or without phosphate amendment. Between plant species, there was a similar pattern of nutrient distribution suggesting that, for the tested conditions, the used plants did not directly affect the nutrients distribution but factors such as the application of a DC electric field did it. Urease slightly decreased in the presence of EK but increased in the presence of ryegrass with or without phosphate amendment and also increased in the presence of Indian mustard. The activity of neutral phosphatase did not significantly change (p<0.05) between the applied treatments.

The concentration of As and Sb in Indian mustard shoot and root tissues was statistically higher (p<0.05) than the one observed in ryegrass (Table 3.7). Comparing with ryegrass root system, Indian mustard accumulated more 64% As and 62% Sb, with P-amendment more 89 and 81%, with EK process more 71 and 48% and with the coupled technology (P-amendment and EK process) more 91 and 72%, respectively. But attending to the higher biomass of ryegrass total uptake may be counteracted.

Table 3.7. pH values and As and Sb levels in ryegrass and Indian mustard after the different applied treatment (mean and standard deviation are shown n = 3).

			As (µg/pot)			Sb (µg/pot)		
Exp.	**Plant**	**pH final**	**Root δ**	**Shoot δ**	**Total¥**	**Root δ**	**Shoot δ**	**Total¥**
T1	Indian mustard	≈ 6.5 *	0.9±0.4	78.4±8.1 i, j	79.3	3.2±1.2	108.2±15.1 k, l	111.4
	ryegrass	≈ 6.5 *	1.2±0.6	85.7±14.9	86.9	1.3±0.6 a	118.1±9.2 a	119.4
T2	Indian Mustard	≈ 6.5 *	2.0±0.6 m	287.7±32.9 b, i, m, n, o	289.7	2.3±1.1 p	404.4±99.5 d, k, n, p, q	406.3
	ryegrass	≈ 6.5 *	1.8±1.0	94.6±52.0 b	96.4	1.3±0.6 c	123.1±53.9 c, d	124.4
T3	Indian Mustard	6.2 - 7.2	1.1±0.7 r	174.9±72.8 o, r, s	176	5.0±2.5 t	197.4±22.1 q, t, u	202.4
	ryegrass	6.1 - 6.9	1.8±0.4	94.9±4.7	96.7	1.5±0.6 e	118.6±9.3 e	120.1
T4	Indian Mustard	5.9 - 7.5	1.9±0.5 v	333.7±63.7 g, j, s, v, w	335.6	2.6±0.8 x	440.6±84.2 h, l, u, w, x	443.2
	Ryegrass	6.3 - 7.2	1.2±0.2 f	142.5±13.9 f, g	143.7	1.2±0.2	195.0±16.8 h	196.2

Legend: box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK

* Minimum and maximum values between 6.4 and 6.7

δ Same letters indicate statistically significant differences among different treatments, metalloids or plant tissues ($p<0.05$).

¥Total As and Sb levels (calculated using metalloids concentration and biomass values of each plant tissue) in ryegrass and Indian mustard after different treatments (µg/pot).

Taking into consideration total biomass at the end of the experiments, the total uptake of Indian mustard (T1) *per* pot achieved less ca. 9% of As and 7% for Sb than ryegrass. Indian mustard total uptake *per* pot significantly increased in all applied treatments (Table 3.7) compared with plant alone. Phosphorus amendment may also help improving metalloids uptake and this was of particular importance for Indian mustard. Compared with plant alone (T1), P-ammendment and EK process (T4) increased As (25 and 48%) and Sb (25 and 30%) uptake for ryegrass and Indian mustard *per* gram of plant, respectively. Soil metal concentrations decreased after the applied treatments although higher treatment time would have provided more extensive remediation.

The combination of phytoremediation and electrokinetics has been proposed in an attempt to avoid, in part, the limitations of phytoremediation while the adverse effect of the electric field caused by the electric current on the soil microorganisms and enzymatic activity is partially counteracted by the plant.

3.3. Organic contaminants removal from soil

3.3.1. Soil characterization

Table 3.8 presents the physical and chemical characteristics of th tree soils used, SO1 was used as a suported medium and soils SO2 and SO3 were used as spiked matrices. Soil SO1 presents a sandy texture, low content of mineral and organic colloids, which lead to a poor CEC. Soil SO2 presents a silty loam texture (with 53.4% clay), high mineral and organic colloids content, which lead to a higher CEC, whereas SO3 presents a loamy sand texture (with only 8% of clay) and lower mineral and organic colloids, which conducts to a poor CEC.

Table 3.8. Physical and chemical characteristics of the soils used in the experiments.

Parameters	Content		
	SO1	SO2	SO3
Origin	Valadares	Paul de Magos	Paul de Magos
Sand (%)	94.0	19.7	88.0
Silt (%)	3.5	26.9	4.0
Clay (%)	2.5	53.4	8.0
Textural classification	Sandy	Silty loam	Loamy sand
$pH_{(H2O)}$	6.0	5.8	5.1
Total carbon (g/kg)	-	24.6	6
Organic matter content (g/kg)	0.41	42.4	10
Cation exchange capacity ($cmol_{(+)}$/kg)	1.47	22.7	2.4
Exchangable cations ($cmol_{(+)}$/kg)			
Ca^{2+}	0.35	11.3	1.5
Mg^{2+}	0.07	5.7	0.6
K^{+}	0.07	0.5	0.1
Na^{+}	0.07	1.2	0.2
Sum of exchangable cations ($cmol_{(+)}$/kg)	0.56	18.7	2.4

3.3.2. General results

According to the experimental conditions (presented in Table 2.3, page 45) when no pH adjustment was performed, the experiment conducted with 10 mA (exp. B) presented always lower voltage than the experiment with 20 mA (exp. C), for SO2 (Table 3.9). In exp. B and C the final voltage was always higher than the initial voltage (+17.6 and +33.8 V, respectively), presenting a positive relation with current intensity (r^2 of 0.999). When pH was adjusted in the anolyte to approx. 13 (exp. D) the voltage at the beginning of the experiment was higher than at its end (-13.2 V).

In the experiments conducted with SO3 and 10 mA, voltage increased (41.5 V). As soil SO3 presents 4.5 times higher sand content comparatively to SO2, the depletion of the ions was faster and consequently the resistance in the medium increased faster.

The electrolytes and soil pH of the experiments varied as expected (Table 3.9) being acid in the anolyte and alkaline in catholyte of the EK experiments. The generation of the acid front from the anode to the cathode, transported via electromigration and electroosmosis [101], caused a pH decrease in the anode compartment of experiment B and F (between 2.2 and 2.5). A higher pH increase in the soil of the cathode region was observed in exp. D.

In the same conditions (exp. B and F), a higher pH decrease was observed when loamy sand soil was used. This is probably due to an easier mobility of the H^+ ions towards the cathode end due to loamy sand soil characteristics and EOF.

In exp. D, the anolyte that was entering the cell had pH 13 and, consequently, the soil pH near the anode chamber ($SO1_{anode}$) was higher than in the other experiments (7.54). The final SO2 pH in experiment D was 7.88, and pH 11 for $SO1_{cathode}$.

The higher volumes of catholyte obtained at the end of the experiments suggests that the EOF developed towards the cathode in all the experiments (Table 3.9), except in experiment F, but the magnitude of its flow rate was different due to the effect of electric field intensity (10 and 20 mA) and pH. When SO3 was used, initially EOF was slightly higher towards the cathode end but, after 72 h, it moved towards the anode (reverse EOF), due to the low soil pH which conducts to a positive soil zeta potential [200].

Soil characteristics also influence EOF. For example, clays have the highest electroosmotic permeability due to a high surface charge density [101]. Consequently, it was expected a higher EOF associated to the silty loam soil (SO2, 53.4% clay) compared to the loamy sand (SO3, with only 8% of clay). For the same EK conditions and the different soils used (exp. B and F), it can be observed that when the loamy sand (SO3) was used, higher accumulated volumes were collected in the cathode end when comparing to exp. B where the silty loam (SO2) was used. This result may be explained by the differences observed in soil pH (explained above). The presence of SO1 as a support medium in the middle compartment that presents a texture more similar to SO3 than SO2 (Table 3.8), may also have influenced the EOF results.

Table 3.9. Soil sections and electrolytes pH means; accumulated volume for the electrokinetic experiments.

			SO2				SO3	
	Cell section	Initial	A [b]	B [c]	C [d]	D [e]	E [b]	F [c]
pH [a]	Anolyte	7.00 ± 0.09	5.03 ± 0.35	2.34 ± 0.18	2.27 ± 0.12	2.94 ± 0.92	5.68 ± 0.58	2.90 ± 1.1
	$SO1_{anode}$	6.00 ± 0.21	5.89 ± 0.07	4.15 ± 0.12	6.59 ± 0.20	7.54 ± 0.73	5.71 ± 0.74	3.95 ± 0.11
	SO2/SO3	5.81 ± 0.13 / 5.12 ± 0.10	5.97 ± 0.05	4.67 ± 0.19	5.39 ± 0.32	7.88 ± 1.28	5.12± 0.08	3.65 ± 0.13
	$SO1_{cathode}$	6.00 ± 0.21	6.36 ± 0.26	7.65 ± 0.06	6.94 ± 0.06	9.36 ± 0.07	5.73± 0.19	5.06 ± 0.15
	Catholyte	7.00 ± 0.09	5.73 ± 0.42	11.38 ± 0.26	11.65 ± 0.14	10.97 ± 0.19	5.32 ± 0.78	10.55 ± 2.3
Voltage drop (V)	Initial	-	-	11.4	24.1	38.2	-	15.9
	Final	-	-	29.0	57.9	25.0	-	57.3
$V_{accumulated}$ (mL)	Anolyte	-	5382	4791	2520	5935	5571	5368
	Catholyte	-	5435	4992	2612	6628	5634	5263

[a] Soil sections pH was measured at the end of the experiments whereas the electrolytes were measured along the time; [b] Conducted with 0mA; [c] Conducted with 10mA; [d] Conducted with 20mA; [e] Conducted with 10 mA and pH adjustment to 13 in the anolyte.

3.3.3. Organic contaminants remediation

The percentage of OCs removed (to cathode and anode end), remaining in the contaminated soil and degraded (amount not detected comparing to the initial concentration) by EK are presented in Table 3.10 (experiments A and E were conducted without current, so the results are not shown). In the control experiments (A and E) all studied compounds were detected in SO1 soil sections (initial non-

contaminated soil) meaning that diffusion is occurring. Using soil SO2, between 0 and 2% of the OCs were detected in soil sections near the anode and cathode but slightly higher maximum amounts were detected in the control experiment using soil SO3, up to 6%.

Table 3.10. Percentage of each organic contaminant remaining, removed and degraded from the soil through the electrokinetic process carried out in experiments B, C, D and F.

	SO2									SO3		
	B			C			D			F		
Compound	**RS[a]**	**Rem.[b]**	**Deg.[c]**	**RS[a]**	**Rem.[b]**	**Deg.[c]**	**RS[a]**	**Rem.[b]**	**Deg.[c]**	**RS[a]**	**Rem.[b]**	**Deg.[c]**
BPA	21	1	68	18	n.d.	73	17	16	63	27	2	61
E2	39	n.d.	58	30	n.d.	69	45	9	45	41	n.d.	57
EE2	50	n.d.	46	35	n.d.	62	35	11	44	47	n.d.	46
TCS	26	n.d.	74	33	n.d.	66	31	4	64	28	n.d.	68
OP	24	n.d.	74	24	n.d.	74	24	1	73	36	n.d.	63
NP	50	n.d.	50	44	n.d.	54	49	n.d.	48	48	n.d.	51

[a] % OC in remaining in SO2 or SO3 = [(mass of OC detected in the SO2 or SO3 soil fraction)/(mass of OC added to the soil)]*100; [b] % OC removed = [∑(mass of OC detected in the cathode and anode end)/(mass of OC added to the soil)]*100; [c] % OC degraded = [1- ∑(mass of OC detected in all cell compartments)/(mass of OC added to the soil)]*100

n.d.: not detected, below LD

When 10 mA were applied to the cell with SO2 (exp. B), only BPA was removed from the soils with 1% being detected in the cathode end and 0.03% in the anode end. In the experiment using SO3 and 10 mA (exp. F) 2 and 0.4% of BPA were detected in the cathode and anode end, respectively. The analysis of the soil section near the anode and cathode ($SO1_{anode}$ and $SO1_{cathode}$) for both experiments showed that, although the most OCs were not detected in the anode and cathode end, they were being mobilized. In experiment B the compounds E2, EE2 and BPA were detected in $SO1_{cathode}$, and in experiment C, NP was also detected. Controlling the pH in experiment D allowed increasing OCs removal mainly towards the cathode end, after 96 h. As the best EK removal efficiencies were obtained in these conditions, this experiment will be further on discussed

The differences between compounds structure influenced their removal. For the steroids, when 10 mA were applied 39% of E2 and 50% of EE2 remained in SO2 (exp. B). When 20 mA were applied the amount remaining in the SO2 decreased to 30 and 35% of EE2 and E2, respectively (exp. C). As EE2 is more soluble than E2, when the EOF increased (exp. D), EE2 the amount present in $SO1_{cathode}$ and cathode end also increased comparatively to E2. For the plasticizers, the degradation order is BPA > OP >> NP mainly due to NP presenting low solubility and high log K_{OW}. Between 26 to 28% of TCS remained in the contaminated soils, SO2 and SO3, in all experiments.

At the end of all experiments the percentage of contaminants that remained in the soil ranged between 17% (BPA) and 50% (NP) for SO2 and between 27% (BPA) and 48% (NP) for SO3, with no statistical differences between treatments.

The parallel photo and electrodegradation experiments (section 2.2.2.3, page 45) showed that the percentage of OCs not detected in the cell is similar to the percentage that potentially may suffer photo

and electrodegradation. Therefore, was assumed that all compounds suffer photo and/or electrodegradation with estimated percentages of 52 ± 23% for BPA, 66 ± 7% for E2, 65 ± 12% for EE2, 68 ± 4% for TCS, 64 ± 9% for OP and 60 ± 7% for NP. Hydrogen peroxide, that may promote degradation of the OCs, was below LD (0.5 mg/L H_2O_2) meaning that even if it was formed during EK, it was not detected. Along the experiments the differences found in the degradation percentages could be mainly related to their chemical structures (Table 1.5, page 33).

Several studies have been conducted to assess the degradation mechanisms of the OCs [201, 202]. In the case of TCS, the phenolic ring can be activated by the two O-containing groups and may be attacked by ·OH radicals, with production of hydroxylated TCS [201]. Bisphenol A has only one electron-donating group (–OH) linked with the benzene ring. This can result in an electrophilic attack of the carbon in the aromatic ring by ·OH radicals [201]. Both NP and OP can also suffer an attack on the group (–OH) linked with the benzene ring. The E2 can be oxidized mainly by the addition of ·OH radicals through two possible ways: abstraction of hydrogen bonded with the C6 atom in the aliphatic ring (that links to the aromatic ring) or oxidation of its hydroxyl group [202]. Finally, EE2 should present a similar behaviour to E2 although the presence of the ethinyl group in EE2 may stabilize the phenolic ring and improve its resistance to an attack by reactive ·OH radicals [202]. Besides the possible reactions with the ·OH radical, all studied compounds contain a phenolic functional group, which makes them susceptible to photodegradation.

The formation of new peaks correspondent to new or related compounds was not detected in the analysis performed by HPLC-DAD (scan from 200 to 800 nm). Still, in other experiments using electro-Fenton process with Ti/MMO cathode, all the intermediates of BPA and TCS disappeared after 60 min degradation, suggesting the breakage of conjugate structures such as benzene ring [201]. Naimi *et al.*, [203] also tested the electro-Fenton process with a carbon felt cathode and platinum anode for the study of E2 degradation in aqueous-acetonitrile mixture, and after 40 min, depending on the initial concentration, a complete degradation was observed. This suggests that in the conditions here presented, 6 h at 10 mA, a complete degradation of the intermediates is a strong hypothesis.

3.3.3.1. Electrokinetic mobilization

In experiment D, OCs removal was higher due to the increased EOF towards the cathode, comparing to the other experiments. As it can be seen in Figure 3.9a, OCs mobilization due to EK along the experiment was not constant. Contaminants removal was low during the first 48 h (Figure 3.9a, point t1), after which it increases for the following 24 h (Figure 3.9a, point t2). The mobilizations rates (v), presented in Table 3.11, are defined as the amount of compound detected in catholyte in relation to the time each 24 h.

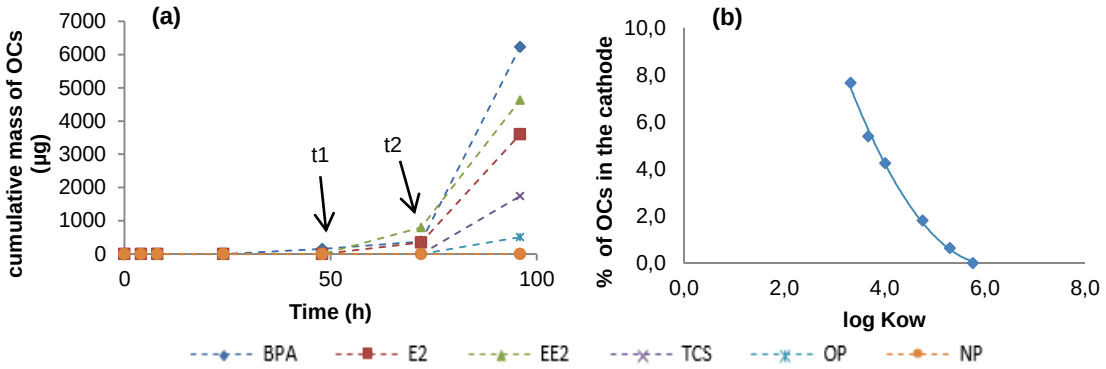


Figure 3.9. Experiment D (a) cumulative mas of organic contaminants found in the catholyte and (b) relation between the percentages of organic contaminants found in the catholyte and the logarithm of octanol-water partition coefficient.

Table 3.11. Mass of organic contaminants found in the different parts of the cell at the end of the electrokinetic process for experiment D and mobilization rate.

	µg					µg/min	
Compound	Anode end	$SO1_{anode}$	SO2	$SO1_{cathode}$	cathode end	v_{t1}	v_{t2}
BPA	n.d.	528	8307	1506	7649	0.15	4.07
E2	n.d.	95	21521	730	4235	0.24	2.26
EE2	n.d.	242	17250	4610	5379	0.55	2.66
TCS	n.d.	n.d.	15393	535	1807	0.00	1.21
OP	n.d.	76	12095	749	642	0.00	0.36
NP	n.d.	n.d.	23924	1270	0	0.00	0.00

v: mobilization rate; t1: between 48 and 72 hours; t2: between 72 and 96 hours; n.d.: not detected, below LOD

Compounds mobilization was mainly dependent on their physico-chemical properties. The lower the log K_{OW} and the highest the solubility the higher its mobilization. In Figure 3.9 can be seen the experimental direct correlation (polynomial regression, $y = 1.1374x^2 - 13.376x + 3.405$, $r^2 = 0.9961$) between the amount of OCs that were mobilized to the catholyte and the logarithm of octanol-water partition coefficient. The compounds that presented a log K_{OW} ≥4 are more tightly sorbed to the soil particles, being more difficult to solubilize and consequently more difficult to remove. Some OCs where also detected in the $SO1_{anode}$, but not in the anode end

Still, some OCs physico-chemical properties also depend on the environmental pH to which they are exposed. In the case of TCS, the soil pH near the cathode ($SO1_{cathode}$, pH 9.36) was above its pKa (7.9). This means that in this soil section, TCS that is adsorbed to the soil will be ionised, resulting in a higher solubility and faster mobilization to the cathode end (1.21 µg/min).

3.4. Microcystins removal and phosphorus recovery from membrane concentrate

3.4.1. Membrane concentrate characteristics

The membrane concentrates (from now on designated by concentrates) were produced using water from two different dams located in the southern Portugal, *Funcho* and *Amoreiras*. The characteristics of the concentrates can be observed in Table 3.12. In all concentrates produced P concentration was between 876 and 1660 µg/L. Conductivity varied between 804 and 4357 µS/cm, turbidity 5 and 300 NTU, DOC between 32 and 54 mgC/L and the UV absorbance between 0.21 and o.63 at 254 nm. The differences found are mainly related to the distinct characteristics of each water sample used in the NF process. Four of the concentrates used in the work were spiked with MC-LR with a concentrations range between 16 and 43 µg/L.

Table 3.12. Characteristics of the membrane concentrates used in the experiments.

Memb Conc.	Dam	pH	Conductivity (µS/cm)	Turbidity (NTU)	DOC (mg C/L)	UV254nm (1/cm)	P (µg/L)	MC-LR (µg/L)
1	Funcho	8.4	4357	5.1	-	0.63	1660	-
2		8.4	2630	30.0	-	0.39	1429	-
3		8.3	1476	188	32.0	0.36	1495	-
4		8.3	1276	146	26.2	0.31	1245	42.9
5		8.2	804	80.7	31.0	0.20	900.5	36.7
6	Amoreiras	8.5	1635	33.0	28.8	0.25	876.2	16.5
7		8.3	2980	281	42.8	0.51	1442	21.1
8		8.4	3000	300	54.1	0.48	1250	-

Legend: DOC – Dissolved organic carbon.

3.4.2. Phosphorus recovery

In the first set of experiments (Table 2.4, page 47), the ED process in a 3c-cell was carried out till the current intensity reached zero. At the end of the experiments, in the 3c-cell set-up there was a decrease in the concentrates pH (Table 3.13) probably due to water splitting at the surface of the AEM and the H^+ that pass through (as it is not a perfect rectifier) in the 3c-cell setup. Conductivity of the concentrates also decreased in all experiments. Different applied currents resulted in differences in the voltage drop between the two working electrodes when the same concentrate was used (T1 and T2, #1). When a concentrate with lower conductivity was used (T3, #2) the experiment finished after 6.5 h.

Phosphorus ED removal from the concentrates presented recovery rates above 70% (Figure 3.10). In T3 the final P concentration in the concentrate was even lower than LQ (0.05 mg/L). Due to concentrates pH, P was mainly in its anionic forms ($H_2PO_4^-$/HPO_4^{2-}), implying its preferential movement from the central cell compartment towards the anode compartment. The best P recovery was achieved in experiment T3, with a total P recovery of c.a. 72%. The mobilization of P during the ED process was also followed and being similar between experiments, as an example, its mobilization during T3 experiment is shown in Figure 3.11.

Table 3.13. pH, conductivity and voltage drop between working electrodes obtained in the electrodialytic experiments of set-1.

Experiment	Anolyte		Catholyte		Membrane Concentrate					
	pH		pH		pH		Conductivity (µS/cm)		Voltage drop (V)	
	Initial	final	Initial	final	Initial	final	Initial	final	Initial	final
T1	7.54	2.08	7.53	9.29	8.16	7.70	4357	23	7.1	97.3
T2	7.50	2.32	7.52	8.34	8.16	7.81	4357	24	11.2	97.2
T3	8.00	2.15	7.50	8.30	8.50	7.00	2630	7	12.3	97.3

During the first 2 h of experiment, almost no movement of P was inferred by observation. In fact, the observed lag time period till P started to be detected in the anolyte was observed in all experiments (between 2 and 3 h after the beginning of the experiments). This may be related to the time needed to promote the conditions and movement of the negative charged P (electromigration). This transport phenomena was considered the main transport mechanism in the system. In a total of 6.5 h, *ca*. 72% of P (T3) was found in the anolyte, due to electromigration. As no losses were found in the system, the remaining 28% of P could be retained in the ED cell components e.g. membranes (no additional analysis were performed).

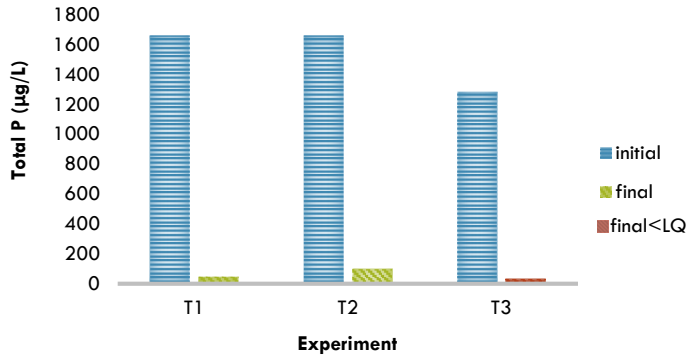


Figure 3.10. Total P present in membrane concentrate at the beginning and at the end of the electrodialytic experiments from set-1 (LQ = 30 µg/L).

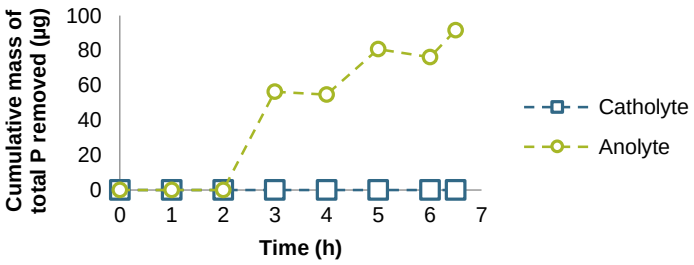


Figure 3.11. Total P measured in electrolyte solutions collected during experiment T3 (membrane concentrate #5, initial =126 µg P; values below LQ were considered as zero, LQ = 30 µg/L).

This first set of experiments showed that it was indeed possible to recover P from the concentrates in a 3c-cell. Taking, these results in consideration, further experiments were designed aiming to further study P recovery (set-2) in a 3c and 2c-cell.

In the controls of 3c (C1) and 2c (C2) cells the pH did not vary significantly between compartments but, in control C3 (electrodegradation) it followed the same tendency as in the ED experiments. In experiments A to K the pH final values varied between 2.3 and 2.9 in the anode compartment, between 5.2 and 8.3 in the central compartment and between 10.3 and 12.1 in the cathode compartment. In experiments A to F and I and K, the conductivity in the central compartment decreased (Table 3.14) compared with the initial values (Table 3.12) due to the movement of ions towards the electrode compartments. In the controls there was no significant change in the conductivity.

In both controls C1 and C2, the sum of P found in the cathode and anode compartments was less than 5% of total P. In the electrodegradation control (C3), a similar trend was observed. In this case, the low P migration (less than 5%) towards the anode compartment is explained by the used cell design as the compartments were linked through a filter paper (Figure 2.5, page 48).

Table 3.14. Final values of pH and conductivity for the experiments of set-2.

		pH			Conductivity (µS/cm)		
CODE	**Memb. Conc.**	Anolyte	Central	Catholyte	Anolyte	Central	Catholyte
C1	6	8.1	8.2	8.2	1370	802	1755
C2	6	8.1	8.0	δ	1319	δ	958
A	3	2.7	6.9	11.1	3266	28	2119
B	3	2.6	5.2	11.0	3594	36	1948
C	4	2.8	8.0	10.3	3007	31	2056
D	5	2.5	8.3	11.2	2450	51	1969
E	8	2.2	5.5	11.1	3382	266	2078
F	8	2.1	5.2	10.9	3982	47	2641
G	8	2.3	δ	10.7	2652	δ	1620
H	8	2.3	δ	9.9	2699	δ	1736
I	7	2.5	5.2	10.9	2910	109	2373
J	7	2.9	δ	12.1	3035	δ	2436
K	6	2.5	5.2	10.9	3352	23	2822

Legend: membrane concentrate in central compartment in controls C1, and experiments A to F and I to K; membrane concentrate in cathode compartment in control C2 and experiments G to H and J.
δ sample does not exist as experiments were carried out in the 2c-cell.

Throughout the experiments, the pH values in the central compartment (between 5.2 and 8.3), still corresponded to an equilibrium between $H_2PO_4^-$ and HPO_4^{2-} anions. Therefore, the majority of P migrated towards the anode compartment, with minor quantities remaining in the central (membrane concentrate) and cathode compartments (Figure 3.12).

The main parameters affecting the migration o P in the 3c-cell setup were the applied voltage and concentrates characteristics. In the 3c-cell using the same concentrates, when 10 mA were applied 84% of P migrated towards the anode compartment (exp. A) whereas the use of 20 mA (exp. B) decreased

the amount of P recovered, less 19%. By using the same ED conditions as in exp. A, but using a different concentrates, 10% less P was recovered in the anode compartment with 11% remaining in the concentrates. It was observed that conductivity influenced P recovery in the anolyte as they present a correlation coefficient (r^2) of 0.7638. In this case, P recoveries in the anolyte increased as the concentrates conductivity decreased (Appendix 2, page 151). Most likely this concentrates with lower conductivity contained less "competing species" (sulfate, carbonate, chloride, etc.) to P ions, which would benefit its migration. It was also observed that the initial P concentration was not directly influencing P recoveries (r^2 = 0.1227).

The ED 3c-cell has shown higher P recoveries comparing to the 2c-cell, in the tested conditions. For example, in the ED experiment conducted with a 2c-cell (experiments G and H; Figure 3.12g and 3.12h) only 38% and 32% of P was recovered in the anode compartment whereas in the 3c-cell recoveries were 48% and 70% (experiment E and F; Figure 3.12e and 3.12f).

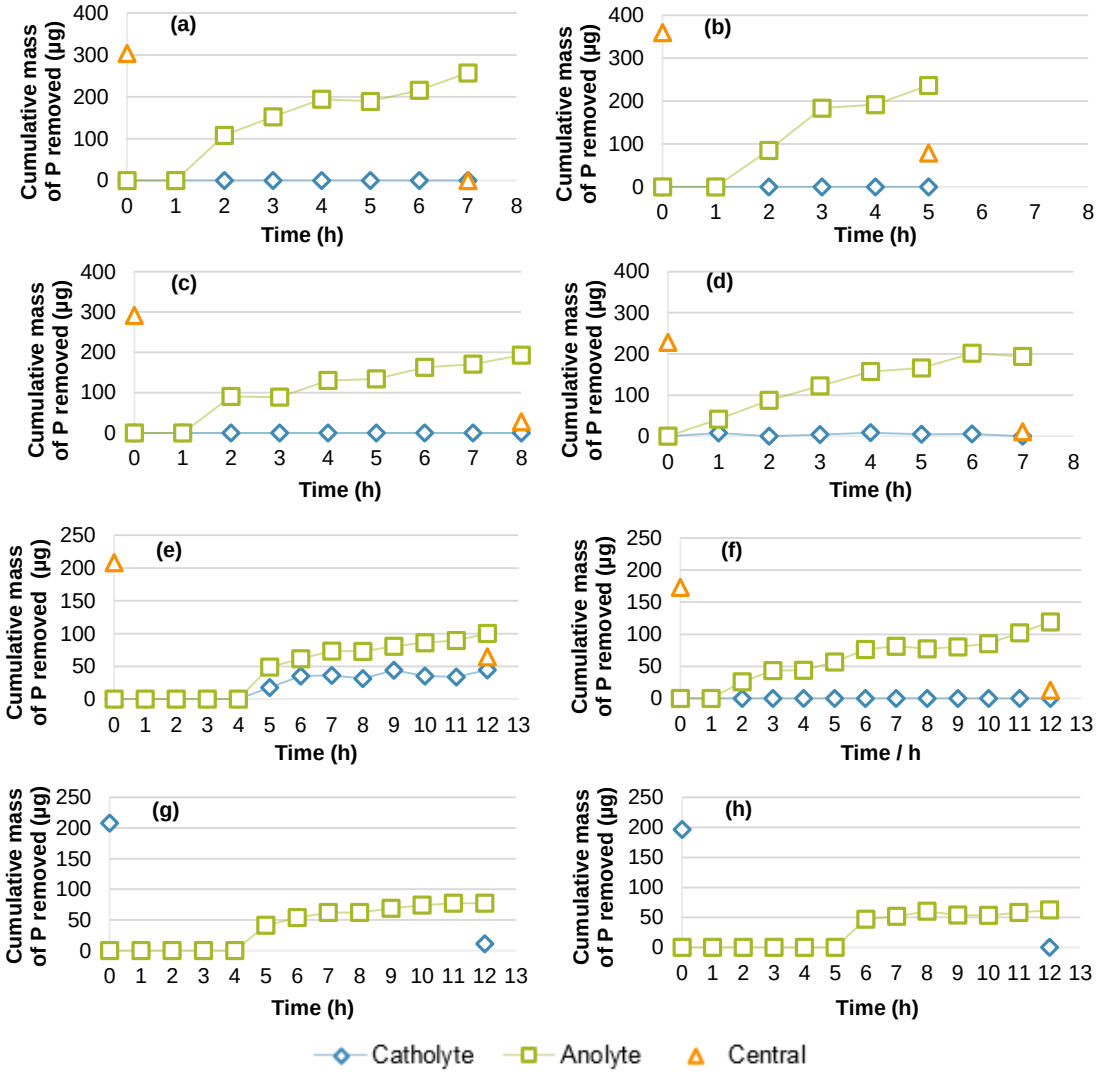


Figure 3.12. Cumulative mass of P during the ED process with: (a) to (f) 3c-cell (A to F); and (g) and (h) 2c-cell (G and H), respectively.

3.4.3. Phosphorus and microcystin separation

To the tested conditions (Table 2.4, page 47), the higher P recovery was observed in the ED 3c-cell design. As so, two different concentrates were used in this cell design to assess the performance of this configuration to simultaneously remove microcystin. Additionally, one of the concentrates was also used in the ED 2c-cell design.

The cumulative mass of P recovered in the anode compartment of ED cell designs with 2c and 3c-cell is shown in Figure 3.13.

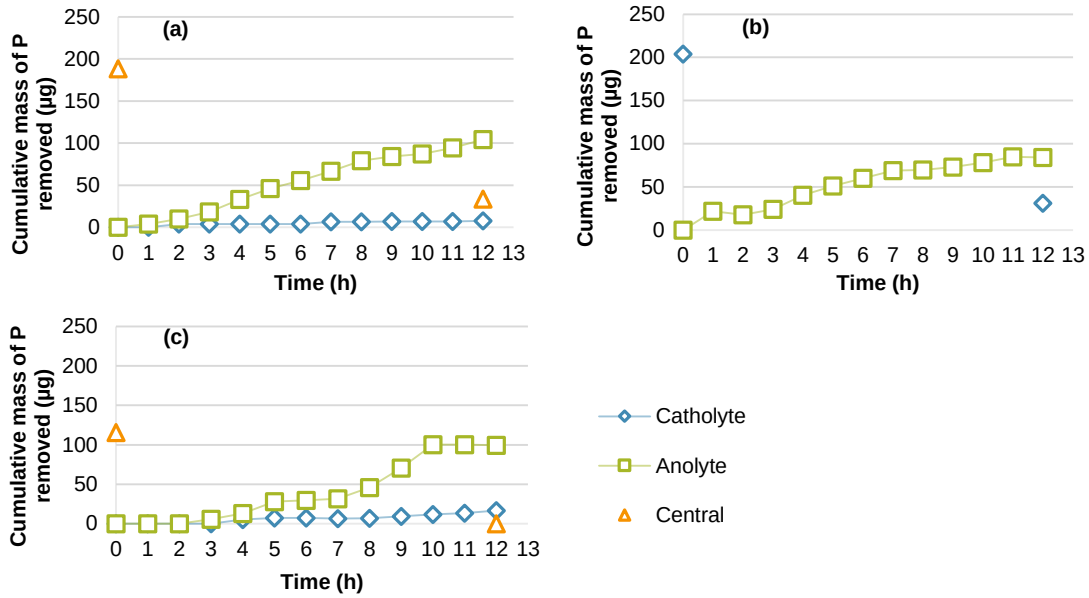


Figure 3.13. Cumulative mass of P in two ED cell designs: (a) and (c) 3c-cell (I and K); and (b) 2c-cell (J), respectively.

In terms of P recovery, in the 3c-cell 56% (exp. I) and 84% (exp. K) of P were recovered in the anolyte and 42% in the 2c-cell (exp. J). The differences between the 3c-cell experiments were mainly related with the different characteristics between concentrates. The concentrate #6 (exp. K) presents lower conductivity and lower initial P content (almost half the concentration).

The ED process not only promoted P recovery as it also showed potential to decrease microcystin concentration in the concentrates. The final concentration of microcystin at the end of the experiments is shown in Table 3.15.

In the cell controls with three (C1) and two (C2) compartments, microcystin was detected in the electrolytes compartments showing that it may pass through the AEM and CEM. In the electrodegradation experiments (C3), performed in a different cell design (see section 2.2.3.1, page 46), microcystin was not detected in all compartments. This observation supports the hypothesis that microcystin may suffer electrodegradation.

Table 3.15. Final concentration of microcystin (MC-LR) obtained for different experiments.

		Final microcystin-LR (µg/L)		
Experiment	**Memb. Conc.**	**Anolyte**	**Central**	**Catholyte**
C1	6	1.37	10.5	1.35
C2	6	1.30	-	11.9
C3	7	nd/pns	nd/pns	nd/pns
I	7	nd/pns	4.67	0.68
J	7	nd/pns	-	0.52
K	6	nd/pns	0.17	0.57

Legend: nd/pns - not detected /peak not solved

The charge of MC-LR (Figure 3.14) depends on the structure of each derivate [204]. MC-LR has a D-methylaspartic acid and a D-glutamic acid both being ionized to the anionic carboxylate forms (pKa of 2.09 and 2.19), as well as it also contains an L-arginine unit with a basic amino group (pKa of 12.48) [205, 206]. As so, MC-LR is singly positively charged in a pH lower than 2.09. With increasing pH (between 2.19 and 12.48), MC-LR loses the two protons from the carboxylic groups, presenting an overall negative charge of -1, whereas at extremely basic pH (>12.48), MC-LR loses the proton from the protonated basic group presenting an overall negative charge of -2 [204, 207, 208].

In the beginning of the experiments, the pH of concentrates was around 8, meaning that microcystin is in the form of a negatively charged ion. So, in both exp. I and K, microcystin electromigrated to the anode compartment where it may have been degraded. Reactions in the membrane concentrate compartment may have also increased removals. So, in the experiments carried out in a 3c-cell the amount of microcystin in the concentrate decreased to 4.67 µg/L in exp. I and to 0.17 µg/L in exp. K. In the 2c-cell the final concentration in the concentrate was 0.52 µg/L.

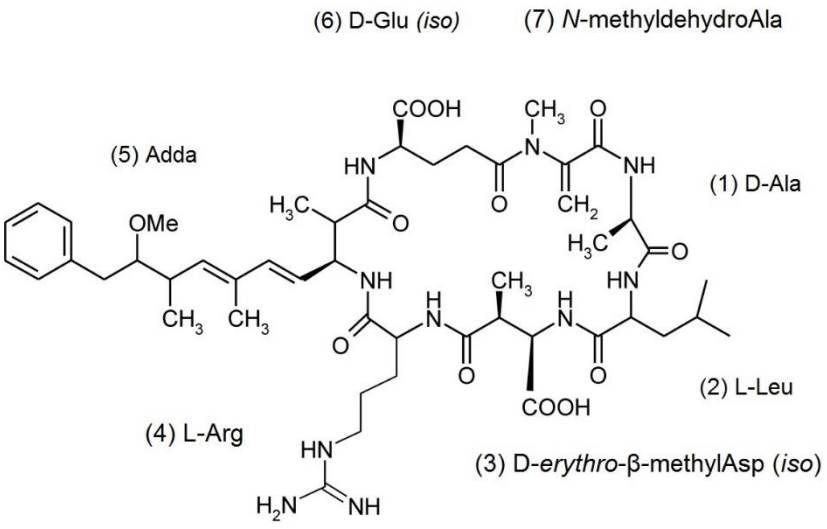


Figure 3.14. Structure of microcystin-LR [209].

It is important to mention that the performance of P recovery and MC-LR removal could have been different in the presence of a concentrate prepared from a field “natural” contamination. Nevertheless, the obtained results encourage further research for the application of this hybrid technology.

3.5. Phosphorus recovery and heavy metals removal from sewage sludge ashes

3.5.1. Chemical characterization of different Danish SSA

The characterization of fresh sewage sludge Avedøre ash (2012 and 2014), deposited (2013) and fresh/deposited Lynetten ash (2012) is presented in Table 3.16. The differences found in pH and conductivity were mainly attributed to samples heterogeneity, incineration process and sampling point (fresh or deposited). The difference in water content between deposited (up to 16%) and fresh (≤ 0.1%) ash is related with the storage conditions (e.g. e.g. air humidity, rain).

The concentration of the different elements was in the same range in all studied SSA. The P content was generally high in all SSA (between 7 and 16 wt. %). Differences in P are majorly attributed to population diet, type of wastewater treatment plant system, and type of detergents used.

Most of the studied Danish SSA were in accordance with reported literature (reported in Table 3.16). The exception was higher Cu (up to +18%), Zn (up to +22%) and Pb (up to +88%), values or lower Fe (-23%) and Ni less (-30%) concentrations. Cr concentrations was lower (between less 22 and 72%) in all studied samples compared to the literature values.

The Danish EPA has two set of limiting values for heavy metals when spreading waste at agricultural land. The dry matter (DM) related concentrations met the requirements for application in all SSA, except for Cd [2.16-3.54 mg/kg] and Ni [35.2-62 mg/kg], and Pb for one sampling period in Lynetten and Avedøre (Table 3.16). Comparing to the Portuguese limiting values, only Lynetten samples collected in 2012 (1st and 2nd samplings) do not met the requirements for application due to the Zn values (Table 3.16). However, even if the SSA complied with the legislation to be spread in agricultural land, a pre-treatment is needed to get plant available P.

Table 3.16. Characteristics of the Danish sewage sludge ash studied, including heavy metal concentrations in relation to the total dry mass (mean ± STD) and limiting values for spreading at agricultural land. Values reported in literature are also presented for comparison.

		Lynetten						***Avedøre***		**Limiting values (mg/kg)** [a]	***Literature*** [b]
		2012 (1st sampling)		***2012 (2nd sampling)***		***2013***		***2012***	***2014***		
	Parameter	***Fresh*** (1)	***Deposited*** (1)	***Fresh***	***Deposited***	***Fresh***	***Deposited***	***Fresh***	***Fresh***		
Physical and chemical characteristics	pH (H_2O)	12.44 ± 0.01 *#	8.85 ± 0.03 *	12.4 ± 0.05 *#	8.3 ± 0.03 *	12.6 ± 0.02 #	12.6 ± 0.01 #	10.4 ± 0.0 *	9.6 ± 0.10 *		
	Water content (%)	0.10 ± 0.18 *	16 ± 0.38 *	0.09 ± 0.03	14.4 ± 0.09	3.70 ± 0.04 #	3.93 ± 0.07 #	-	0.16 ± 0.01		
	Conductivity (mS/cm)	3.23 ± 0.51 *	4.81 ± 0.13 *#	7.81 ± 0.02 *	5.59 ± 0.11 *#	10.54 ± 0.21 #	9.97 ± 0.82 #	2.12 ± 0.02 *#	2.52 ± 0.14 *#		
	Loss on ignition (550 ºC; %)	0.15 ± 0.05 *#	0.92 ± 0.08 *	0.25 ± 0.05 *#	0.16 ± 0.00 *	2.58 ± 0.01 *	0.47 ± 0.04 *	0.3 ± 0.1 *#	0.57 ± 0.07 *		
	Solubility in water (%)	1.8 ± 0.1 *	3.1 ± 0.0 *	5.12	0.84	5.3 ± 0.0	5.6 ± 0.79	-	29.5		
	Gas production (mL gas/g)	1.6 ± 0.1	1.9 ± 0.2	-	-	-	-	-	-		
Elements	P (g/kg)	134 ± 1	130 ± 5	161 ± 12	-	72.5 ± 0.01 *	68.3 ± 1.5 *	112 ± 2 #	105.4 ± 3.8 #		39-123
	Al (g/kg)	22.6 ± 0.5 *	21.5 ± 0.7 *	21.2	19.5	14.2 ± 0.0	-	20.3 ± 0.5 *	22.1 ± 0.6 *		19.7-218
	Fe (g/kg)	60.0 ± 1.4	62.0 ± 2.3	44.0	-	36.3 ± 0.1	-	78.2 ± 2.9 *	53.2 ± 1.5 *		47-200
	Zn (mg/kg)	3335 ± 77 *#	3157 ± 128 *	3060 ± 222 #	2810 ± 117	2414 ± 10 *#	2270 ± 66.7 *#	2160 ± 60 *#	2410 ± 72 *#	***4000***	448-2737
	Cu (mg/kg)	758 ± 4.9 *	733 ± 9 *	711 ± 5.65 *	694 ± 6.49 *	512 ± 4 #	507 ± 7.58 #	550 ± 10 *	815 ± 18 *	***1000***	417-690
	Pb (mg/kg)	293 ± 44 #	297 ± 9	102 ± 2.15 #	99.5 ± 1.08 #	102 ± 2 #	98.8 ± 5.44 #	90 ± 1 #	253 ± 181 #	***120***	18-158
	Cr (mg/kg)	45.5 ± 0.4 #	44.9 ± 0.7 #	29.7 ± 0.66	28.6 ± 0.61	45.0 ± 0.5 #	44.9 ± 0.40 #	80 ± 2 *	47 ± 1 *#	***100***	102-136
	Cd (mg/kg)	3.25 ± 0.04 #	3.14 ± 0.08	2.21 ± 0.05	2.16 ± 0.09 #	2.2 ± 0.1 #	2.2± 0.1 #	3.4 ± 0.1 #	3.54 ± 0.35 #	***0.8***	0.4-3.9
	Ni (mg/kg)	54.6 ± 0.6	55.7 ± 1.0	35.2 ± 0.72	35.4 ± 0.58	38.9 ± 0.6	37.8 ± 0.14	60 ± 1	62 ± 1.6	***30***	50-93

* indicate statistically significant differences among pairs (columns in grey) ($p<0.05$) – t-test
\# indicate the absence of statistically significant differences inside the group of non-deposited and deposited SSA ($p<0.05$) – ANOVA
a [216]
b [217]
c [156, 192, 212, 218]
(1) samples used in the experiments aiming P-recovery (acid washing and ED process).

3.5.2. Morphology and mineral composition of deposited and fresh Lynetten SSA (2012)

Deposited and fresh Lynetten SSA from the first 2012 sampling (Table 3.16) were further analysed to assess if the deposition influenced morphology and mineral composition to assess.

SEM analysis shows that the Lynetten SSA particles generally were irregular shaped (Figure 3.15) and no major differences were found between fresh and deposited samples. Additionally, SEM/EDX analysis revealed that O, P, Fe, Al, K, Na, Mg, Si, S, and Ca were distributed all over the particle surfaces in both SSA.

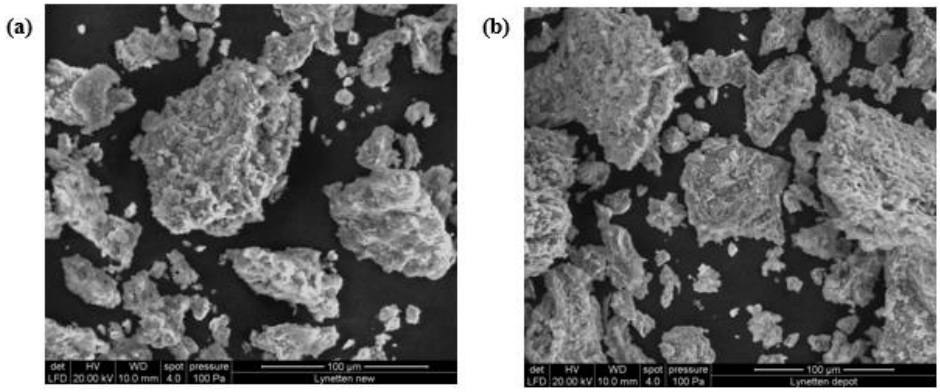


Figure 3.15. SEM micrographs of (a) fresh Lynetten SSA 2012 (b) deposited Lynetten SSA 2012.

The major mineral phases identified by XRD (presented in Figure 3.16) showed no significant differences between deposited and fresh SSA. There was $CaSO_4$ in both samples, however difficult to completely identify. In the fresh sample, it was likely present as anhydrite ($CaSO_4$) and in the deposited, it was not clear, although not anhydrite nor gypsum ($CaSO_4 \cdot 2H_2O$). However, anhydrite can be present in SSA when they are fresh but as a result of "hydration" of the SSA, gypsum may start to form [210], though this was not confirmed by XRD in the present work. In SEM/EDX a S rich region was observed and can belong to (i) an amorphous $CaSO_4$, or (ii) $Na_2SO_4/K_2SO_4/NaKSO_4$ condensed on this Ca-rich particle.

In terms of P, phosphates were indicated as calcium phosphates, but the only chemical formula clearly identified was whitlockite [$Ca_9(MgFe)(PO_4)_6PO_3OH$],

From the XRD patterns of fresh and deposited SSA samples it can be inferred that some amorphous phases are present, due to the slight hump between 2θ of 10 and 30˚, but the material is not prevalently amorphous. The amorphous phase in other ashes has been reported in literature to be between 40-74% [211].

The RIR method indicated that the mass distribution of the major crystalline phases in both SSA were as following: calcium phosphate and quartz > iron oxide and calcium sulphate.

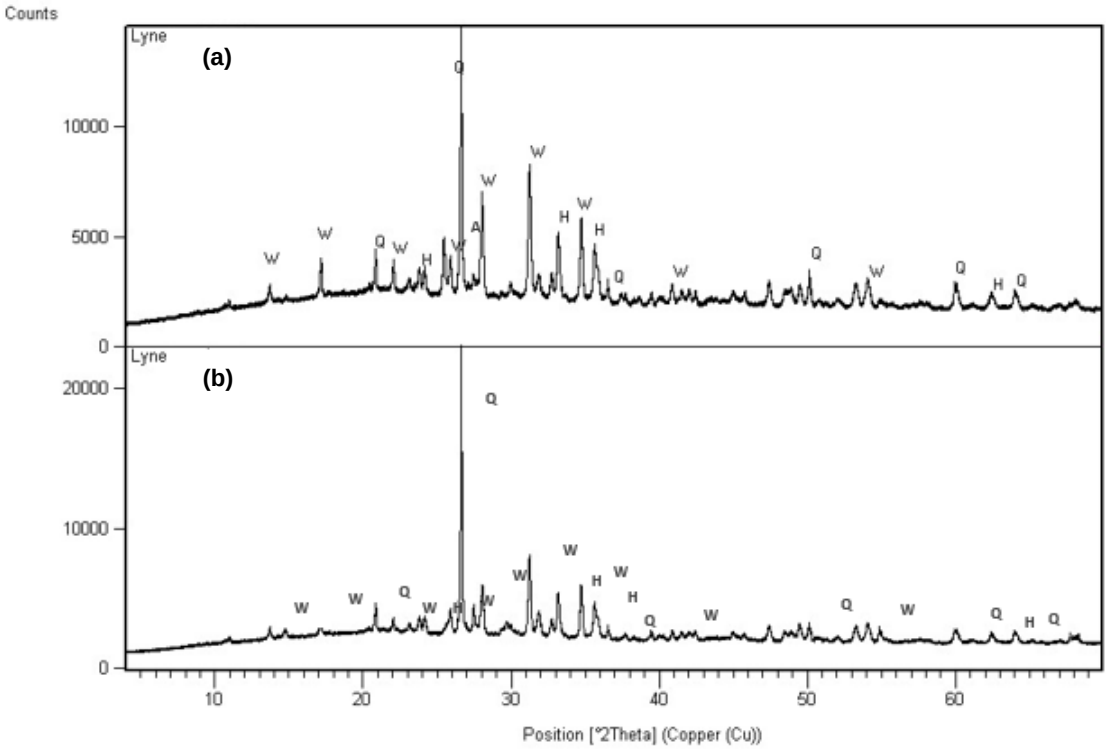


Figure 3.16. XRD diffractograms of (a) fresh Lynetten SSA 2012 (b) deposited Lynetten SSA 2012. Q – Quartz, W – Whitlockite, H – Hematite, A – Anhydrite.

3.5.3. Acid washing of ash

A total of 40% of P was extracted from the both SSA at pH approx.1.8 (Figure 3.17). Storage did not affect the extent of P extraction. Differences were observed for Cd between pH 2 and 3 as more 14% were extracted in the deposited SSA. The metals more mobilized were Zn (65%), Cu (approx. 55%) and Ni and Al (approx. 33%, Figure 6.4). Iron was strongly bound in both SSA, and even at the lowest pH, less than 2% was solubilized. This is in accordance to what was expected as the identified Fe_2O_3, is insoluble in acid [86]. As the XRD also showed the presence of $Ca_9(MgFe)(PO_4)_6PO_3OH$ but, since at low pH, only a small amount of Fe was extracted in contrast to more than 35% of P in both samples (Figure 3.17) it can be inferred that: either these two elements were generally not associated in the SSA or after solubilization Fe re-precipitated [190].

As heavy metals mobilization started approximately at the same pH than P mobilization, the obtained acidic liquid solution was a mixture with P and heavy metals, meaning that a further separation step is needed.

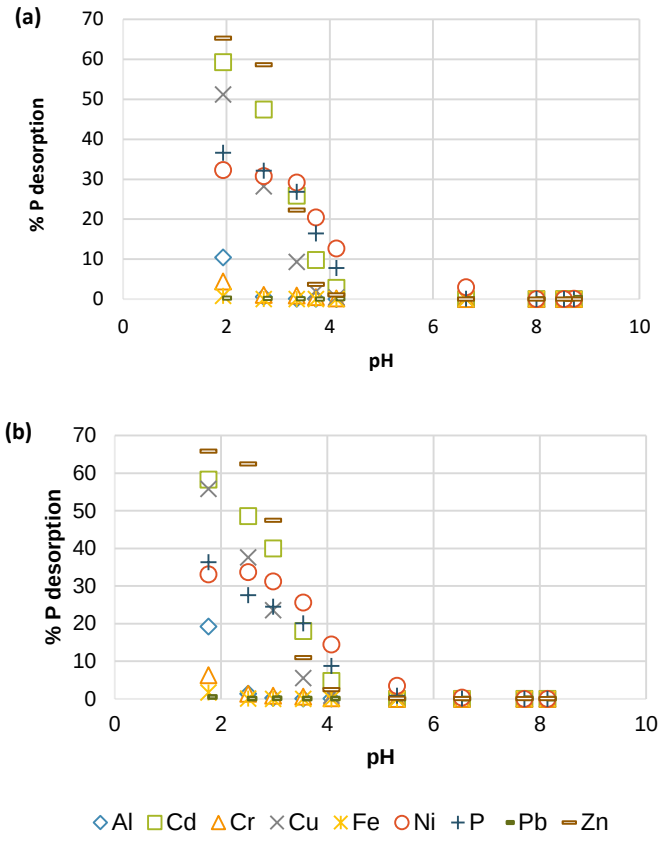


Figure 3.17. Phosphorus extraction as a function of pH in batch extraction experiments using HNO_3 on (a) fresh and (b) deposited Lynetten SSA of 2012.

3.5.4. Electrodialytic separation

3.5.4.1. Mobilization of phosphorus and heavy metals

In this study, the 3c-cell was used. The ED removal efficiency was defined as the percentage of the element removed from the SSA towards the cathode end and the anode end (cathode, electrolyte solutions and membranes). Elements found in the solid and liquid phase of the central cell compartment were not considered removed. The removal percentages were calculated dividing the mass of element removed to different parts of the cell by the initial mass. Figure 3.18 presents the distribution of elements within the cell after the ED process.

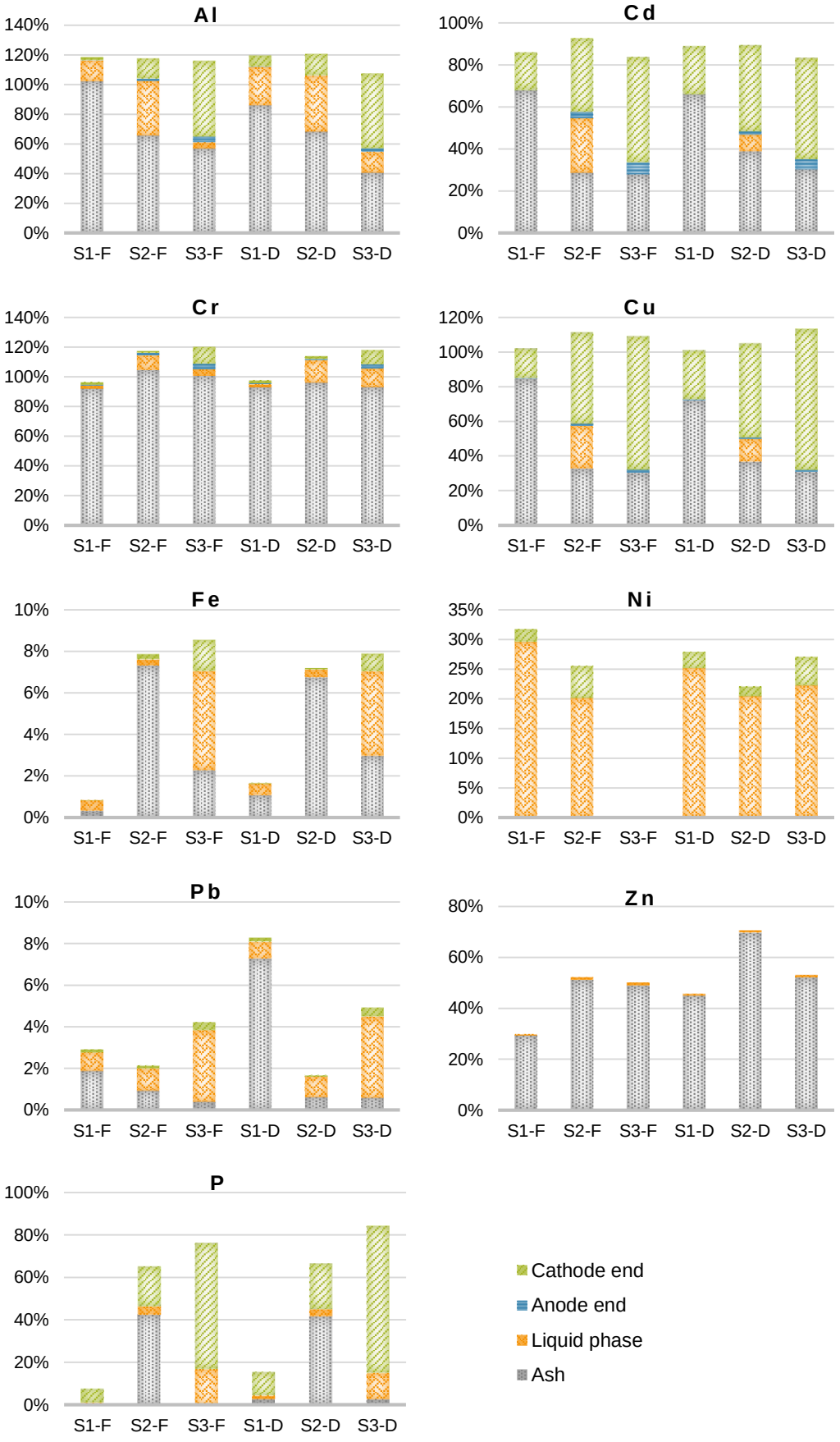


Figure 3.18. Percentage of heavy metals and P in the ED cell sections at the end of the experiments of 3 (S1), 7 (S2) and 14 (S2) days for the fresh and deposited SSA.

Time was a very important factor in these experiments with removal efficiencies increasing along the days. Along the experiments the species are continuously being solubilized from the SSA during the treatment process and transported towards the anode end or cathode end depending on their speciation. Some remain in the liquid phase, either as uncharged species or as ionic forms, to be removed as the experiments proceed. In general the desorbed metals were mainly transported towards the cathode end, showing that they were mostly present in cationic forms, whereas P was transported towards the anode end, supporting the overall separation objective of P-recover for further reuse.

The highest removal efficiency was obtained for Cu, 79 and 82% after 14 days (S3-F and S3-D, respectively) followed by Al, Zn and Cd (ca. 50%). For Fe and Pb the removal towards the electrode compartments were low (*ca*. 6%), indicating that these metals are tightly bounded to the less soluble SSA particles. After 7 days, only 20% of total P was recovered in the anode end, with almost 42% of remaining in the liquid phase of the suspension. After 14 days, 59 and 69% of P had been transported towards the anode end, while 17 and 12% P was transported towards the cathode end for the new and deposited SSA, respectively. Less than 3% of P remained in the liquid phase of the central compartment (Figure 3.18).

Similarly to the results obtained in acid washing, Fe and P were generally not associated in SSA samples as little Fe was extracted in contrast to P. However, as referred before, solubilized Fe could have re-precipitated during the ED process [190].

Using ED treatment for 14 days resulted in an anolyte solution rich in P with low heavy metal content. The anolyte has in total *ca.* 98% of P in relation to the studied elements (P plus heavy metals, Table 3.17). The ED separation of P and heavy metals was thus successful.

The analysis performed on the anolyte of SSA samples showed that 91 and 85% of total P was present in its inorganic form, for the S3-F and S3-D respectively All inorganic P in the S3-D anolyte sample was present as orthophosphate that are readily bioavailable for plants [212, 213]. In S3-F anolyte sample, the inorganic P is 92% orthophosphate and 8% polyphosphate. The presence of polyphosphates may be associated with the colorimetric method uncertainty. Still, the polyphosphate once in contact with environmental conditions may be converted to orthophosphate through hydrolysis.

Table 3.17. Concentration of elements present in the anode end after 14 days of electrodialytic treatment (mg/Kg).

Element *	S3-F	S3-D
P	79319	89018
Al	849	498
Fe	883	521
Zn	35.7	26.0
Cu	14.4	9.05
Pb	1.14	1.22
Cr	1.65	1.27
Cd	0.19	0.15
Ni	2.60	-

* Initial concentrations can be seen in Table 3.16.

3.5.4.2. Influence of cell design and acid concentration

Experiments were conducted using two cell designs, 2c and 3c-cell. Aiming at increasing the P recovery in 7 days, the acid concentration was doubled and used in the experiments with 2c and 3c-cell. An experiments with 2c-cell with 0.08 M H_2SO_4 was also done.

In the 3c-cell which main objective was to remove the P from the SSA placed in the central compartment and, through its electromigration, recover it in the anolyte to where a low migration of heavy metals is expected (mainly electromigrating to the cathode). In contrast to this, in the 2c-cell the SSA is placed in the anolyte from where the heavy metals are expected to migrate to the cathode end promoting the separation.

Table 3.18 presents the initial conditions and the changes in pH, conductivity and mass loss resulting from the ED experiments. The initial pH in the central cell compartment varied between 1.0 and 2.6 for the SSA. During the ED experiments, pH in the SSA decreased in all experiments reaching lower values in the 2c-cell (pH 1.24 in S6-D) due to the generation of H^+ in the anode compartment were the SSA is placed. The dissolution of SSA particles during the ED treatment results in a SSA mass loss [117]. In these experiments, the mass loss was between 36 and 43% (Table 3.18).

Increasing amount of ions present in the SSA suspension was seen in the 2c-cell experiments as well as an increasing conductivity at the end of the experiments. This is due to the solubilisation of ions from the SSA that remain in the anode compartment or that migrate towards the cathode, contrary to what is seen in the 3c-cell. In the 3c-cell, as the ions that are being solubilized from the SSA suspension migrate either to the anode or cathode compartments, there is a depletion of ions in the central compartment which decreases the medium conductivity.

Table 3.18. Parameters measured at the beginning and at the end of the electrodialytic experiments.

Experiment	Voltage drop (V)	SSA suspension [1]		Mass loss (%)
		pH	Conductivity (mS/cm)	
S4-F	5.1 - 4.2	2.25 - 1.61	22.2 - 11.7	41
S4-D	6.8 - 4.4	2.04 - 1.84	32.4 - 13.2	40
S5-F	6.7 - 4.3	2.63 - 1.68	9.6 - 22.5	43
S5-D	5.7 - 4.7	2.47 - 1.55	14.1 - 32.8	41
S6-F	5.0 - 4.5	2.11 - 1.28	15.9 - 32.6	42
S6-D	4.8 - 4.7	2.80 - 1.24	26.7 - 33.3	36

[1] Central compartment in the 3c-cell and anode compartment in the 2c-cell

In general, higher removals were achieved when 0.19 M of H_2SO_4 was used compared to the use of 0.08 M, independently of the cell design used (3c or 2c-cell, Figure 3.17 and Figure 3.18). The exception was Cd which removal was higher in the 3c-cell, 82% in both experiments (S4-F and S4-D) contrasting to the 23.3 and 26.7% in the S6-F and S6-D, respectively. In terms of P, approximately more 7 and 11%

of P were removed in the 3c-cell with 0.19 M of acid, comparing to the use of 0.08M (S3-F and S3-D), mainly present as H_3PO_4, (Table 3.19).

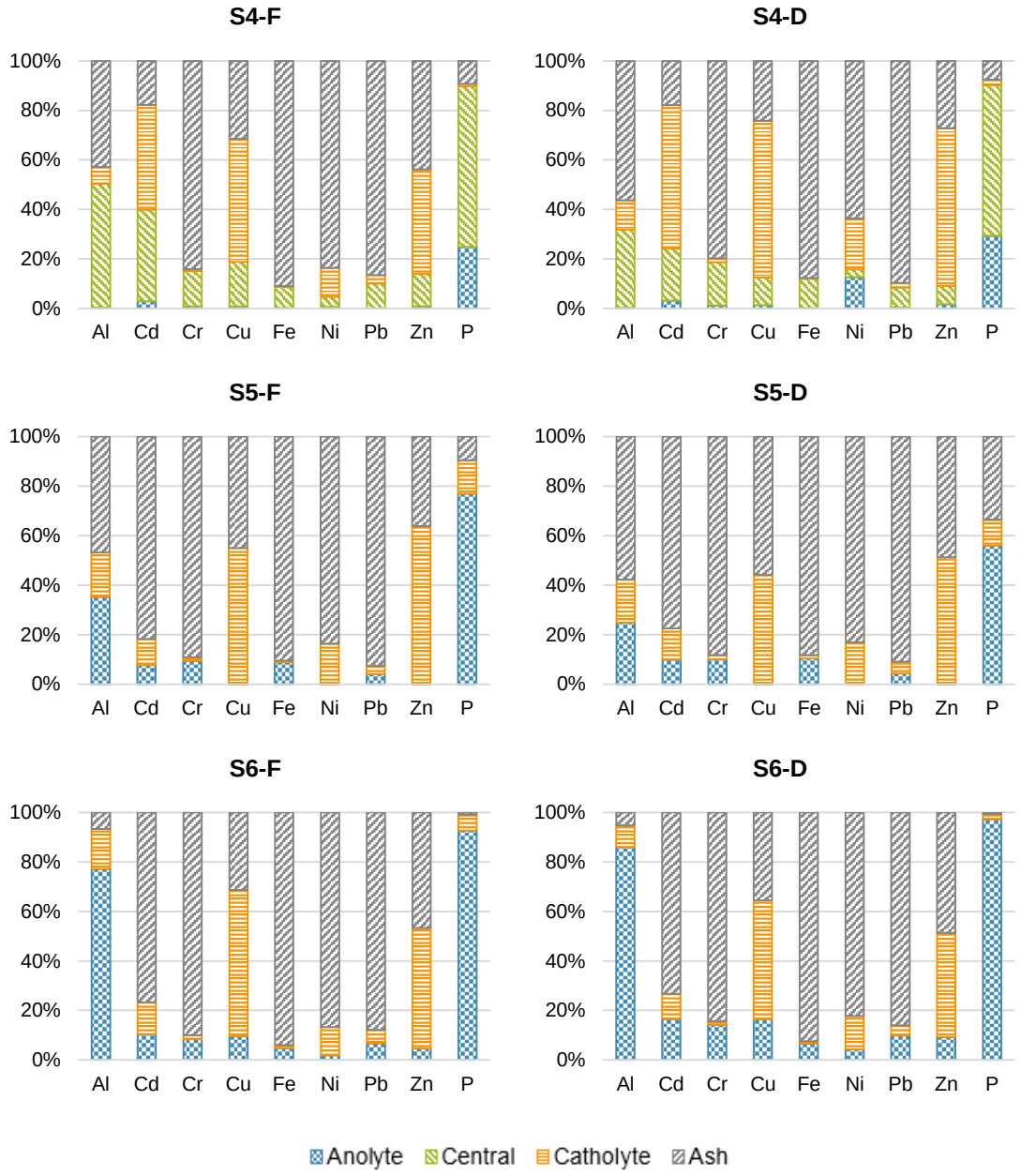


Figure 3.19. Percentage of heavy metals and P in the different matrices after the electrodialytic treatments in the 3c and 2c-cell design.

Between cell designs, the 2c-cell setup increased overall efficiency of P recovery after 7 days of experiment, under the conditions tested here. Dissolution of P seems to be faster and more complete in the 2c-cell experiments than in the 3c-cell. In the 2c-cell set-up when 0.19 M of H_2SO_4 were used, resulted in higher P solubilization from the SSA, approx. 99% in both SSA (S6-F and S6-D). From these, 93 and 97% in the S6-F and S6-D, respectively, remained in the anolyte as H_3PO_4 and $H_2PO_4^-$ (Table

3.19). Only 7% in S6-F and 2% in S6-D electromigrated toward the cathode compartment. Still, in the 2c-cell set-up, the P was not completely separated from the heavy metals as, for example, 32% of Al for S6-F and 45% for S6-D remained in the anolyte.

From the total amount of elements analysed, the anolyte solution of S6-F was constituted by 90% of P and 10% of heavy metals, whereas S6-D anolyte contained 93% of P and the remaining 8% were heavy metals. In total, approx. 125 g of P/kg of SSA were recovered in the anolytes of the S6-F and S6-D.

The type of SSA influenced the total P solubilization in 2c-cell when 0.08M of H_2SO_4 and, consequently, the amount collected in the anolyte solution. In this case, 91% of P for S5-F and only 67% for S5-D were solubilized from the SSA. From these, 14 and 11% of P (S5-F and S5-D, respectively) electromigrated to the cathode compartment, probably due to the complexation with Al, Fe and Ca forming positively charged species (Table 3.19) and 77% of P in S5-F and 56% in S5-D remained in the liquid phase (Figure 3.19).

Table 3.19. MINTEQ calculation of major species of phosphate ions for the anolyte concentrations at the end of the treatments.

Experiments	**S4-F**		**S4-D**		**S5-F**		**S5-D**		**S6-F**		**S6-D**	
Fe oxidation state	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
$H_2PO_4^-$	6.19	6.19	6.69	6.69	27.6	27.6	22.8	22.6	14.6	14.2	13.7	13.3
H_3PO_4	92.8	92.8	92.2	92.1	57.4	57.1	67.2	66.6	73.7	71.6	76.5	74.2
$AlHPO_4^+$	-	-	-	-	4.50	4.44	2.29	2.23	1.73	1.68	1.39	1.34
$Al_2PO_4^{+3}$	-	-	-	-	0.27	0.27	0.07	0.06	0.08	0.08	0.06	0.05
$CaH_2PO_4^+$	0.93	0.93	1.02	1.02	5.96	5.92	3.17	5.92	3.71	3.62	2.84	2.76
$FeH_2PO_4^{2+}$	-	0.08	4.26	0.15	4.31	3.09	4.48	3.75	6.17	7.30	5.55	7.05
$FeHPO_4^+$	-	-	-	0.01	-	-	-	1.64	-	1.49	-	1.33

* Not applicable

3.6. Phosphorus recovery and organic contaminants removal from sewage sludge

3.6.1. Test of different cell designs

3.6.1.1. General results

a) pH and voltage drop

In the first set of experiments (Table 2.6, page 52) three cell designs were used in which the SS was placed in the (i) anode with a CEM, (ii) cathode with a CEM and (iii) anode with an AEM. Experiments were also conducted with 20 or 50 mA.

During the ED treatments, pH variations were recorded along the experiments (Figure 3.20a) and results can be divided into three groups according to final SS pH: acidic, kept close to neutral and alkaline. When the SS was placed in the anode compartment with a CEM, pH decreased till approx. 2.5 (Exp-1

and Exp-2). While in the cathode compartment, also with a CEM, only slight pH variations (RSD ± 0.6) were observed comparing to Control-1 and Control-2, final pH approx. 7.0 (Exp-3 and Exp-4). This slight pH variation in relation to the initial SS pH may be explained by the migration of H^+ ions to the cathode compartment that are counteracting the OH^- effect. The use of an AEM prevented this migration, Exp-5, resulting in an alkaline pH being observed in the final SS pH, approx. 12.5.

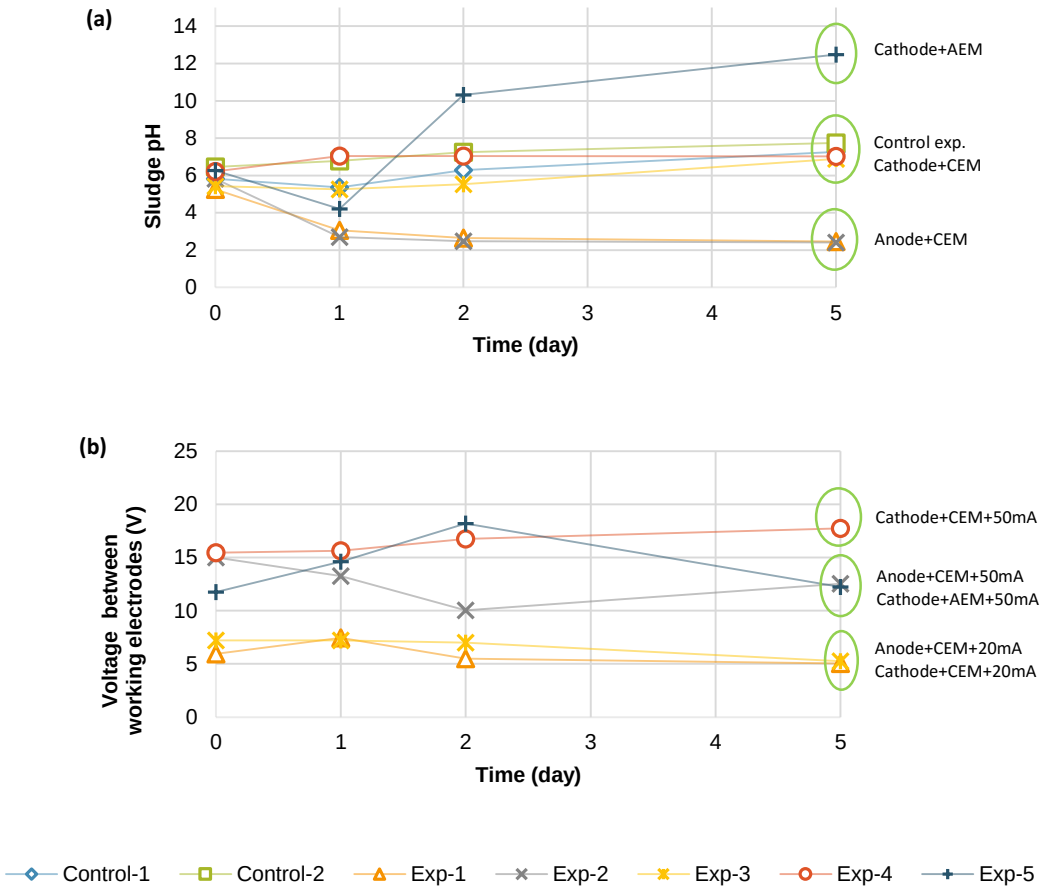


Figure 3.20. The development of (a) pH in the SS compartment during ED and (b) voltage drop between the working electrodes for set-1 experiments

When the experiments were conducted at 20 mA, independently of the cell design, the voltage measured between working electrodes was kept between 6.0 and 5.1 V (Figure 3.20b). In experiment Exp-2 (SS in the anode compartment, CEM, 50 mA) the initial voltage was higher, 15 V, than when 20 mA were applied (Exp-1, same cell design, 20 mA, 6.0 V), but after the first day it started to decrease till 12.5 V. When the SS was placed in the cathode compartment and 50 mA were applied, Exp-4 and Exp-5, the voltage increased, being more pronounced when a CEM was used (Exp-4). Exp-4 also presented a higher voltage along the experiment (between 15 and 18 V) meaning that this cell design resulted in higher resistivity.

b) Microbiological observation

Biological processes are extensively used in urban WWTP and the changes promoted by ED (e.g. pH) may affect the microbial community. In this first set, a preliminary survey in the microbiological community was done to assess the bioremediation potential of the medium. Therefore, a microscope observation was conducted for qualitative control. Samples prior to ED experiments were defrosted overnight and immediately observed under the light microscope, presenting large compacted flocs with only death bacteria and other animal remains being detected. It was possible to observe protozoa (*Thecamoebae*, swimmers, sessile and bottom cleaners), and rotifer but without activity. After 5 days in the ED cell without direct current, control experiments (Control-1 and Control-2) the appearance of foam on top of the SS was detected. After microscope observation a filamentous bacteria, *Thiothrix spp.* was identified and other filamentous bacteria presenting activity were observed. The presence of the hyphae of *fungi* was noticed, probably due to the pH and temperature conditions (no thermal control was done). Death *Arcella hemisphaerica*, algae and vegetal detritus were also observed. In Exp-2, the flocs were more condensed resulting in a very dense sample with high organic content in suspension (very similar to when flocculants are added to the sludge). In both experiments Exp-1 and Exp-2, final pH was below 3 making good conditions for the growth of filamentous bacteria, but only detritus were seen. Algae were also present in the samples. In experiment Exp-4, SS was characterized by condensed organic matter with large flocs. These flocs characteristics are a positive outcome as it may decrease the amount of polyelectrolyte that is needed, as well as the energy used to dehydrate the sludge and, consequently, the cost may decrease in WWTP. In terms of biology, less *A. hemispaherica* were detected comparing to control experiments (Control 1 and Control-2). The filamentous bacteria that were observed in control samples, appear–destroyed in the Exp-4 sample. The samples presented spiral shaped bacteria, possibly *spirillum* as well as bacteria colonies. In the final samples of experiment Exp-5, *Thecamoebae*, microalgae, filamentous bacteria and vegetal detritus were observed.

These results sustain the hypothesis that the electric current, pH changes will affect the microbial community present in the SS, supporting the need for further studies to be conducted in order to assess more comprehensively these changes.

3.6.1.2. Phosphorus separation

The distribution of P in the different parts of the cell at the end of the ED experiments is shown in Figure 3.21, sludge (solid collected after filtration of the SS), effluent (aqueous phase of the SS) and electrolyte. In the experiment Control-1 (CEM), after 5 days, 67% of the P was present in the sludge, 28% in the effluent and 5% in the electrolyte solution (probably due to diffusion). When the control was performed with an AEM more 12% of P was able to pass to the electrolyte (Control-2). In total, 16% of P was collected in the electrolyte of Control-2 being statistically significantly different from Control-1 (p<0.05). In total, 95% of P in Control-1 and 84% in Control-2 remained in the sludge compartment.

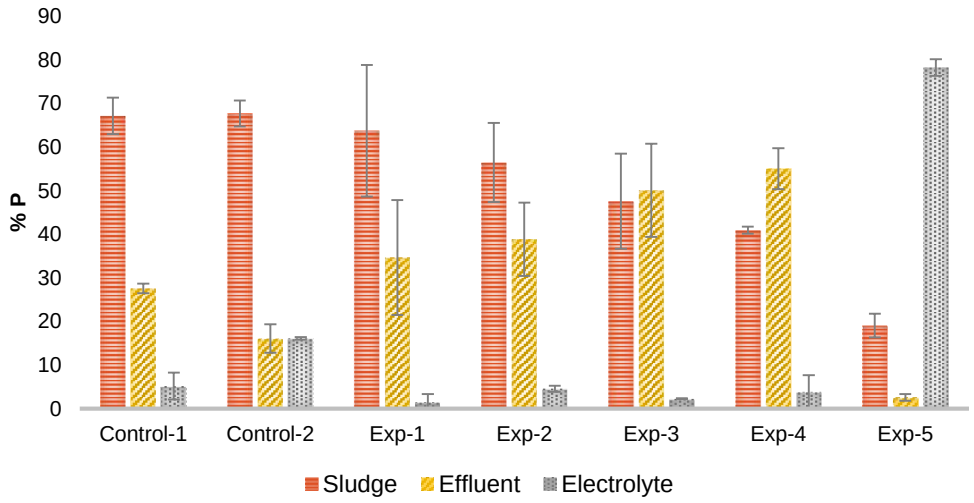


Figure 3.21. Distribution of P at the end of the electrodialytic experiments of set-1.

After applying ED, the amount of P in the effluent increases (Figure 3.21) along the different experiments as the pH in the SS compartment increases (Figure 3.20). The placement of the SS in cathode+CEM (Figure 2.7a, page 51) and applying 50 mA, Exp-4, resulted in statistically significantly differences (p<0.05) between the amount of P in the sludge (41%) and effluent (55%), comparing to control Control-1 and Control-2. When the SS was in the cathode+AEM (Figure 2.7c, page 51) and 50 mA were applied, Exp-5, 78% of P were mobilized to the electrolyte with only 19% remaining in the sludge. Contrary to the other experiments, in Exp-5 only 22% of P remained in the sludge compartment whereas in the other experiments the values were above 84%. In Exp-5, the combination of the high pH (P mainly present as HPO_4^{2-}/PO_4^{3-}) and the use of an AEM allowed the P to be transported to the anode end via electromigration being this statistically significantly different from the Control-1 and Control-2 (p<0.05). The other experiments did not present significant differences (p<0.05) in relation to Controls (1 and 2).

The results show that in the ED tested conditions, P can either be: (i) equally divided between the sludge and the effluent, cell design with SS in anode+CEM at 20 or 50 mA, and cathode+CEM at 20 mA; (ii) recovered in the effluent, cathode+CEM at 50 mA; or (iii) in the electrolyte, cathode+AEM at 50 mA.

If the sludge is free of contaminants and rich in P, it can be further treated and if it complies with the legislation it may be applied in agriculture. In experiments Exp-3 and Exp-4, the sludge presents a neutral pH but in the case of experiments Exp-1 and Exp-2, the sludge presents an acidic pH, needing further treatment. In these cases, the effluent also contains P and it can be recovered by promoting, e.g., P precipitation. The same option can be applied for the P recovered in the electrolyte (Exp-5).

3.6.1.3. Organic contaminants profile

The percentage of contaminants detected at the end of the ED experiments in the sludge, effluent and electrolyte are presented in Table 3.20.

Table 3.20. Percentage of contaminant detected in the sewage, effluent and electrolyte at the end of the experiments in relation to the initial amount for the experiments of set-1 (n=2, RSD can be seen in Appendix 3, page 152).

		Compound					
		Caf	**BPA**	**E2**	**EE2**	**IBU**	**MPBh**
Control-1	Sludge	18	32	21	46	93	36
	Effluent	17	7.4	0.7	5.1	6.0	<LQ
	Elect.	22	2.0	<LD	14	7.3	<LD
Control-2	Sludge	19	37	32	51	87	38
	Effluent	7.0	3.2	1.1	3.6	2.0	5.5
	Elect.	23	0.3	0.5	0.2	26	1.5
Exp-1	Sludge	<LD	33	18	59	43	41
	Effluent	2.3	11	1.3	3.1	2.6	1.8
	Elect.	7.7	<LD	<LD	<LD	<LQ	<LD
Exp-2	Sludge	9.1	35	23	58	37	43
	Effluent	2.0	7.5	1.1	1.1	2.5	<LQ
	Elect.	3.4	5.7	1.6	2.6	<LQ	<LQ
Exp-3	Sludge	4.2	46	8.7	44	20	57
	Effluent	10	4.9	1.0	1.9	0.77	0.20
	Elect.	6.6	1.2	<LQ	0.19	3.0	<LQ
Exp-4	Sludge	29	86	14	80	36	87
	Effluent	15	11	0.30	2.0	15	<LQ
	Elect.	12	14	2.0	19	3.2	<LQ
Exp-5	Sludge	<LQ	<LQ	<LD	<LQ	<LD	17
	Effluent	<LQ	1.5	0.87	3.0	0.33	<LQ
	Elect.	29	12	6.0	14	2.9	<LQ

The majority of the OCs (except Caf) in the Control-1 and Control-2 were mainly detected in the sludge (>70% of the total amount detected), together with P, due to the high log K_{OW}. Some differences in the contaminants profile within the cell were observed in the control experiments according to the use of a CEM (Control-1) or AEM (Control-2). When a CEM was used the electrolyte contained approx. more 14% of EE2 than when the AEM was used. A contrary result was observed for Ibu that presented more 19% in the electrolyte when the AEM was used. For Ibu the pH in the sludge was between 7.3-7.7, being mainly in its ionized form, making it more soluble and able to pass through the AEM. Caf was able to pass through both membranes, 22 and 23% for the CEM and AEM, respectively.

The lowest percentage of OCs in the sludge was obtained in Exp-5 (cathode+AEM, 50 mA). In this experiment the sludge presented all compounds, except MBPh, below method limits. Whereas the electrolyte presented high amount of OCs, except MBPh that was below LQ. This may be explained by the increased degradations obtained in Exp-5, further on explained. The lowest amount of OCs in the electrolyte was obtained in Exp-1, with all compounds, except Caf, below method limits.

The parallel degradation experiments conducted for 6 hours in the controlled conditions (two beakers linked by a CEM; spiked electrolyte; section 2.2.5.3, page 53) support the hypotheses that the OCs may potentially suffer electrodegradation with estimated percentages between 7.5 and 25% in the anode

end, and between 5.5 and 27% at the cathode end, with no statistically significant differences at $p<0.05$ (Table 3.21).

Table 3.21. Degradation percentage* for the experiments of set-1 (n=2).

			Contaminant					
			Caf	BPA	E2	EE2	Ibu	MBPh
Electrode-gradation tests	**Anode end**	$\bar{X}$	7.5	8.5	19	13	25	11
		SD	2.1	3.5	7.1	4.2	4.9	7.8
	Cathode end	$\bar{X}$	5.5	15	16	15	27	19
		SD	2.1	5.7	1.4	0.7	1.4	4.2
Electrodialytic cell experiments	**Control-1**	$\bar{X}$	43 [a]	59 [b]	78	35	WD [c]	64 [d]
		SD	13	7.7	5.2	27	4.3	5.9
	Control-2	$\bar{X}$	51	60 [e]	66 [f]	45	WD [g]	55 [h]
		SD	5.0	1.8	0.5	2.8	1.5	0.6
	Exp-1	$\bar{X}$	90 [a,i]	56 [j]	81	38	54 [c,g,k]	57 [l]
		SD	8.5	0.2	1.0	4.2	13	6.8
	Exp-2	$\bar{X}$	85	52 [m]	74 [n]	38	61 [c,g,o]	57 [p]
		SD	9.2	0.9	2.9	11	3.2	0.2
	Exp-3	$\bar{X}$	79	48 [q]	90 [f,n]	54 [r]	76 [c,g]	43 [s]
		SD	19	2.5	4.0	8.7	13	0.2
	Exp-4	$\bar{X}$	43 [i]	WD [b,e,j,m,q,t]	84 [f]	WD [r,u]	46 [c,g,v]	13 [d,h,l,p,w]
		SD	7.9	2.3	6.9	3.9	9.7	15
	Exp-5	$\bar{X}$	71	87 [b,e,j,m,q,t]	93 [f,n]	83 [u]	97 [c,g,k,o,v]	83 [s,w]
		SD	4.6	15	3.6	12	4.2	12

* % OC degraded = [1- ∑(mass of OC detected in all cell compartments)/(mass of OC added to the SS)]*100; WD – Without observed degradation. *Statistics:* degradation statistically significantly different at $p<0.05$ comparing to: [a] Caf Control-1; [b] BPA Control-1; [c] Ibu Control-1; [d] MBPh Control-1; [e] BPA Control-2; [f] E2 Control-2; [g] Ibu Control-2; [h] MBPh Control-2; [i] Caf Exp-1; [j] BPA Exp-1; [k] Ibu Exp-1; [l] MBPh Exp-1; [m] BPA Exp-2; [n] E2 Exp-2; [o] Ibu Exp-2; [p] MBPh Exp-2; [q] BPA Exp-3; [r] EE2 Exp-3; [s] MBPh Exp-3; [t] BPA Exp-4; [u] EE2 Exp-4; [v] Ibu Exp-4; [w] MBPh Exp-4;

According to experimental data, all compounds degradation follow a first order kinetics with correlations (r^2) between 0.8252 and 0.9879 (Appendix 4, page 153). The formation of new peaks, corresponding to new or related compounds, was assessed by HPLC-DAD in the samples collected during the experiments. In the anode samples, 6 new peaks were identified and none in the cathode samples. So the formation of by-products needs to be taken into account and the mechanisms should be further on investigated.

In the control experiments, with no applied current (Control-1 and Control-2), the compound that presented higher degradation was E2, followed by MBPh and BPA, Caf and EE2, whereas Ibu was not degraded (Table 3.21). This degradation is mainly attributed to bioremediation mechanisms, as after the 5 days experiment, bacteria activity was observed in the collected samples. Although differences were observed in contaminants profile within the cell, no statistical significant differences ($p<0.05$) were observed for the contaminants degradation between the two control experiments (Control-1 and Control-2).

When ED is applied to SS, besides the bio and electrodegradation mechanisms (direct anodic oxidation or cathodic reduction) strong oxidants such as chloride have been considered for indirect oxidation [214].

The higher degradation improvement was found when 50 mA were applied to the SS placed in the cathode+AEM (Exp-5). In this case, all degradations were between 71% (Caf) and 97% (Ibu). Comparing to the control experiments, a general tendency for higher degradations was observed for all compounds being statistically different for BPA, Ibu comparing to Control-1 and BPA, E2 and Ibu comparing to Control-2 (p<0.05). In the case of MBPh this was the only experiment in which its degradation seems to have improved compared to control tests. By comparing Exp-5 with the other ED experiments, higher degradations were achieved for: BPA than for all the others, EE2 comparing to Exp-4, Ibu in all experiments except Exp-3 and MBPh in Exp-4 and Exp-3, being all statistically different (p<0.05).

As the final objective is to remove P from the sludge to the electrolyte, the data suggests the use of an ED cell where the SS is placed at the cathode and an AEM is the most viable option as it also promoted the highest OCs remediation. So, this cell design as used in the second set of experiments.

3.6.2. Influence of current intensities

3.6.2.1. General results

The initial SS presented an average P content (n=12) of 4.68 ± 0.62% (Table 3.22), mostly present as ortho-P (90%). Total suspended solids (TSS) range from a maximum of 33.6 g/L in the sample collected on May 5, 2015, and 22.7 g/L in the sample collected on July 9, 2015. As the previous experiments were conducted for 5 days, another control experiment without current was performed. During the Control-3 experiment (SS separated from the electrolyte by an AEM, 3 days) SS pH slightly increased from 6.4 to 7.4. After applying ED, due to the formation of OH^-, SS pH increased to values between 9.8 and 10.6 (Table 3. 22).

The initial SS conductivity varied between 873 and 1054 µS/cm. After the application of the electric current, the SS conductivity increased to values between 1502 µS/cm in Exp-6 and 2920 µS/cm in Exp-7. In terms of voltage drop, a decrease was always observed between the initial and the final of the experiments, suggesting that during the 3 days, fouling was not occurring.

Table 3. 22. Parameters measured at the beginning and at the end of the electrodialytic experiments of set-2.

	before ED							after ED						
	SS					Electrolyte		SS			Electrolyte		Voltage drop (V)	
Exp.	P (g/kg d.w.)	TSS (mg/L)	pH	Conductivity (µS/cm)	% H_2O	pH	Conductivity (µS/cm)	pH	Conductivity (µS/cm)	% H_2O	pH	Conductivity (µS/cm)	Initial	Final
Control-3	45.5 ± 3.1	33600	6.4	873	93.0	5.5	1211	7.4 ± 0.4	1703 ± 501	96.6 ± 0.4	7.8 ± 0.3	1042 ± 11	-	-
Exp-6	51.1± 8.5	32600	6.5	1054	94.1	6.1	1342	10.6 ± 0.5	1502 ± 81	96.9 ± 0.2	2.1 ± 0.0	3945 ± 318	32 ± 3	19 ± 0
Exp-7	45.5 ± 3.0	28250	6.7	983	93.2	5.2	1194	10.1 ± 1.2	2920 ± 1499	91.3 ± 1.0	1.6 ± 0.1	6515 ± 2044	48 ± 2	32 ± 10
Exp-8	56.9± 1.3	32550	7.0	1054	91.9	5.7	1158	10.0 ± 0.9	2418 ± 1531	93.5 ± 0.5	1.9 ± 0.1	4705 ± 431	38 ± 3	25 ± 4
Exp-9	41.0± 5.5	27400	6.8	989	93.0	6.9	1146	10.0 ± 1.4	2161 ± 1300	90.6 ± 2.8	1.6 ± 0.0	4985 ± 78	27 ± 0	29 ± 1
Exp-10	41.0± 6.4	22700	6.8	974	92.1	7.2	1372	9.8 ± 0.7	1824 ± 198	92.5 ± 1.7	1.4 ± 0.0	6620 ± 269	50 ± 3	17 ± 6

3.6.2.2. Microbiological changes

The 35 Taxa initially identified in the SS were divided in 12 groups: algae, bacteria, amoebae without shell, shelled amoebae, free-living flagellates, free-living ciliates, crawling ciliates, stalked ciliates, rotifers, nematodes, tardigrades and others (Table 3.23).

Table 3.23. Groups and species counted and identified in the SS samples.

Group	***Taxa***
Algae	*Navicula* spp.
	Nitzschia spp.
	Pirobotrys sp.
	Filamentous algae n.i.
	Filamentous Chlorophyta n.i.
	Centric Diatom n.i.
Bacteria	*Oscillatoria* spp.
	Spirillum sp.
	Spirulina sp.
	Zoogloea spp. (dendritic growth)
	Zoogloea spp. (globular growth)
	Cyanobacteria n.i.
Amoebae without shell	Naked amoeba n.i.
Shelled amoebae	*Arcella gibbosa*
	Difflugia sp.
Free-living flagellates	*Bodo* sp.
	Euglena sp
Free-living ciliates	*Litonotus* sp.
	Didinium sp.
Crawling ciliates	*Aspidisca cicada*
Stalked ciliates	*Epistylis* spp.
	Opercularia sp.
	Vorticella spp.
	Zoothamnium spp.
	Podophrya spp.
	Stalked ciliate n.i.
Rotifer	*Philodina* sp.
	Rotatoria sp.
	Rotifer n.i.
Nematode	Free-living Nematode n.i.
Tardigrade	Tardigrade n.i.
Others	*Pinus* spp.
	Toxocara canis egg
	Rotifer mastax
	Rotifer egg

Legend: n.i. – not identified; sp. (plural spp.) - is used when the specific name of a species cannot be specified; spp. - indicates several species of the same genus.

A slight variation in the total number of individuals was found along the different SS sampling dates (Table 3.24). The highest counting was observed in the initial sample, t0, of Exp-9 and the lowest for Exp-7, 273 000 and 81 600 individuals *per* gram of SS, respectively. This is mainly attributed to the climatic conditions (e.g. temperatures, rain) and WWTP biological reactor parameters that influenced the SS characteristics collected on the secondary settling tank.

Table 3.24. Minimum and maximum number of individuals *per* gram of SS (ind/g x10^3, n=2)

	t0 [a]	t⅓	t1	t2	t3
Control-3	251.7	[δ]	126.0 – 245.7	68.4 – 94.5	20.1 – 20.7
Exp-6	131.7	45.6 – 45.6	5.4 – 29.1	4.5 – 13.2	1.2 – 3.3
Exp-7	81.6	130.5 – 186.9	28.2 – 35.1	22.5 – 28.8	16.8 – 19.8
Exp-8	252.0	146.6 – 186.4	128.4 – 188.7	47.4 – 122.7	57.9 – 89.1
Exp-9	273.0	[δ]	93.3 – 136.2	78.9 – 108.3	83.7 – 171.3
Exp-10	181.9	[δ]	140.3 -186.0	167.6 – 108.6	69.4 – 123.0

[a] In the t0 samples only one analysis was carried out; [δ] Samples not collected.

In the Control-3 experiment the number of individuals decreased (Figure 3.22). After 24 h, the microbiological population decreased in 26% and kept decreasing till the end of the experiments. At the end, the population mean was 92% lower than in the beginning. This was mainly attributed to the agitation system that fragmented the flocs and to the low oxygenation conditions as the cell was almost completely closed (the only oxygenation was done through the hole from which the agitator was inserted).

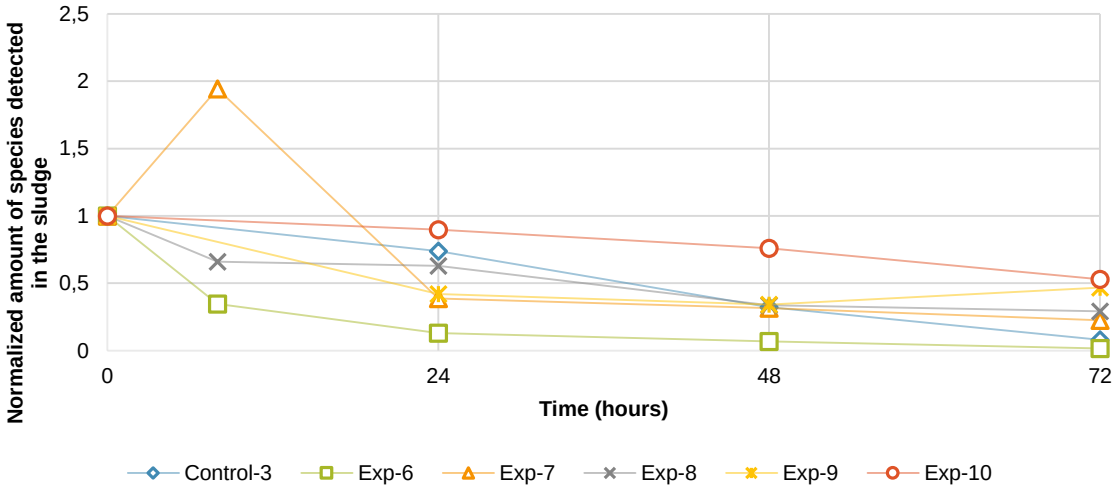


Figure 3.22. Amount of individuals normalized to the initial amount counted in the SS samples.

When the electric current was applied the population also decreased (Figure 3.22). The highest change was observed in the experiment conducted with 50 mA (Exp-6) in which t3 (72 h) sample presented less

93% ind/g of SS. In Exp-4 and Exp-5 the population number only decreased 53 and 47%, respectively. In Exp-7, an increase in the number of individuals of t⅓ in relation to t0 was observed. In this sample, more *Arcella gibbosa* individuals were counted compared to the t1 sample, being this mainly attributed to sample heterogeneity.

3.6.2.3. Biodiversity and abundance

Richness (*R*), Simpson's diversity index (*D*) and Evenness (*J'*) were calculated for all experiments (group represented as *others* in Table 3.23 was excluded from calculus) and the results can be seen in Figure 3.23.

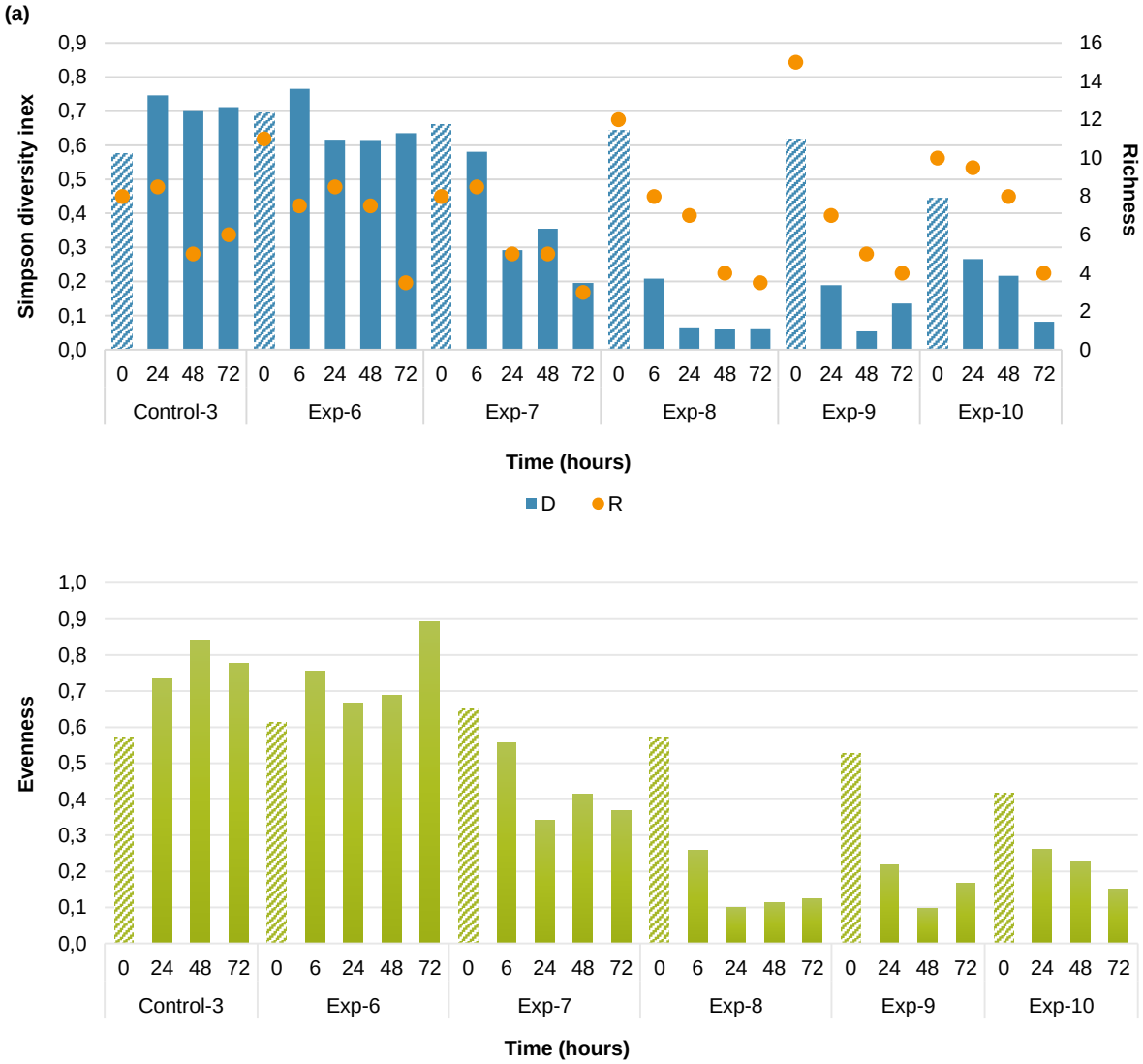


Figure 3.23. Biodiversity indexes (a) Simpson diversity index and richness and (b) evenness for the sewage sludge samples.

In terms of samples richness (Figure 3.23a), the values varied between 7.0 (Exp-7) and 14.0 (Exp-9) meaning that Exp-7 initial sample presented less species (in relation to the number of individuals) than Exp-9 (p<0.05). Control-3 richness decreased from 8.0 to 5.5, although without statistical differences (p<0.05). All experiments performed with DC resulted in lower richness at the end of the experiments comparing to the initial samples, being this statistically different (p<0.05) for all experiments except Exp-7. Although not statistically different, p<0.05, at the end of all experiments, Control-3 SS was richer than the SS of the experiments performed with DC.

Simpson diversity (Figure 3.23a) varied between 0.45 (Exp-10) and 0.69 (Exp-6) in all initial samples, without statistical differences (p<0.05). Although without statistical differences (p<0.05), *D* increased by 22% after 72 h in the Control-3 experiment (from 0.58 to 0.70). This means that the probability of two individuals randomly selected from an area belonging to different species also increased. This result can be associated with the decrease in the number of individuals of Control-3 (Table 3.24) but not on the identified *Taxa* (total of 8). When the DC was applied, a decrease in *D* was observed in the samples after 72 h, being more pronounced in the experiments with currents higher than 75 mA (between 70% and 90 %). Comparing to Control-3, statistically differences (p<0.05) were observed for Exp-7 (75 mA), Exp-8 (100 mA), Exp-9 (50-75-100 mA) and Exp-10 (100-75-50 mA). The application of 50 mA, Exp-6, resulted in a final *D* value higher than the other applied currents (between 75 and 100 mA), with statistical differences (p<0.05).

Evenness, initial values ranged between 0.42 in Exp-10 and 0.65 in Exp-7 (Figure 3.23b). Evenness of the final samples (72 h) of each experiment were statistically different (p<0.05) comparing to initial samples (0 h). Contrary to richness, evenness increased in the Control-3 and Exp-6 (more 33% and 55%, respectively) meaning that the SS presents less variation in communities between the species. This increase can be explained by the decrease in the total number of individuals that were more evenly distributed among the species. For the other experiments a decrease was observed, being the value 44% lower when 75 mA were applied (Exp-7) and 74% for the 100 mA (Exp-8). The use of current steps also resulted in a 64% decrease in Exp-10 and 94% in Exp-9. The final SS samples of the Control-3 and Exp-6 presented higher evenness values than Exp-7, Exp-8, Exp-9 and Exp-10 (p<0.05).

The obtained results show a negative effect of the ED treatment on the protozoa and metazoa community either by: (i) agitation system used; (ii) direct effect of the applied current; (iii) physico-chemical changes of the medium (e.g. pH).

Figure 3.24 shows the total abundance of protozoa and small metazoa considered of particular importance, either because they were the most abundant or frequent and/or because of their recognized value as bio-indicators of degrading conditions in the aeration tank of activated sludge. As so, for these results only the individuals belonging to key groups: free-living flagellates, free-living ciliates, crawling ciliates, stalked ciliates, amoebae without shell, shelled amoebae and small metazoa (rotifer and nematode), were considered.

In terms of abundance (Figure 3.24), the sample t0 from Control-3 and Exp-6 was mainly constituted by stalked ciliates (83% and 86%, respectively) followed by shelled amoebae, free living ciliates and free-

living flagellates. In the other experiments (Exp-7, Exp-8, Exp-9 and Exp-10) the amount of shelled amoebae present in t0 samples was higher. Exp-7 contained 52% of shelled amoebas, 54% in Exp-8, 59% in Exp-9 and 73% in Exp-10.

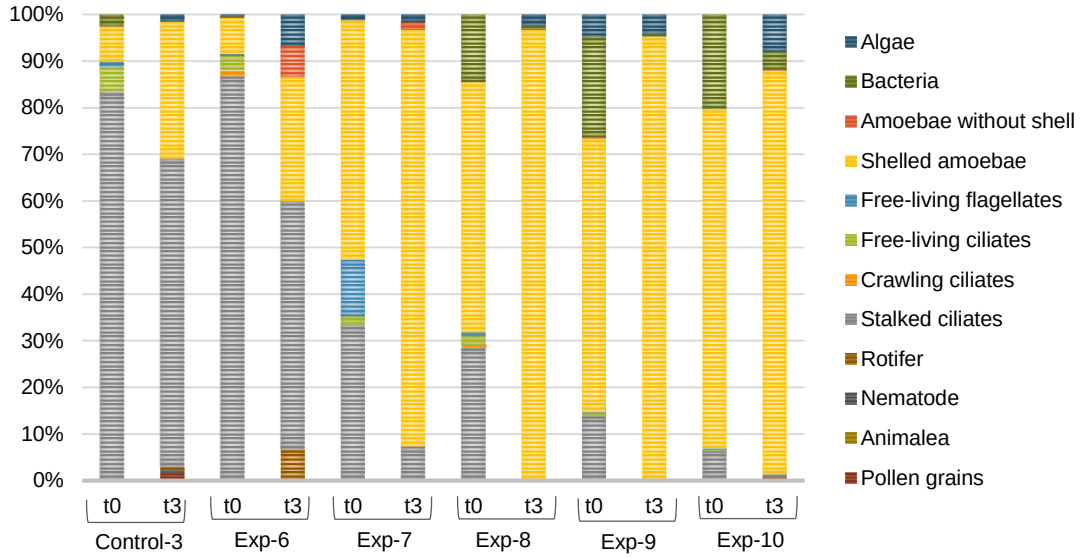


Figure 3.24. Percentage of each microbiological group in relation to the total amount of organism counted in each the sample.

In general, the sludge composition changed as the sludge was mainly constituted by shelled amoebae whereas the percentage of ciliates, flagellates and bacteria decreased. Their physiognomy may explain the obtained results. Stalked ciliates, *Epistylis* spp. (Figure 3.25a), *Opercularia* sp., *Vorticella* spp. (Figure 3.25b), *Zoothamnium* spp., *Podophrya* spp. and other unidentified pedunculated ciliates, are usually attached to a piece of floc by a peduncle possibly being more sensitive to the changes in flocs structure. On the other hand, the identified shelled amoebae, *Arcella gibbosa* (Figure 3.25c) and *Difflugia* sp., are single-celled protists partially enclosed in a simple test which may have protected them from the electric current and pH changes.

Figure 3.25. Microscope photograph of (a) *Epistylis* spp. colony (100x), (b) *Vorticella* spp. (400x), (c) *Arcella gibbosa* (400x).

Crawling ciliates and shelled amoebae have shown a strong association with effluent biochemical oxygen demand (BOD_5) [215]. In these experiments a decrease in the number of testate amoebae (between 25% for Exp-9 and 94% in Exp-6) and crawling ciliates (approx. 100%) was observed, meaning that the process may be result in poor quality effluent. Carnivorous ciliates (e.g. *Litonotus* sp.) and flagellates have significant positive correlations with sludge volumetric index (SVI), suggesting that these two groups may be indicators of bad settlement conditions of sludge [215, 216]. Their number also decreased along the experiments. The obtained results suggest that the conditions within the cell were not appropriated to the protozoa and metazoan communities, influencing the SS quality. Aiming to improve the conditions, the agitation of the SS in the cell should be carried out by pumping air into the system instead of using the stirrer, aiming at mimetizing the conditions of the WWTP bioreactor while promoting a better oxygenation and a softer agitation of the sludge.

3.6.2.4. Organic contaminants degradation and profile

In the Control-3 experiment degradations, mainly attributed to bioremediation (ED cell were protected from direct sunlight exposure), range between 65% for EE2 and 87% for Caf without statistically significantly differences (p<0.05) between compounds (Table 3.25). By comparing these results with the study carried out with frozen sludge (Table 3.21) higher degradations were achieved by using the fresh SS. More 36, 26, 20 and 17% of degradation was achieved for Caf, BPA, EE2 and MBPh, respectively. Although removal efficiencies vary, in other studies the reported average for BPA in full-scale facilities was 84% [217], for Caf was greater than 80% in full scale, pilot scale membrane bioreactor, subsurface flow, and a batch system [218]. For the EE2 removals were 75% and 85% in anaerobic digesters, whereas in batch experiments they were 100% and 20% [217]. Using a membrane bioreactor MBPh removal achieved 41% and 50% in pilot-scales and 99% in batch experiments [217].

After the application of a direct current the compounds degradation was generally improved (between more 2 and 18% of degradation), with some exceptions (Figure 3.26). The best degradation improvement was observed for EE2 that was always 10% higher in all experiments with current, although no statistically significant differences were observed (p<0.05). MBPh also presented good results with improvements between 8% and 14%. The lowest degradation improvement was seen for Caf in Exp-4, which decreased approx. 24% when compared to the Control-3 (no statistically significant differences were observed, p<0.05). BPA was the compound that presented lowest results after the application of a direct current. Its degradation only improved in Exp-6 and Exp-10 (5 and 6%, respectively) comparing to the Control-3.

Table 3.25. Percentage of contaminant detected in the sewage, effluent, electrolyte and degraded at the end of the experiments in relation to the initial amount for the set-2 experiments (n=2).

		Compound			
		Caf	**BPA**	**MBPh**	**EE2**
Control	Sludge	<LD [a, b]	13 ± 6 [a]	28 ± 7[B]	34 ± 1[A]
	Effluent	11 ± 12	1.2 ± 1.3	0.28 ± 0.16 [b]	0.93 ± 0.48 [a]
	Elect.	2.7 ± 0.3	<LD	<LD [b]	<LD [a]
	Degradation	87 ± 12	86 ± 7	72 ± 7	65 ± 1
Exp-6	Sludge	8.6 ± 0.4	<LD	16 ± 1	13 ± 3 [a]
	Effluent	3.1 ± 4.4[d]	2.2 ± 1.2	1.3 ± 0.2	1.1 ± 0.6
	Elect.	[δ]	6.0 ± 3.4	1.2 ± 0.5	2.7 ± 0.4
	Degradation	88 ± 4	92 ± 5	82 ± 1	83 ± 2
Exp-7	Sludge	4.5 ± 0.2 [c]	13 ± 11	18 ± 2	26 ± 8 [C]
	Effluent	6.0 ± 2.7	5.1 ± 0.4	0.83 ± 0.34	2.2 ± 0.5 [c]
	Elect.	[δ]	7.9 ± 2.9	0.21 ± 0.23	2.4 ± 2.1 [c]
	Degradation	89 ± 3 [f]	74 ± 8	81 ± 1	70 ± 5
Exp-8	Sludge	<LD	4.1 ± 5.9	14 ± 2	18 ± 3
	Effluent	3.8 ± 0.2	5.1 ± 2.8	0.90 ± 0.45	2.7 ± 0.8
	Elect.	<LD	10.0 ± 13.1	0.67 ± 0.85	0.15 ± 0.21
	Degradation	96 ± 0[f]	81 ± 5	85 ± 1	79 ± 2
Exp-9	Sludge	14 ± 9	6.3 ± 8.9	19 ± 14	17 ± 0
	Effluent	22.7 ± 4.2 [D]	3.8 ± 4.4	0.76 ± 0.34 [d]	2.2 ± 1.0 [d]
	Elect.	<LD [d]	6.7 ± 8.8	0.76 ± 0.73	<LD
	Degradation	63 ± 13 [F]	83 ± 5	79 ± 14	80 ± 1
Exp-10	Sludge	6.9 ± 1.0	6.9 ± 0.2	16 ± 4	25 ± 8 [E]
	Effluent	0.57 ± 0.19 [d]	2.0 ± 1.0	0.57 ± 0.19	<LD [e]
	Elect.	<LD	0.64 ± 0.91	0.24 ± 0.09	<LD[e]
	Degradation	93 ± 10 [f]	91 ± 2	83 ± 5	75 ± 8

% OC degraded = [1- ∑(mass of OC detected in all cell compartments)/(mass of OC added to the SS)]*100
<LD: Below limit of detection; [δ] Compound not quantified due to co-elution during the analysis; *Statistics:* percentage statistically significantly different at $p<0.05$ comparing to: [a]EE2 sludge Control-3; [b] MBPh sludge Control-3; [c] EE2 sludge Exp-7; [d] Caf effluent Exp-9; [e] EE2 sludge Exp-10; [f] Caf degradation Exp-9.

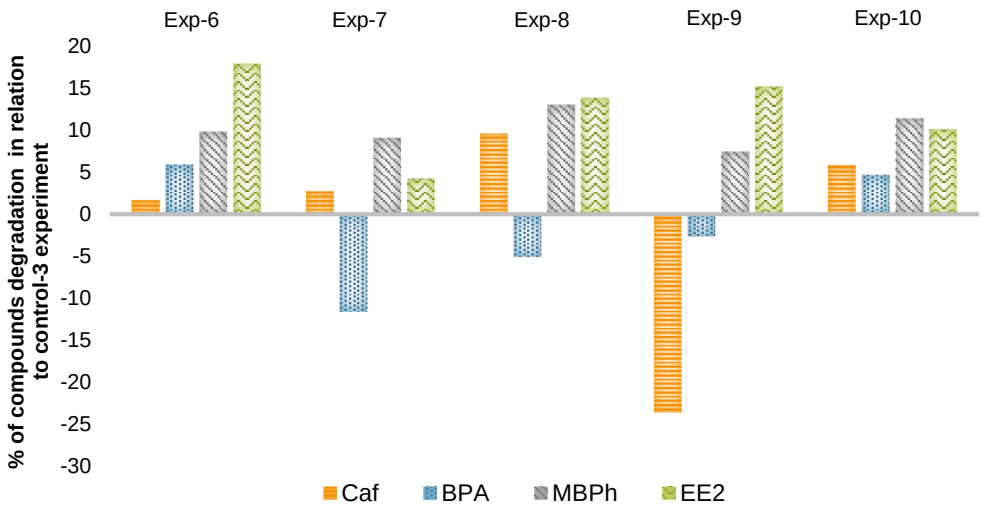


Figure 3.26. Percentage of organic contaminants degraded in the electrodialytic separation experiments comparing to Control-3.

In general, the increase in the current intensity (from 20 to 50 mA) did not show improvements in contaminants degradation. The only statistical difference (p<0.05) was found for Caf, which degradation in Exp-9 (50-75-100 mA) was lower than Exp-7, Exp-8 and Exp-10. This may be attributed to the current used (steps) but also to a decrease in biodegradation potential of the medium.

In terms of OC profile within the cell, it can be seen that the percentage of compound detected in sludge increases 0% Caf < 13% BPA < 28% MBPh ≈ 34% EE2 as the log K_{OW} increases and the solubility decreases (Table 1.5, page 33). In the case of EE2 and MBPh, that have very similar log K_{OW} (3.67 and 3.82, respectively), the lower solubility of EE2 (11.3 mg/L *vs* 69 mg/L) may have influenced the results. In the sludge, the amount of EE2 is statistically higher than the amount of the others compounds (except MBPh). In the effluent, although without statistically differences (p<0.05), the opposite trend is observed as the amount of compound detected decreases as the log K_{OW} increases. The percentage of EE2 detected in the sludge of the control experiment was also statistically different (p<0.05) from the amounts detected in the effluent and electrolyte. Diffusion through the AEM after 3 days was only observed for Caf (3% in the electrolyte). One hypotheses, is that caffeine was able to pass through the AEM due to similarities between its functional group and membrane charged groups (e.g. $–NH_3^+$, $–NRH_2^+$, $–R_2H^+$, $–NR_3^+$) as well as its high solubility.

When the current was applied, the pH in the cathode compartment increased in all experiments to values above the compounds pKa, except for Caf (pKa 14). This means that BPA, EE2 and MBPh suffered deprotonation, being mainly present as anions, and were able to electromigrate to the anode compartment. Once in the anode compartment, these compounds may suffer anodic oxidation. In Exp-10, the electrolyte presented the lower amounts of compounds comparing to the other experiments with current, as only two compounds were detected in the anolyte at very low concentrations (below 0.64 ppm).

Changes in the compounds profile due to the application of a direct current was also observed in the experiments. Differences (p<0.05) were found in the amount of EE2 detected in the sludge of Exp-6 comparing to Control-3, showing that the application of 50 mA, decreased the amount of compound adsorbed to the sludge. This may be due to the increase in the degradation and, as the compound was mainly ionized (pKa<pH), to its distribution within the cell.

In these tested conditions, compounds degradation was not complete. Still, a very high concentration was used in the experiments to allow assess OCs profile within the cell. The use of different electrodes may also be an option in trying to increase degradations [219-223]. Also, in this study the organic compounds were considered removed as the elimination of parent organic compound. The extent of biodegradation and the loss of the parent compound indicates biotransformation of an unknown degree, and not necessarily mineralization. Furthers studies are needed to assess degradation extent, mechanisms and by-product formation.

3.6.2.5. Phosphorus separation

Phosphorus desorption was initially assessed at pH values between 1 and 14. The highest desorption as obtained at pH approx. 13, at which 123 mg P/L were solubilized from sludge. As for the other tested pH, 48 mg/L of P at pH 1.06 of and only 7 and 12 mg/L of P at pH 5.84-6.19 were desorbed. So, it is expected that in the ED experiments, the high pH reached in the cathode compartment (Table 3. 22), results in high P solubilization from the sludge to the effluent and, once it is present in an ionic form, be able to migrate to the anolyte.

All SS samples used in the experiments were initially analysed to assess P distribution and 7.2 ± 3.9% of the total P (n = 12) was present in the effluent whereas 93.0 ± 2.6% was in the sludge. The distribution of P in the different parts of the cell at the end of the ED experiments, sludge (solid collected after filtration of the SS), effluent (aqueous phase of the SS) and electrolyte is presented in Table 3.26. After 3 days in the EK cell, Control-3 experiment, 29% of P were able to pass through the AEM and were detected in the electrolyte, with 62% remaining in the sludge.

Table 3.26. Parameters measured at the beginning and at the end of the electrodialytic experiments of set-2 with SS (n = 2).

Compart.	Control-3	Exp-6	Exp-7	Exp-8	Exp-9	Exp-10
Electrolyte	29.2 ± 1.1 ^{a,G}	53.3 ± 9.7 ^{b,g,i}	62.9 ± 0.7 ^{c,g}	70.3 ± 2.0 ^{d,g,I}	59.9 ± 3.6 ^{e,g}	56.7 ± 2.1 ^{f,g}
Effluent	8.90 ±2.13 ^{a}	5.91 ± 1.41 ^{B}	2.06 ± 0.77 ^{c}	3.68 ± 2.48 ^{d}	2.52 ± 0.50 ^{e}	2.47 ± 1.97 ^{F}
Lama	61.9 ±3.2 ^{a,H}	40.7 ± 1.1 ^{b,h}	35.0 ± 0.1 ^{c,h}	26.0 ± 0.5 ^{d,h}	37.5 ± 4.1 ^{e,h}	40.8 ± 0.3 ^{f,h}

Statistics: percentage statistically significantly different at $p<0.05$: ^{b} between Control-3 matrices; ^{b} comparing to Exp-6 effluent; ^{c} between Exp-7 matrices; ^{d} between Exp-8 matrices; ^{e} between Exp-9 matrices; ^{f} comparing to Exp-10 effluent; ^{g} comparing to Control-3 electrolyte; ^{h} comparing to Control-3 sludge; ^{i} comparing to Exp-8 electrolyte.

When the electric current was applied, the amount of P detected in the electrolyte at the end of the experiments increased in all treatments compared to Control-3 (more 24-41%), whereas the amount in the sludge decreased (statistically significantly different in all treatments, $p<0.05$). Between the experiments conducted with current, no statistical differences ($p<0.5$) were found in the amount of P detected in the sludge, although a tendency can be seen: increasing the current seems to increase the amount of P extracted from the sludge (Exp-6, Exp-7 and Exp8; m = 0.3399, r^2 = 0.9949). In all experiments the percentage of P detected in the sludge ranged between 26% (Exp-8) and 41% (Exp-10). The highest recovery in the electrolyte was 70% in Exp-8 (100 mA) and the lowest 53% in Exp-6, being these two values statistically different ($p<0.5$). The use of current steps (Exp-9 and Exp-10) did not improve P recovery.

Initially, P was mainly present as inorganic-P (90%) but after ED the electrolyte contained between 57% (Exp-6) and 99% (Exp-10) of the P detected was organic-P. One hypotheses is that P reacted with other compounds containing carbon that were present in the system either in the sludge compartment or in the anode compartment.

Looking at the amount of P reaching the anolyte along the 3 days, 72 h, of experiment (Figure 3.27), it can be seen that the maximum parentage of P recovered was reached during the first 24 h of all

experiments. The highest recovery velocity was achieved in Exp-8 (100 mA), 22 mg P *per* kg d.w. *per* min in the first 24 h. A similar pattern was also reported by Ebbers et al. [156]. This can be explained by the precipitation of P as calcium phosphate e.g. in the form of Hydroxyapatite (eq. 3.1) at higher pH values (8~10) [224].

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \longrightarrow Ca_5(PO_4)OH \quad (3.1)$$

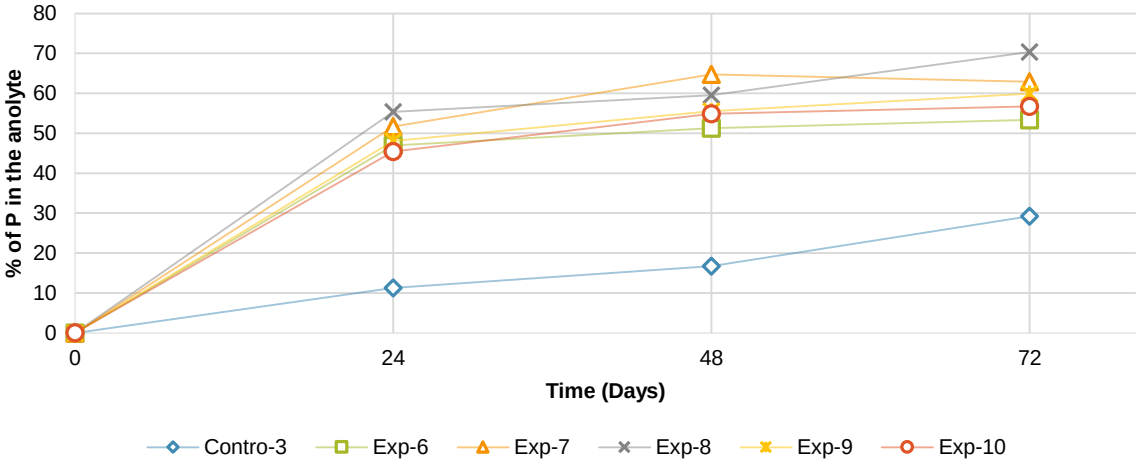


Figure 3.27. Percentage of P detected in the anolyte along the experiments (t1, t2 and t3).

Also, ED is not ion selective meaning that other species, like OH^-, will also carry current instead of P, decreasing extraction efficiency.

In these experiments, a slightly lower P recovery were achieved in 3 days than the ones achieved in 5 days with sludge at 50 mA, Exp-6 (Figure 3.21). Still, the decrease in P recoveries was only 8% not justifying the need to run the recovery for 5 days. Also, in the here tested conditions, ED process aiming P recovery could be carried out only for 24 h, decreasing the associated energy costs. Still, anolyte was only collected for P analysis every 24 h and, further experiments should be carried out to assess the P mobilization during the first 24 h aiming to optimize the process and decrease even more the time needed for recovery.

In none of the experiments a P solution a free of OCs was achieved. The lowest percentage of contaminants in the anolyte was found in Exp-10, and this still needs further optimization aiming to increase contaminants degradation and recovering a P clean solution in 24 h.

SECTION IV

4. CONCLUSIONS

Soil contamination is a worldwide problem and technologies are needed to tackle it. Simultaneously, there is a need to move towards more sustainable solutions that combine, or use successively, already proven technologies. EK remediation is an environmental technique especially developed for the removal of contaminants in soil, sediments and sludge, although it can be applied to any solid porous material [98].

When EK was applied, for 90 days, to a mine soil contaminated with As and Sb, removal efficiencies were very low, 0.6 and 0.1%, respectively. NaOH conditioning in the anolyte and phosphate amendment enhanced contaminants removal to 17 and 2% for As and Sb (after 90 days), but is still a very low rate. The couple of EK with phytoremediation, combining the advantages of both technologies and overcoming the limitations of each one, seems to be a more viable option for the removal of As and Sb (in 15 days, 143 and 196 µg/pot for ryegrass; 336 and 443 µg/pot for Indian mustard). The use of P amendment also helped to improve contaminants uptake: either by competing with the metalloids for the soil adsorption sites, or by increasing plant biomass, which consequently increases the uptake capacity of the plant. Results showed that both tested plants (ryegrass and Indian mustard) can accumulate metalloids, and for that they are considered to be valuable for phytoremediation schemes of mining areas co-contaminated with As and Sb.

Concerning soils contaminated with OCs (BPA, E2, EE2, TCS, OP and NP), the EK promoted their removal by the combined effect of electroosmosis mobilization towards the catholyte and by degradation mechanisms (photo and electrodegradation). The pH control (≈13) in the anolyte improved the EOF rate. The extent of mobilization towards the cathode end was dependent on compound solubility and octanol-water partition coefficients. The rate of compounds degradations (between 44 and 74%) were mainly related to their chemical structures.

The EK remediation of a contaminated soil with OCs is largely dependent on the physico-chemical properties of soil, OCs, and their interactions along time. No statistically differences were found for the degradation percentages between OCs nor between the spiked experimental soils (silty loam and loamy sand).

Phosphorus is a macronutrient, indispensable for plant growth. As phosphate rock, its primary source, is non-renewable, included in the EU 2014 list as one of the 20 Critical Raw Materials,

there is a need to re-assess current use of P, recover it from 'waste' and reuse it in various applications. This is the basis of preserving P as a valuable resource. It would significantly contribute to resolving the issue of environmental degradation, as well as resource scarcity, while ensuring global food security. Taking into consideration that the increased utilization of secondary resources is an important issue in waste strategies of EU, it makes sense to search for the upgrade of these wastes while recycling P. The major aim in using the ED process to recover P from the waste matrices is the possibility to separate it from contaminants. In this study, three waste matrices that may be potential P sources were studied: membrane concentrates resulting from nanofiltration in drinking water treatment, SS from wastewater treatment, and SSA from incineration of SS. These matrices present very distinct P concentrations (from micrograms in the membrane concentrates to grams in the SS and SSA). Although concentrates contain a very little P amount, the eventual presence of microcystins makes it a hazardous waste that needs to be disposed of accordingly. In this case, ED treatment presents a good opportunity, as it removes microcystin-LR reducing the risk associated with the waste, also allowing the recovery of P, avoiding its loss.

Regarding membrane concentrates, two ED cell setups (3c and 2c-cells) were used in the experiments. The 3c-cell presented the highest recoveries (P collected in the anolyte) while applying the lowest current tested (up to 84% with 10 mA or 0.06 mA/cm^2), whereas the 2c-cell gave the best microcystin degradation results being obtained in the cathode compartment where the concentrate was placed (10 mA or 0.06 mA/cm^2). In these experiments, the concentrates used presented differences, namely conductivity, and this influenced the obtained results (r^2 = 0.7638). For the same experimental time, when the concentrates presented higher conductivity and P content, lower recoveries were achieved compared to a concentrate with lower conductivity and P content. Also for the same MC, lower current intensity (10 *vs* 20 mA) allowed higher recoveries.

For SSA, data supported ED as a viable method to separate P from the heavy metals. P and heavy metals are tightly bounded to the ash, and thus the matrix was suspended in sulfuric acid to increase their solubilization. Two acid concentrations were tested in two ED cell designs (2c- and 3c-cells). Independently of the cell design, a higher acidic concentration allowed a higher solubilization.

The highest P solubilization and recovery (up to 99% of P solubilized using H_2SO_4 0.19M; 93 and 97% recovery for the fresh and deposited Lynetten SSA, respectively) from the SSA were achieved in the 2c-cell, in which the SSA was placed in the anode end and a CEM was used. In this design the heavy metals electromigrate to the cathode end being therefore separated from the P that stays in the anode. The influence of storage conditions of the SSA prior to the ED treatment on P recoveries was also accessed. The two different SSA collected showed no trending differences in metal contents and physico-chemical parameters (except for moisture content, which was directly related with the ash disposal conditions). However, the SSA collected after the incineration or from the deposit influenced the total P solubilization in the 2c-cell, when

0.08M of sulfuric acid was used. The deposition of the SSA promoted the decrease in the amount of P solubilized (less 24%), and consequently decreased in 21% the P collected in the anolyte.

The application of a low level DC improved the degradation of all OCs (Caf, BPA, E2, EE2, Ibu, MBPh) in the SS while allowing P recovery. In contrast to the SSA, a high pH favoured P solubilization from the SS. The 2c-cell design in which the SS was placed in the cathode end using an AEM was the best option. This design allowed the migration of P to the anode end. In total, 78% of P were recovered after 5 days using 50 mA (0.10 mA/cm^2) and 70% of P in 3 days using 100 mA (0.21 mA/cm^2). Still, the obtained results showed that 55% were recovered in 24 h using 100 mA. This suggests that P recovery, for the study experimental conditions, should be carried out only for 24 h, decreasing the associated energy costs. The analysis of the microbiological community showed that the conditions within the cell were not appropriated to the protozoa and metazoan communities, as the number of individuals decreased with increasing ED experiments duration.

Comparing the three matrices, the highest amount of P was recovered in the SSA, approx. 125 g of P/kg of SSA in anolyte (93 and 97% for the fresh and deposited Lynetten ash). However, this recovery was achieved after 7 days of ED treatment. With SS, 31 g P/kg SS (55%) were recovered after 1 day and 40 g of P/ kg SS (70%) after 3 days. Membrane concentrates present the lowest potential for P recovery, 1.3 mg of P/L of concentrate (84%), but obtained in only half a day.

Sample-preparation procedure plays a fundamental role in developing analytical methodology for complex matrices, such as SS. Techniques that provide fast, safe and easy preparation procedures, and use smaller amounts of samples and solvents receive significant attention. The application of advanced chromatographic technologies to environmental analysis has opened up the range of compounds that can be analysed, allowing a more comprehensive assessment of environmental contaminants. During this Ph.D. analytical procedures were used and developed for the OCs analysis in the tested different matrices. The extraction of the liquid samples was carried out by SPE, that offers the possibility to simultaneously extract several samples (up to 12 samples in a manifold) in a short time needed (approx. 1 h) with low solvent consumption.

The soil extraction based on UAE was a viable method for the OCs extraction from soil. The major advantage was the simplicity of the UAE equipment (very easy to operate) and relatively cheap. The major drawback is the time needed to perform the extraction (in total 20 min only for the sonication step process alone) and the high amount of solvent used (150 mL).

The innovative SS preparation based on QuEChERS presents as main advantages the simple sample preparation, rapid extraction and clean-up procedures, only requiring approx. 20 min for e.g. 6 samples (number of samples dependent on the centrifuge used).

5. FUTURE DEVELOPMENTS

There are several approaches that can be applied aiming environmental matrices remediation. The processes studied during this Ph.D. showed that EK based technologies are viable for the removal of contaminants, as well as for P recovery. However, optimization for each matrix should be targeted and the following research lines are suggested:

a) Metalloids removal from mine soil

- Test the EK enhanced phytoremediation technology with other plant species that have shown ability to accumulate inorganic contaminants, considering: (i) the use of plants with high accumulation of metals in small volume of biomass, as they are easier and more economic to operate for either metals recovery or safe disposal; (ii) plants with multiple harvests in a single growth period as they have greater potential for phytoextraction;
- Test the influence of AC and DC fields with more plant species and try to elucidate the mechanism of their influence in plant growth, metal uptake and metal translocation.
- Determine the distribution, translocation and environmental risks of heavy metal(loid)s and their influence on plants metal(loid)s accumulation;
- Determine the influence of metalloids speciation in plant metal uptake;
- Test enhancing agents, focusing on natural or biodegradable products.

b) Organic contaminants removal from soil:

- Test EK by applying periodic voltage (cycle of continuous voltage application followed by a period of “down time” with no voltage), to increase the time for the mass transfer, diffusion of the contaminant and polarize the soil particles;
- Study the soil physico-chemical and biological changes after being subjected to the EK process;
- Test other electrodes known to promote OCs degradation, like boron-doped diamond;
- Study the degradation of the OCs to: (i) assess the formation of possible by-products or confirm the complete degradation (mineralization) of the compounds, and (ii) propose degradation pathways;
- Test enhancing agents, focusing on natural or biodegradable products;
- Test the feasibility of EK enhanced phytoremediation aiming at an *in situ* approach.
- Test the EK system with mixed contamination (heavy metals and organic compounds);

c) Microcystins removal and P recovery from MC

- Study other approaches to increase MC-LR degradation like (i) electrodes known to promote OCs degradation and (ii) coupling ED with other process, e.g. UV light (238 nm).
- Study the degradation mechanisms of MC-LR to (i) assess the formation of possible by-products or confirm the complete degradation (mineralization) and (ii) propose degradations pathways;
- Perform the best ED conditions using a “real” contaminated matrix.
- Study the environmental and social costs through life cycle assessment, energy consumption, availability, resource use and pollution, in order the make the process economically viable.

d) P recovery and heavy metals removal from SSA

- Study heavy metals speciation;
- Evaluate the removal of other compounds that may be present in the ash (e.g. Cl, dioxins);
- Evaluate the final physico-chemical characteristics of the ash;
- Test other assisting agents (H_2SO_4 may cause formation of a high quantity of gypsum crystals in the remaining ash and this must be taken into account when considering ash handling in e.g. construction materials or as an increased volume to be deposited);
- Study the possibility of SSA reuse after ED, e.g., in construction materials.

e) P recovery and OCs removal from SS

- Design a cell that allows the agitation of the SS by pumping air into the system (instead of the stirrer), aiming at mimic the conditions of the WWTP bioreactor while promoting the oxygenation and a softer agitation of the sludge.
- Test other cell designs for OCs degradation, e.g. by inserting both anode and cathode directly in the sludge compartment (another anode could be placed in the electrolyte compartment and used for 24 h or less aiming to recover P).
- Test the application of periodic voltage application aiming at reducing the negative effects on the sludge characteristics, namely in the microbiological community.
- Similarly to the suggestion of the soil with OCs, other electrodes known to promote OCs degradation should be tested to assess their potential on P recovery.
- Study the degradation (bio, photo and electro) of the OCs to: (i) assess the formation of possible by-products or confirm the complete degradation (mineralization) of the compounds and (ii) propose degradation pathways;

Although ED proved to be a viable technology to recover P, a life cycle assessment should be done, aiming to assess the environmental impacts associated with all the stages of the product's life from recovery through processing, manufacture, distribution, use and disposal or recycling. Important issues, besides energy consumption and energetic costs, may include the identification of possible uses for the treated SS and SSA. In the case of SSA possible uses of the retrieved heavy metals, carbon footprint and assessing the impacts of implementation and operation should be accounted for. The same should be considered for soils remediation. In the specific case of EK enhanced phytoremediation, the end use

of the plants should be taken into consideration, like the use of the plants for energy (bioenergy) or fibre generation**.**

Mathematical models are currently being developed in collaboration with José Miguel Rodríguez-Maroto and his team from the Department of Chemical Engineering, Málaga University, Spain. Two models are being developed for: (i) EK removal of OCs from the two types of soil and (ii) ED P recovery and heavy metals removal from the SSA. The development of the model will be used for further interpretation of the obtained results.

Future development for the analytical methods are:

f) Analytical methods development for organic contaminants determination

- Development of a method using advanced chromatographic technologies like comprehensive two-dimensional gas chromatography (GCxGC) and liquid chromatography with mass spectrometry (LC-MS);
- Decrease the chromatographic LQ and LD aiming to use the QuEChERS method to analyse SS collected from different WWTPs;
- Develop and optimize the QuEChERS method to soil and plants. This will allow to follow the contaminants pathway/dispersion from the SS to the plant.
- Test new technologies, like microextraction by packed sorbent (MEPS), for the extraction of the OCs from liquid samples. This technology requires little amount of sample for the extraction, allowing a continuous monitoring of the remediation process.

REFERENCES

[1] European Comission, Communication from the commission to the council, the european parliament, the european economic and social committee and the committee of the regions, the Council, the European Economic and Social Committee and the Committee of the Regions, Thematic Strategy for Soil Protection, COM(2006) 231, 2006.

[2] CEC, Proposal for a Directive of the European Parliament and of the Council establishing a framework for the protection of soil and amending Directive 2004/35/EC, COM(2006) 232, 2006/0086 (COD), Commission of the European Communities, Brussels, Belgium, 2006.

[3] European Commission Joint Research Centre, Soil contamination, http://esdac.jrc.ec.europa.eu/themes/soil-contamination, European Soil Data Centre, Accessed the 23th May 2015.

[4] B. Singh, R. Naidu, Cleaning contaminated environment: a growing challenge, Biodegradation, 23 (2012) 785-786.

[5] EEA, Progress in management of contaminated sites (CSI 015/LSI 003) - Assessment published May 2014, European Environmental Agency, 2014.

[6] USEPA, Superfund - Cleaning up the Nation's Hazardous Wastes Sites, United States Environmental Protection Agency, 2014, http://www.epa.gov/superfund/, Accessed the 15th July 2015.

[7] USEPA, Brownfields and Land Revitalization, United States Environmental Protection Agency, 2014, http://www.epa.gov/brownfields/basic_info.htm, Accessed the 15th July 2015.

[8] Q.-Y. Cai, C.-H. Mo, Q.-T. Wu, A. Katsoyiannis, Q.-Y. Zeng, The status of soil contamination by semivolatile organic chemicals (SVOCs) in China: A review, Science of The Total Environment, 389 (2008) 209-224.

[9] S. Khan, Q. Cao, Y.M. Zheng, Y.Z. Huang, Y.G. Zhu, Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China, Environmental Pollution, 152 (2008) 686-692.

[10] L. Niu, F. Yang, C. Xu, H. Yang, W. Liu, Status of metal accumulation in farmland soils across China: From distribution to risk assessment, Environmental Pollution, 176 (2013) 55-62.

[11] Z. Li, Z. Ma, T.J. van der Kuijp, Z. Yuan, L. Huang, A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment, Science of The Total Environment, 468–469 (2014) 843-853.

[12] S. Srinivasa Gowd, M. Ramakrishna Reddy, P.K. Govil, Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India, Journal of Hazardous Materials, 174 (2010) 113-121.

[13] A. Eguchi, T. Isobe, K. Ramu, N.M. Tue, A. Sudaryanto, G. Devanathan, P.H. Viet, R.S. Tana, S. Takahashi, A. Subramanian, S. Tanabe, Soil contamination by brominated flame retardants in open waste dumping sites in Asian developing countries, Chemosphere, 90 (2013) 2365-2371.

[14] G.P. Marc van Liedekerke, S.B. Rabl-Berger, M. Kibblewhite, G. Louwagie, Progress in the Management of Contaminated Sites in Europe, Report EUR 26376 EN, Institute for Environment and Sustainability. Joint Research Center. European Commission (Ed.), Luxembourg, 2014.

[15] S.M. Rodrigues, M.E. Pereira, E.F. da Silva, A.S. Hursthouse, A.C. Duarte, A review of regulatory decisions for environmental protection: Part II-The case-study of contaminated land management in Portugal, Environment International, 35 (2009) 214-225.

[16] R. Naidu, Recent Advances in Contaminated Site Remediation, Water, Air, & Soil Pollution, 224 (2013) 1-11.

[17] BBC news, Report: One fifth of China's soil contaminated, 2014, http://www.bbc.com/news/world-asia-china-27076645, Accessed the 7th May 2015.

[18] J. Zhu, Y. Yan, C. He, C. Wang, China's Environment: Big issues, accelerating effort, ample opportunities, in: Goldman Sachs (Ed.) China: Environmental Services, 2015, http://www.goldmansachs.com/our-thinking/pages/interconnected-markets-folder/chinas-environment/report.pdf, Accessed the 28th May 2015.

[19] Safe Drinking Water Foundation, Mining and Water Pollution, 2014, http://www.safewater.org/PDFS/resourcesknowthefacts/Mining+and+Water+Pollution.pdf, Accessed the 28th May 2015.

[20] M.H. Wong, Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils, Chemosphere, 50 (2003) 775-780.

[21] A.D. Bradshaw, Understanding the fundamentals of succession, in: J. Miles, D.H. Walton (Eds.) Primary Succession on Land, Blackwell, Oxford, 1993.

[22] P.C. Nagajyoti, K.D. Lee, T.V.M. Sreekanth, Heavy metals, occurrence and toxicity for plants: a review, Environmental Chemistry Letters, 8 (2010) 199–216.

[23] J.M. Santos Oliveira, J. Farinha, J.X. Matos, P. Ávila, C. Rosa, M.J. Canto Machado, F.S. Daniel, L. Martins, M.R. Machado Leite, Diagnóstico ambiental das principais áreas mineiras degradadas do país, Boletim de Minas, 39 (2002) 67-85 (in Portuguese).

[24] R. Pereira, R. Ribeiro, F. Gonçalves, Plan for an integrated human and environmental risk assessment in the S. Domingos mine area (Portugal). Human and Ecological Risk Assessment: An International Journal, 10 (2004) 543–578.

[25] G.K. Strauss, J. Madel, Geology of massive sulphide deposits in the Spanish Portuguese Pyrite Belt, Geologische Rundschau, 63 (1974) 191–211.

[26] E. Solgi, A. Esmaili-Sari, A. Riyahi-Bakhtiari, M. Hadipour, Soil contamination of metals in the three industrial estates, Arak, Iran, Bulletin of Environmental Contamination and Toxicology, 88 (2012) 634-638.

[27] A. Facchinelli, E. Sacchi, L. Mallen, Multivariate statistical and GIS-based approach to identify heavy metal sources in soils, Environmental Pollution, 114 (2001) 313-324.

[28] C. Bonaventura, F.M. Johnson, Healthy environments for healthy people: bioremediation today and tomorrow, Environmental Health Perspectives, 105 (1997) 5-20.

[29] J. Dong, Q.-w. Yang, L.-n. Sun, Q. Zeng, S.-j. Liu, J. Pan, X.-l. Liu, Assessing the concentration and potential dietary risk of heavy metals in vegetables at a Pb/Zn mine site, China, Environmental Earth Sciences, 64 (2011) 1317-1321.

[30] G. Nabulo, S.D. Young, C.R. Black, Assessing risk to human health from tropical leafy vegetables grown on contaminated urban soils, Science of The Total Environment, 408 (2010) 5338-5351.

[31] Q. Wang, Y. Dong, Y. Cui, X. Liu, Instances of soil and crop heavy metal contamination in China Soil and Sediment Contamination, 10 (2001) 497-510.

[32] S. Bhattacharya, K. Gupta, S. Debnath, U.C. Ghosh, D. Chattopadhyay, A. Mukhopadhyay, Arsenic bioaccumulation in rice and edible plants and subsequent transmission through food chain in Bengal basin: a review of the perspectives for environmental health, Toxicological & Environmental Chemistry, 94 (2012) 429-441.

[33] C. Gil, J. Ramos-Miras, L. Roca-Pérez, R. Boluda, Determination and assessment of mercury content in calcareous soils, Chemosphere, 78 (2010) 409-415.

[34] C. Gil, R. Boluda, J. Ramos, Determination and evaluation of cadmium, lead and nickel in greenhouse soils of Almería (Spain), Chemosphere, 55 (2004) 1027-1034.

[35] J.J. Ramos-Miras, L. Roca-Perez, M. Guzmán-Palomino, R. Boluda, C. Gil, Background levels and baseline values of available heavy metals in Mediterranean greenhouse soils (Spain), Journal of Geochemical Exploration, 110 (2011) 186-192.

[36] A. Esmaeili, F. Moore, B. Keshavarzi, N. Jaafarzadeh, M. Kermani, A geochemical survey of heavy metals in agricultural and background soils of the Isfahan industrial zone, Iran, Catena, 121 (2014) 88-98.

[37] E. Galán, J.C. Fernández-Caliani, I. González, P. Aparicio, A. Romero, Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South–West Spain, Journal of Geochemical Exploration, 98 (2008) 89-106.

[38] M. Díez, M. Simón, F. Martín, C. Dorronsoro, I. García, C.A.M. Van Gestel, Ambient trace element background concentrations in soils and their use in risk assessment, Science of The Total Environment, 407 (2009) 4622-4632.

[39] T. Tarvainen, E. Kallio, Baselines of certain bioavailable and total heavy metal concentrations in Finland, Applied Geochemistry, 17 (2002) 975-980.

[40] D. Baldantoni, A. Leone, P. Iovieno, L. Morra, M. Zaccardelli, A. Alfani, Total and available soil trace element concentrations in two Mediterranean agricultural systems treated with municipal waste compost or conventional mineral fertilizers, Chemosphere, 80 (2010) 1006-1013.

[41] European Commission, Background values in European soils and sewage sludges, PART III: Conclusions, comments and recommendations, in: B.M. Gawlik, G. Bidoglio (Eds.), Directorate-General Joint Research Centre Institute for Environment and Sustainability, 2006.

[42] Commission of European Communities, Council Directive 91/271/EEC of 21 March 1991 concerning urban waste-water treatment (amended by the 98/15/EC of 27 February 1998).

[43] EEA, The European environment — State and outlook 2005, Copenhagen, 2005.

[44] European Commission, Working document on sludge. 3rd draft, Brussels, 27 April 2000.

[45] B. Clarke, S. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environment International, 37 (2011) 226-247.

[46] U. Bolz, H. Hagenmaier, W. Körner, Phenolic xenoestrogens in surface water, sediments, and sewage sludge from Baden-Württemberg, south-west Germany, Environmental Pollution, 115 (2001) 291-301.

[47] J. Jensen, Fate and effects of linear alkylbenzene sulphonates (LAS) in the terrestrial environment, Science of The Total Environment, 226 (1999) 93-111.

[48] V. Gabet-Giraud, C. Miège, J.M. Choubert, S.M. Ruel, M. Coquery, Occurrence and removal of estrogens and beta blockers by various processes in wastewater treatment plants, Science of The Total Environment, 408 (2010) 4257-4269.

[49] M. Muller, F. Rabenoelina, P. Balaguer, D. Patureau, K. Lemenach, H. Budzinski, D. Barceló, M. López De Alda, M. Kuster, J.P. Delgenès, G. Hernandez-Raquet, Chemical and biological analysis of endocrine-disrupting hormones and estrogenic activity in an advanced sewage treatment plant, Environmental Toxicology and Chemistry, 27 (2008) 1649-1658.

[50] M. Barret, L. Delgadillo-Mirquez, E. Trably, N. Delgenes, F. Braun, G. Cea-Barcia, J.P. Steyer, D. Patureau, Anaerobic removal of trace organic contaminants in sewage sludge: 15 years of experience, Pedosphere, 22 (2012) 508-517.

[51] K. Fent, A.A. Weston, D. Caminada, Ecotoxicology of human pharmaceuticals, Aquatic Toxicology, 76 (2006) 122-159.

[52] H.K. Allen, J. Donato, H.H. Wang, K.A. Cloud-Hansen, J. Davies, J. Handelsman, Call of the wild: antibiotic resistance genes in natural environments, Nature Reviews Microbiology, 8 (2010) 251-259.

[53] A. Sapkota, J. Heidler, R.U. Halden, Detection of triclocarban and two co-contaminating chlorocarbanilides in US aquatic environments using isotope dilution liquid chromatography tandem mass spectrometry, Environmental Research, 103 (2007) 21-29.

[54] R.U. Halden, D.H. Paull, Co-occurrence of triclocarban and triclosan in U.S. water resources, Environmental Science and Technology, 39 (2005) 1420-1426.

[55] M. Ricart, H. Guasch, M. Alberch, D. Barceló, C. Bonnineau, A. Geiszinger, M.l. Farré, J. Ferrer, F. Ricciardi, A.M. Romaní, S. Morin, L. Proia, L. Sala, D. Sureda, S. Sabater, Triclosan persistence through wastewater treatment plants and its potential toxic effects on river biofilms, Aquatic Toxicology, 100 (2010) 346-353.

[56] B. Wilson, R.F. Chen, M. Cantwell, A. Gontz, J. Zhu, C.R. Olsen, The partitioning of Triclosan between aqueous and particulate bound phases in the Hudson River Estuary, Marine Pollution Bulletin, 59 (2009) 207-212.

[57] N. Aryal, D.M. Reinhold, Phytoaccumulation of antimicrobials from biosolids: Impacts on environmental fate and relevance to human exposure, Water Research, 45 (2011) 5545-5552.

[58] R. Rodil, J.B. Quintana, E. Concha-Graña, P. López-Mahía, S. Muniategui-Lorenzo, D. Prada-Rodríguez, Emerging pollutants in sewage, surface and drinking water in Galicia (NW Spain), Chemosphere, 86 (2012) 1040-1049.

[59] D.J. Lapworth, N. Baran, M.E. Stuart, R.S. Ward, Emerging organic contaminants in groundwater: A review of sources, fate and occurrence, Environmental Pollution, 163 (2012) 287-303.

[60] M.S. Díaz-Cruz, M.J. García-Galán, P. Guerra, A. Jelic, C. Postigo, E. Eljarrat, M. Farré, M.J. López de Alda, M. Petrovic, D. Barceló, Analysis of selected emerging contaminants in sewage sludge, TrAC Trends in Analytical Chemistry, 28 (2009) 1263-1275.

[61] R. Salgado, R. Marques, J.P. Noronha, J.T. Mexia, G. Carvalho, A. Oehmen, M.A. Reis, Assessing the diurnal variability of pharmaceutical and personal care products in a full-scale activated sludge plant., Environmental Pollution, 159 (2011) 2359-2367.

[62] N. Ratola, A. Cincinelli, A. Alves, A. Katsoyiannis, Occurrence of organic microcontaminants in the wastewater treatment process. A mini review, Journal of Hazardous Materials, 239–240 (2012) 1-18.

[63] D. Cordell, A. Rosemarin, J.J. Schröder, A.L. Smit, Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options, Chemosphere, 84 (2011) 747-758.

[64] J.J. Schröder, D. Cordell, A.L. Smit, A. Rosemarin, Sustainable Use of Phosphorus, Report 357, EU Tender ENV.B.1/ETU/2009/0025, 2010.

[65] K.M. Smith, G.D. Fowler, S. Pullket, N.J.D. Graham, Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications, Water Research, 43 (2009) 2569-2594.

[66] IFA, Feeding the earth – global phosphate rock production trends from 1961 to 2010: reasons for the temporary set-back in 1988–1994., International Fertilizer Industry Association, Paris, 2011.

[67] S.R. Carpenter, E.M. Bennett, Reconsideration of the planetary boundary for phosphorus, Environmental Research Letters, 6 (2011).

[68] Ostara Nutrient Recovery Technologies, A Food-Water-Resource Balancing Act, Sustainability. The Process Today, http://www.ostara.com/sustainability, Accessed the 28th May 2015.

[69] C. Mitchell, D. Fam, D. Cordell, Effectively managing the transition towards restorative futures in the sewage industry: a phosphorus case study, IWA Publishing, London 2011.

[70] D. Cordell, J.-O. Drangert, S. White, The story of phosphorus: Global food security and food for thought, Global Environmental Change, 19 (2009) 292-305.

[71] D. Cordell, S. White, The Australian story of phosphorus: sustainability implications of global phosphate scarcity for a net food-producing nation, in review, Food Policy, (2009) 23.

[72] J. Lienert, M. Haller, A. Berner, M. Stauffacher, T.A. Larsen, How farmers in Switzerland perceive fertilizers from recycled anthropogenic nutrients (urine). Water Science and Technology, 48 (2003) 47-56.

[73] Y. Liu, G. Villalba, R.U. Ayres, H. Schroder, Global Phosphorus Flows and Environmental Impacts from a Consumption Perspective, Journal of Industrial Ecology, 12 (2008) 229-247.

[74] United Nations Population Fund,, State of World Population, 2007: Unleashing the Potential of Urban Growth, in: United Nations Population Fund (Ed.), 2007.

[75] J.R. Mihelcic, L.M. Fry, R. Shaw, Global potential of phosphorus recovery from human urine and feces, Chemosphere, 84 (2011) 832-839.

[76] B.L. Green, PreP-REX and EIP Water, Arreu Action Group, 26 June 2015, Brussels, Belgium, 2015.

[77] C. Blöcher, C. Niewersch, T. Melin, Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration, Water Research, 46 (2012) 2009-2019.

[78] B.E. Rittmann, B. Mayer, P. Westerhoff, M. Edwards, Capturing the lost phosphorus, Chemosphere, 84 (2011) 846-853.

[79] D.A. Bright, N. Healey, Contaminant risks from biosolids land application: Contemporary organic contaminant levels in digested sewage sludge from five treatment plants in Greater Vancouver, British Columbia, Environmental Pollution, 126 (2003) 39-49.

[80] N.T. Basta, J.A. Ryan, R.L. Chaney, Trace element chemistry in residual-treated soil: key concepts and metal bioavailability, Journal of Environmental Quality, (2005) 49-63.

[81] C.P. Gerba, J.E. Smith, Sources of pathogenic microorganisms and their fate during land application of wastes, Journal of Environmental Quality, 34 (2005) 42-48.

[82] H.A. Elliott, G.A. O'Connor, Phosphorus management for sustainable biosolids recycling in the United States, Soil Biology and Biochemistry, 39 (2007) 1318-1327.

[83] J.P.S. Sidhu, S.G. Toze, Human pathogens and their indicators in biosolids: A literature review, Environment International, 35 (2009) 187-201.

[84] P. Cornel, C. Schaum, Phosphorus recovery from wastewater: needs, technologies and costs, Water Science & Technology, 59 (2009) 1069-1076.

[85] R.A. Gibbs, C.J. Hu, G.E. Ho, I. Unkovich, Regrowth of faecal coliforms and salmonellae in stored biosolids and soil amended with biosolids, Water Science and Technology, 35 (1997) 269-275.

[86] S. Donatello, M. Tyrer, C.R. Cheeseman, EU landfill waste acceptance criteria and EU Hazardous Waste Directive compliance testing of incinerated sewage sludge ash, Waste Management, 30 (2010) 63-71.

[87] S.-C. Pan, C.-C. Lin, D.-H. Tseng, Reusing sewage sludge ash as adsorbent for copper removal from wastewater, Resources, Conservation and Recycling, 39 (2003) 79-90.

[88] M.H. Al Sayed, I.M. Madany, A.R.M. Buali, Use of sewage sludge ash in asphaltic paving mixes in hot regions, Construction and Building Materials, 9 (1995) 19-23.

[89] M. Anderson, M. Elliott, C. Hickson, Factory-scale proving trials using combined mixtures of three by-product wastes (including incinerated sewage sludge ash) in clay building bricks, Journal of Chemical Technology & Biotechnology, 77 (2002) 345-351.

[90] D.-F. Lin, H.-L. Luo, Y.-N. Sheen, Glazed tiles manufactured from incinerated sewage sludge ash and clay, Journal of the Air & Waste Management Association, 55 (2005) 163-172.

[91] C. Sartorius, J. Horn, F. Tettenborn, Phosphorus recovery from wastewater: state-of-the-art and future potencial, in: IWA. Water Environment Federation (Ed.), International Recovery and Management, Miami, Florida, USA, 2011.

[92] P. Hooda, V. Truesdale, A. Edwards, P. Withers, M. Aitken, A. Miller, A. Rendell, Manuring and fertilization effects on phosphorus accumulation in soils and potential environmental implications, Advances in Environmental Research, 5 (2001) 13-21.

[93] M. Yli-Halla, H. Hartikainen, P. Ekholm, E. Turtola, M. Puustinen, K. Kallio, Assessment of soluble phosphorus load in surface runoff by soil analyses, Agriculture, Ecosystems & Environment, 56 (1995) 53-62.

[94] Eurostat, Phosphorus balance in agriculture, European Commission, 2012, http://ec.europa.eu/eurostat/statistics-explained/, Accessed the 27th March 2012

[95] Plano Nacional da Água, Capítulo II, Tema 7, Conservação da natureza, ecossistemas e qualidade biológica, Ministério do Ambiente, Portugal (in Portuguese).

[96] PRGH-Açores, Plano de Gestão da Região Hidrográfica dos Açores, Technical report, Secretaria Regional do Ambiente e do Mar, 2011, http://www.azores.gov.pt/Gra/srrn-drotrh/conteudos/livres/PGRH-A%C3%A7ores.htm, Accessed 27th July 2012 (in Portuguese)

[97] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediation, Environmental Science & Technology, 27 (1993) 2638-2647.

[98] C. Cameselle, S. Gouveia, D.E. Akretche, B. Belhadj, Advances in Electrokinetic Remediation for the Removal of Organic Contaminants in Soils, in: M.N. Rashed (Ed.) Organic Pollutants - Monitoring, Risk and Treatment, 2013, 209-229.

[99] Y.B. Acar, M.F. Rabbi, R.J. Gale, E.E. Ozsu, A.N. Alshawabkeh, Enhance soil bioremediation with electric fields, Chemtec, 26 (1996).

[100] G. Denisov, R.E. Hicks, R.F. Probstein, On the kinetics of charged contaminant removal from soils using electric fields, Journal of Colloid and Interface Science, 178 (1996) 309-323.

[101] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, R. Parker, Electrokinetic remediation: Basics and technology status, Journal of Hazardous Materials, 40 (1995) 117-137.

[102] A. Yeung, C. Hsu, R. Menon, EDTA-Enhanced electrokinetic extraction of lead, Journal of Geotechnical Engineering, 122 (1996) 666-673.

[103] Y. Acar, H. Li, R. Gale, Phenol Removal from Kaolinite by Electrokinetics, Journal of Geotechnical Engineering, 118 (1992) 1837-1852.

[104] A.B. Ribeiro, J.M. Rodríguez-Maroto, Trace Elements in the Environment: Biogeochemistry, Biotechnology and Bioremediation, in: M.N.V. Prasad, K.S. Sajwan, R. Naidu (Eds.), Taylor & Francis, CRC Press (Ed.), Florida, USA, 2006, 341-368.

[105] B.E. Reed, P.C. Carriere, J.C. Thompson, J.H. Hatfield, Electrokinetic (EK) remediation of a contaminated soil at several Pb concentrations and applied voltages, Journal of Soil Contamination, 5 (1996) 95-120.

[106] L. Ottosen, Electrokinetic remediation. Application to soils polluted from wood preservation, Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, 1995.

[107] Y.B. Acar, A.N. Alshawabkeh, Electrokinetic remediation. I: pilot-scale tests with lead-spiked kaolinite, Journal of Geotechnical Engineering, 122 (1996) 173.

[108] J. Virkutyte, M. Sillanpää, P. Latostenmaa, Electrokinetic soil remediation — critical overview, Science of The Total Environment, 289 (2002) 97-121.

[109] A.B. Ribeiro, Use of electrodialytic remediation technique for removal of selected heavy metals and metalloids from soils, Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, 1998.

[110] E. Velizarova, A.B. Ribeiro, L.M. Ottosen, A comparative study on Cu, Cr and As removal from CCA-treated wood waste by dialytic and electrodialytic processes, Journal of Hazardous Materials, 94 (2002) 147-160.

[111] P.E. Jensen, L.M. Ottosen, C. Ferreira, Electrodialytic remediation of soil fines (<63 μm) in suspension—Influence of current strength and L/S, Electrochimica Acta, 52 (2007) 3412-3419.

[112] L.M. Ottosen, P.E. Jensen, H.K. Hansen, A. Ribeiro, B. Allard, Electrodialytic remediation of soil slurry–Removal of Cu, Cr, and As, Separation Science and Technology, 44 (2009) 2245-2268.

[113] L. Ottosen, P. Jensen, G. Kirkelund, H. Hansen, Electrodialytic remediation of different heavy metal-polluted soils in suspension, Water, Air, & Soil Pollution, 224 (2013) 1-10.

[114] L.M. Ottosen, H.K. Hansen, S. Laursen, A. Villumsen, Electrodialytic remediation of soil polluted with copper from wood preservation industry, Environmental Science and Technology, 31 (1997) 1711-1715.

[115] A.B. Ribeiro, E.P. Mateus, L.M. Ottosen, G. Bech-Nielsen, Electrodialytic removal of Cu, Cr and As from chromated copper arsenate-treated timber waste, Environmental Science & Technology, 34 (2000) 784-788.

[116] H.K. Hansen, A. Rojo, L.M. Ottosen, Electrodialytic remediation of copper mine tailings, Journal of Hazardous Materials, 117 (2005) 179-183.

[117] L.M. Ottosen, A.T. Lima, A.J. Pedersen, A.B. Ribeiro, Electrodialytic extraction of Cu, Pb and Cl from municipal solid waste incineration fly ash suspended in water, Journal of Chemical Technology and Biotechnology, 81 (2006) 553-559.

[118] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method, Electrochimica Acta, 52 (2007) 3420-3426.

[119] G.M. Kirkelund, L.M. Ottosen, A. Villumsen, Electrodialytic remediation of harbour sediment in suspension—Evaluation of effects induced by changes in stirring velocity and current density on heavy metal removal and pH, Journal of Hazardous Materials, 169 (2009) 685-690.

[120] P.E. Jensen, C.M.D. Ferreira, H.K. Hansen, J.-U. Rype, L.M. Ottosen, A. Villumsen, Electroremediation of air pollution control residues in a continuous reactor, Journal of Applied Electrochemistry, 40 (2010) 1173–1181

[121] M. Pazos, G.M. Kirkelund, L.M. Ottosen, Electrodialytic treatment for metal removal from sewage sludge ash from fluidized bed combustion, Journal of Hazardous Materials, 176 (2010) 1073-1078.

[122] E. Mateus, J. Zrostlíková, M. Gomes da Silva, A. Ribeiro, P. Marriott, Electrokinetic removal of creosote from treated timber waste: a comprehensive gas chromatographic view, Journal of Applied Electrochemistry, 40 (2010) 1183-1193.

[123] H.I. Gomes, C. Dias-Ferreira, A.B. Ribeiro, Electrokinetic remediation of organochlorines in soil: Enhancement techniques and integration with other remediation technologies, Chemosphere, 87 (2012) 1077-1090.

[124] A.T. Lima, L.M. Ottosen, A.B. Ribeiro, Assessing fly ash treatment: Remediation and stabilization of heavy metals, Journal of Environmental Management, 95, Supplement (2012) S110-S115.

[125] A.T. Lima, L.M. Ottosen, A.B. Ribeiro, Electroremediation of straw and co-combustion ash under acidic conditions, Journal of Hazardous Materials, 161 (2009) 1003-1009.

[126] H.K. Hansen, A. Rojo, D. Pino, L.M. Ottosen, A.B. Ribeiro, Electrodialytic remediation of suspended mine tailings, Journal of Environmental Science and Health, Part A, 43 (2008) 832-836.

[127] C. Ferreira, P. Jensen, L. Ottosen, A. Ribeiro, Removal of selected heavy metals from MSW fly ash by the electrodialytic process, Engineering Geology, 77 (2005) 339-347.

[128] G.M. Kirkelund, C. Magro, P. Guedes, P.E. Jensen, A.B. Ribeiro, L.M. Ottosen, Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension – test of a new two compartment experimental cell, Electrochimica Acta, *in press.*

[129] H.H. Ali, E. Khan, M.A. Sajad, Phytoremediation of heavy metals—Concepts and applications, Chemosphere, 91 (2013) 869-881.

[130] C. Qi, F. Wu, Q. Deng, G. Liu, C. Mo, B. Liu, J. Zhu, Distribution and accumulation of antimony in plants in the super-large Sb deposit areas, China, Microchemical Journal, 97 (2011) 44-51.

[131] A.M. Murciego, A.G. Sánchez, M.A.R. González, E.P. Gil, C.T. Gordillo, J.C. Fernández, T.B. Triguero, Antimony distribution and mobility in topsoils and plants (*Cytisus striatus, Cistus ladanifer* and *Dittrichia viscosa*) from polluted Sb-mining areas in Extremadura (Spain), Environmental Pollution, 145 (2007) 15-21.

[132] J. Pratas, M.N.V. Prasad, H. Freitas, L. Conde, Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation, Journal of Geochemical Exploration, 85 (2005) 99-107.

[133] M. Vaculík, Ľ. Jurkovič, P. Matejkovič, M. Molnárová, A. Lux, Potential risk of arsenic and antimony accumulation by medicinal plants naturally growing on old mining sites, Water, Air, & Soil Pollution, 224 (2013) 1-16.

[134] U. Jana, V. Chassany, G. Bertrand, M. Castrec-Rouelle, E. Aubry, S. Boudsocq, D. Laffray, A. Repellin, Analysis of arsenic and antimony distribution within plants growing at an old mine site in Ouche (Cantal, France) and identification of species suitable for site revegetation, Journal of Environmental Management, 110 (2012) 188-193.

[135] G. Levresse, G. Lopez, J. Tritlla, E.C. López, A.C. Chavez, E.M. Salvador, A. Soler, M. Corbella, L.G.H. Sandoval, R. Corona-Esquivel, Phytoavailability of antimony and heavy metals in arid regions: The case of the Wadley Sb district (San Luis, Potosí, Mexico), Science of The Total Environment, 427–428 (2012) 115-125.

[136] C. Pérez-Sirvent, M.J. Martínez-Sánchez, S. Martínez-López, J. Bech, N. Bolan, Distribution and bioaccumulation of arsenic and antimony in Dittrichia viscosa growing in mining-affected semiarid soils in southeast Spain, Journal of Geochemical Exploration, 123 (2012) 128-135.

[137] H.I. Gomes, Phytoremediation for bioenergy: challenges and opportunities, Environmental Technology Reviews, 1 (2012) 59-66.

[138] P.J.C. Favas, J. Pratas, M. Varun, R. D'Souza, M. Paul, Chapter 17: Phytoremediation of soils contaminated with metals and metalloids at mining areas: Potential of native flora, in: M.C.H. Soriano (Ed.) Environmental Risk Assessment of Soil Contamination, In Tech2014.

[139] P. Madejón, J.M. Murillo, T. Marañón, F. Cabrera, R. López, Bioaccumulation of As, Cd, Cu, Fe and Pb in wild grasses affected by the Aznalcóllar mine spill (SW Spain), Science of The Total Environment, 290 (2002) 105-120.

[140] C.S. O'Connor, N.W. Lepp, R. Edwards, G. Sunderland, The combined use of electrokinetic remediation and phytoremediation to decontaminate metal-polluted soils: A laboratory-scale feasibility study, Environmental Monitoring and Assessment, 84 (2003) 141-158.

[141] L. Cang, Q.Y. Wang, D.M. Zhou, H. Xu, Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard, Separation and Purification Technology, 79 (2011) 246-253.

[142] R.S. Putra, Y. Ohkawa, S. Tanaka, Application of EAPR system on the removal of lead from sandy soil and uptake by Kentucky bluegrass (*Poa pratensis L.*), Separation and Purification Technology, 102 (2013) 34-42.

[143] H. Aboughalma, R. Bi, M. Schlaak, Electrokinetic enhancement on phytoremediation in Zn, Pb, Cu and Cd contaminated soil using potato plants, Journal of Environmental Science and Health, Part A, 43 (2008) 926-933.

[144] R. Bi, M. Schlaak, E. Siefert, R. Lord, H. Connolly, Influence of electrical fields (AC and DC) on phytoremediation of metal polluted soils with rapeseed (*Brassica napus*) and tobacco (*Nicotiana tabacum*), Chemosphere, 83 (2011) 318-326.

[145] C. Cameselle, R.A. Chirakkara, K.R. Reddy, Electrokinetic-enhanced phytoremediation of soils: Status and opportunities, Chemosphere, 93 (2013) 626-636.

[146] L. Cang, D.-M. Zhou, Q.-Y. Wang, G.-P. Fan, Impact of electrokinetic-assisted phytoremediation of heavy metal contaminated soil on its physicochemical properties, enzymatic and microbial activities, Electrochimica Acta, 86 (2012) 41-48.

[147] Saifullah, E. Meers, M. Qadir, P. de Caritat, F.M.G. Tack, G. Du Laing, M.H. Zia, EDTA-assisted Pb phytoextraction, Chemosphere, 74 (2009) 1279-1291.

[148] J. Bech, I. Corrales, P. Tume, J. Barceló, P. Duran, N. Roca, C. Poschenrieder, Accumulation of antimony and other potentially toxic elements in plants around a former antimony mine located in the Ribes Valley (Eastern Pyrenees), Journal of Geochemical Exploration, 113 (2012) 100-105.

[149] A. Bhargava, F.F. Carmona, M. Bhargava, S. Srivastava, Approaches for enhanced phytoextraction of heavy metals, Journal of Environmental Management, 105 (2012) 103-120.

[150] V. Antoniadis, C. Tsadilas, V. Samaras, J. Sgouras, Availability of heavy metals applied to soil through sewage sludge, in: M.N.V. Prasad, K.S. Sajwan, R. Naidu (Eds.) Trace Elements in the Environment: Biogeochemistry, Biotechnology and Bioremediation, Taylor and Francis, Florida, 2006.

[151] Y. Teng, Y. Shen, Y. Luo, X. Sun, M. Sun, D. Fu, Z. Li, P. Christie, Influence of *Rhizobium meliloti* on phytoremediation of polycyclic aromatic hydrocarbons by alfalfa in an aged contaminated soil, Journal of Hazardous Materials, 186 (2011) 1271-1276.

[152] C.M. Mehta, W.O. Khunjar, V. Nguyen, S. Tait, D.J. Batstone, Technologies to recover nutrients from waste streams: A critical review, Critical Reviews in Environmental Science and Technology, 45 (2015) 385-427.

[153] G. Sturm, H. Weigand, C. Marb, W. Weiß, B. Huwe, Electrokinetic phosphorus recovery from packed beds of sewage sludge ash: yield and energy demand, Journal of Applied Electrochemistry, 40 (2010) 1069-1078.

[154] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, Electrodialytic separation of phosphorus and heavy metals from two types of sewage sludge ash, Separation Science and Technology, 49 (2014) 1910-1920.

[155] B. Ebbers, L.M. Ottosen, P.E. Jensen, Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash, Chemosphere, 125 (2015) 122-129.

[156] B. Ebbers, L.M. Ottosen, P.E. Jensen, Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus, Electrochimica Acta, *in press.*

[157] K. Danzer, The Analytical Process, Analytical Chemistry, Springer Berlin Heidelberg, 2007, 13-41.

[158] O. Zuloaga, P. Navarro, E. Bizkarguenaga, A. Iparraguirre, A. Vallejo, M. Olivares, A. Prieto, Overview of extraction, clean-up and detection techniques for the determination of organic pollutants in sewage sludge: A review, Analytica Chimica Acta, 736 (2012) 7-29.

[159] L. Sanchez-Prado, C. Garcia-Jares, M. Llompart, Microwave-assisted extraction: Application to the determination of emerging pollutants in solid samples, Journal of Chromatography A, 1217 (2010) 2390-2414.

[160] USEPA, Microwave assisted acid digestion of sediments, sludges, soils, and oils, United States Environmetal Protection Agency, 2007.

[161] K. Vilkhu, R. Mawson, L. Simons, D. Bates, Applications and opportunities for ultrasound assisted extraction in the food industry — A review, Innovative Food Science & Emerging Technologies, 9 (2008) 161-169.

[162] H.M. Santos, C. Lodeiro, J.-L. Capelo-Martínez, The Power of Ultrasound, Ultrasound in Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2009, 1-16.

[163] USEPA, Method 3550C, United States Ennvironmental Protection Agency, 2000, 1-16.

[164] R. Rial-Otero, Ultrasonic Assisted Extraction for the Analysis of Organic Compounds by Chromatographic Techniques, Ultrasound in Chemistry, Wiley-VCH Verlag GmbH & Co. KGa A, 2009, 55-79.

[165] A.V. Filgueiras, J.L. Capelo, I. Lavilla, C. Bendicho, Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of magnesium, manganese and zinc in plant samples by flame atomic absorption spectrometry, Talanta, 53 (2000) 433-441.

[166] F.W. Fifield, D. Kealey, Principles and Practice of Analytical Chemistry, 5th Edition, Blackwell Science Ltd., 2000, 73-80.

[167] Sigma Aldrich Co., Guide to Solid Phase Extraction, 1998, http://www.sigmaaldrich.com/Graphics/Supelco/objects/4600/4538.pdf, Accessed the 9th September 2015.

[168] M. Anastassiades, K. Maštovská, S.J. Lehotay, Evaluation of analyte protectants to improve gas chromatographic analysis of pesticides, Journal of Chromatography A, 1015 (2003) 163-184.

[169] A.R. Fontana, A. Camargo, L.D. Martinez, J.C. Altamirano, Dispersive solid-phase extraction as a simplified clean-up technique for biological sample extracts. Determination of polybrominated diphenyl ethers by gas chromatography–tandem mass spectrometry, Journal of Chromatography A, 1218 (2011) 2490-2496.

[170] Phenomenex, QuEChERS, https://www.phenomenex.com/sample-preparation/quechers, Accessed the 4th September 2015.

[171] Y. Wang, L. DU, X. Zhou, H. Tan, L. Bai, D. Zeng, H. Tian, QuEChERS extraction for high performance liquid chromatographic determination of pyrazosulfuron-ethyl in soils, Journal of the Chemical Society of Pakistan, 34 (2012) 28-32.

[172] Method AOAC 2007, Official Methods of Analysis, Pesticide Residues Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulfate, 2007, http://www.weber.hu/PDFs/QuEChERS/AOAC_2007_2001.pdf, Accessed the 21th September 2015.

[173] EN15662, Foods of plant origin - Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE, https://shop.austrian-standards.at/Preview.action;jsessionid=0591FE94A94C9C6E7117064F9A22C0CE?preview=&dokkey=321612&selectedLocale=en, Accessed the 12th September 2015, (2009).

[174] C.G. Pinto, M.E.F. Laespada, S.H. Martín, A.M.C. Ferreira, J.L.P. Pavón, B.M. Cordero, Simplified QuEChERS approach for the extraction of chlorinated compounds from soil samples, Talanta, 81 (2010) 385-391.

[175] M.Á. González-Curbelo, B. Socas-Rodríguez, A.V. Herrera-Herrera, J. González-Sálamo, J. Hernández-Borges, M.Á. Rodríguez-Delgado, Evolution and applications of the QuEChERS method, TrAC Trends in Analytical Chemistry, 71 (2015) 169-185.

[176] P.W.S. Raymond, Instrumentation for High-Performance Liquid Chromatography, Analytical Instrumentation Handbook, Third Edition, CRC Press, 2004, 687-726.

[177] M.W. Dong, Modern HPLC for Practicing Scientists, John Wiley & Sons Inc., 2006.

[178] Waters, How Does High Performance Liquid Chromatography Work?, 2015, http://www.waters.com/waters/en_US/How-Does-High-Performance-Liquid-Chromatography-Work%3F/nav.htm?cid=10049055&locale=en_US, Accessed the 14th September 2015.

[179] Waters, HPLC Separation Modes, 2015, http://www.waters.com/waters/en_US/HPLC-Separation-Modes/nav.htm?cid=10049076&locale=en_US, Accessed 4th September 2015.

[180] RELACRE, Validação de métodos internos de ensaio em análise química, Guia RELACRE 12, 2000 (in Portuguese).

[181] M. Ribau Teixeira, M.J. Rosa, Microcystins removal by nanofiltration membranes, Separation and Purification Technology, 46 (2005) 192-201.

[182] J.B. Jensen, A. Villumsen, Method and apparatus for the decontamination of products containing heavy metal, PCT/DK95/00209, 1995.

[183] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, B. Ebbers, Electrodialytic recovery and purification of phosphorous from sewage sludge ash, sewage sludge and wastewater, PCT/EP2014/068956, 2014.

[184] R.K. Lu, Analysis Methods of Soil Agricultural Chemistry, Agricultural Science Press, Beijing, China, 2000, 12, 106, 477 (in Chinese).

[185] Y. Cai, J.C. Cabrera, M. Georgiadis, K. Jayachandran, Assessment of arsenic mobility in the soils of some golf courses in South Florida, Science of The Total Environment, 291 (2002) 123-134.

[186] J. Meriluoto, L. Spoof, SOP: Solid phase extraction of microcystins in water samples. , Abo Akademi University, Finland, 2005.

[187] A.D. Boney, Phytoplankton, in: Edward Arnold (Ed.) Institute of Biology's studies in biology ; no. 52, London, 1975.

[188] J.W.G. Lund, C. Kipling, E.D. Le Cren, The inverted microscope method of estimating algal numbers and the statistical basis of estimations by counting, Hydrobiologia, 11 (1958) 143-170.

[189] DS259, Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry in flame, Dansk Standardiseringsråd, 2003 (in Danish).

[190] L.M. Ottosen, G.M. Kirkelund, P.E. Jensen, Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminum, Chemosphere, 91 (2013) 963-969.

[191] Standard Methods 1998, Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA - AWWA - WEF, USA, 1998.

[192] A.B. Ribeiro, E.P. Mateus, J.-M. Rodríguez-Maroto, Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Experimental and modeling, Separation and Purification Technology, 79 (2011) 193-203.

[193] W. Peysson, E. Vulliet, Determination of 136 pharmaceuticals and hormones in sewage sludge using quick, easy, cheap, effective, rugged and safe extraction followed by analysis with liquid chromatography–time-of-flight-mass spectrometry, Journal of Chromatography A, 1290 (2013) 46-61.

[194] S. Kegley, B. Hill, S. Orme, PAN Pesticide Database; Pesticide Action Network, North America, San Francisco, CA., 2015.

[195] Waters, Oasis HLB cartridges and 96-well plates, http://www.waters.com/webassets/cms/support/docs/715000109.pdf, Accessed the 12th September 2015.

[196] J.M. Dzenitis, Steady state and limiting current in electroremediation of soil, Journal of the Electrochemical Society, 144 (1997) 1317-1322.

[197] B.-G. Ryu, G.-Y. Park, J.-W. Yang, K. Baek, Electrolyte conditioning for electrokinetic remediation of As, Cu, and Pb-contaminated soil, Separation and Purification Technology, 79 (2011) 170-176.

[198] C. Yuan, T.-S. Chiang, Enhancement of electrokinetic remediation of arsenic spiked soil by chemical reagents, Journal of Hazardous Materials, 152 (2008) 309-315.

[199] K. Baek, D.-H. Kim, S.-W. Park, B.-G. Ryu, T. Bajargal, J.-S. Yang, Electrolyte conditioning-enhanced electrokinetic remediation of arsenic-contaminated mine tailing, Journal of Hazardous Materials, 161 (2009) 457-462.

[200] A. Asadi, B.B.K. Huat, M.M. Hassim, T.A.M. Mohamed, M.M. Hanafi, N. Shariatmadari, Electroosmotic phenomena in organic soils, American Journal of Environmental Sciences, 5 (2009) 310-314.

[201] S. Yuan, N. Gou, A.N. Alshawabkeh, A.Z. Gu, Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode, Chemosphere, 93 (2013) 2796-2804.

[202] N. Xu, Y. Zhang, H. Tao, S. Zhou, Y. Zeng, Bio-electro-fenton system for enhanced estrogens degradation, Bioresource Technology, 138 (2013) 136-140.

[203] I. Naimi, N. Bellakhal, Removal of 17β-estradiol by electro-fenton process, Materials Sciences and Applications, 3 (2012) 880-886.

[204] M.G. Antoniou, J.A. Shoemaker, A.A. de la Cruz, D.D. Dionysiou, LC/MS/MS structure elucidation of reaction intermediates formed during the TiO2 photocatalysis of microcystin-LR, Toxicon, 51 (2008) 1103-1118.

[205] W. Liao, M. Murugananthan, Y. Zhang, Electrochemical degradation and mechanistic analysis of microcystin-LR at boron-doped diamond electrode, Chemical Engineering Journal, 243 (2014) 117-126.

[206] M. Ribau Teixeira, M.J. Rosa, Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration, Water Research, 40 (2006) 2837-2846.

[207] G. Liu, Y. Qian, S. Dai, N. Feng, Adsorption of Microcystin LR and LW on Suspended Particulate Matter (SPM) at Different pH, Water, Air, and Soil Pollution, 192 (2008) 67-76.

[208] P. Maagd, A. Hendriks, W. Seinen, D. Sijm, pH dependent hydrophobicity of the cyanobacteria toxin microcystin-LR, Water Research, 33 (1999) 677-680.

[209] J. Meriluoto, Chromatography of microcystins, Analytica Chimica Acta, 352 (1997) 277-298.

[210] A.P. Bayuseno, W.W. Schmahl, Characterization of MSWI fly ash through mineralogy and water extraction, Resources, Conservation and Recycling, 55 (2011) 524-534.

[211] M. Cyr, M. Coutand, P. Clastres, Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials, Cement and Concrete Research, 37 (2007) 1278-1289.

[212] C.S. Reynolds, P.S. Davies, Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective, Biological Reviews, 76 (2001) 27-64.

[213] D.P. Schachtman, R.J. Reid, S. Ayling, Phosphorus uptake by plants: from soil to cell, plant physiology, 116 (1998) 447–453.

[214] F. Oliveira, M. Osugi, F.M. Paschoal, D. Profeti, P. Olivi, M. Zanoni, Electrochemical oxidation of an acid dye by active chlorine generated using Ti/Sn(1−x)Ir x O2 electrodes, Journal of Applied Electrochemistry, 37 (2007) 583-592.

[215] K. Zhou, M. Xu, B. Liu, H. Cao, Characteristics of microfauna and their relationships with the performance of an activated sludge plant in China, Journal of Environmental Sciences, 20 (2008) 482-486.

[216] M. Martín-Cereceda, S. Serrano, A. Guinea, A comparative study of ciliated protozoa communities in activated-sludge plants, FEMS Microbiology Ecology, 21 (1996) 267-276.

[217] H. Melcer, G. Klečka, Treatment of wastewaters containing bisphenol A: State of the science review, Water Environment Research, 83 (2011) 650-666.

[218] K. Onesios, J. Yu, E. Bouwer, Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review, Biodegradation, 20 (2009) 441-466.

[219] C. Indermuhle, M.J. Martín de Vidales, C. Sáez, J. Robles, P. Cañizares, J.F. García-Reyes, A. Molina-Díaz, C. Comninellis, M.A. Rodrigo, Degradation of caffeine by conductive diamond electrochemical oxidation, Chemosphere, 93 (2013) 1720-1725.

[220] V.H. Cong, S. Iwaya, Y. Sakakibara, Removal of estrogens by electrochemical oxidation process, Journal of Environmental Sciences, 26 (2014) 1355-1360.

[221] M.J. Martín de Vidales, M. Millán, C. Sáez, J.F. Pérez, M.A. Rodrigo, P. Cañizares, Conductive diamond electrochemical oxidation of caffeine-intensified biologically treated urban wastewater, Chemosphere, 136 (2015) 281-288.

[222] J. He, H. Yu, B. Fugetsu, S. Tanaka, L. Sun, Electrochemical removal of bisphenol A using a CNT-covered polyester yarn electrode, Separation and Purification Technology, 110 (2013) 81-85.

[223] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review, Environment International, 40 (2012) 212-229.

[224] J.F. Ferguson, D. Jenkins, J. Eastman, Calcium phosphate precipitation at slightly alkaline pH values, Water Pollution Control Federation, 45 (1973) 620-631.

APPENDICES

Appendix 1. List of the organic compounds most frequently detected in environmental compartments.

	Compound	log K_{ow}	Categories	WWTP[a]	Ref.
A					
	acetaminophen (paracetamol)	0.46	Analgesic	y	[1-6]
	acetylsalicylic acid	1.2	Analgesic	y	[3, 4]
	6-acetylmorphine	1.3	Heroin metabolite	y	[7]
	abieta-8,11,13-triene diterpenoid		Diterpenoid derivate		[8]
	allopurinol	-0.55	Gout treatment	y	[4]
	alprazolam	2.1	Anxiolytic, tranquilizer	y	[2, 4]
	alkylphenol ethoxylates	3.0-3.3	Non-ionic surfactants		[9]
	alkylphenol ethoxy acetic acids		Anti-Infective agents, local		[9]
	amitriptyline	-0.32	Adrenergic uptake inhibitors, analgesic non-narcotic, antidepressive		[10]
	atenolol	0.16	(Beta)-blocker	y	[4-6, 10]
	amphetamine	1.8	Central nervous system stimulant and sympathomimetic		[10]
	4-aminoantipyrine	0.1	Analgesic, anti-inflammatory		[11]
	amoxicillin	-2	Antibiotic	y	[2, 4]
	ampicillin	4.2	Antibiotic		[4]
	androsterone	3.7	Testosterone metabolite	y	[12]
	androstanediol	4.3	Anabolic agents, metabolite of testosterone		[12]
	5-androstenediol	3.5	Intermediate in testosterone biosynthesis	y	[12]
	aromadendrene	4.7	Coil compound		[8]
	azithromycin	4.0	Antibiotic	y	[2, 4]
	azulene	3.45	Oil compound		[8]
B					
	bezafibrate	3.8	Antilipemic agent	y	[2, 5, 6]
	benzylparaben	3.06	Pharmaceutical and personal care products		[9]
	benzoylecgonine	-0.3	Metabolite of cocaine		[10]
	betamethasone	1.9	Corticosteroid (SAID)	y	[4]
	biochanin A	3	Anticarcinogenic agents; phytoestrogens		[13-15]
	bisphenol A	3.3	Plasticizer		[9, 13-15]
	bisoprolol	1.9	Beta-1 adrenergic blocker		[2]
	bromazepam	1.7	Anxiolytic, tranquilizer	y	[2, 4]
	budesonide	2.5	Corticosteroid (asthma)	y	[4]
	α-bulnesene	4.6	Oil compound	y	[8]
	butylparaben	3.6	Antimicrobial in cosmetics, medication suspensions, flavouring additive		[9]
	(1-butylnonyl)-benzene	8.5			[8]
C					
	cadina-1(10),4-diene	6.5	flavouring		[8]
	α-calacorene	4.4	Anti-inflammatory and anti-microbial		[8]
	calamenene	5.1	Natural substance and extract		[8]
	cashmeran	3.3	Musk	y	[4]
	caffeine	-0.07	CSN stimulant	y	[1, 3-6, 10, 11, 16]
	carbamazepine	2.5	Antiepileptic	y	[1, 4-6, 10, 16-18]
	captopril	0.34	Antihypertensive	y	[4]

	celestolide	5	Musk	y	[4]
	chlortetracycline	-1.3	Anti-bacterial	y	[1]
	cholesterol	8.7	Sterol	y	[12]
	ciprofloxacin	0.28	Antibiotic	y	[2, 4]
	clarithromycin	3.2	Antibiotic		[10]
	clorazepate	3.3	Anxiolitic	y	[4]
	clofibric acid	2.6	Lipid modifying agent	y	[3-6]
	clofibrate ethyl	3.3	Lipid modifying agent	y	[4]
	cocaine	2.3	Anaesthetics, dopamine uptake inhibitors, vasoconstrictor agents		[10]
	codeine	1.1	Analgesic	y	[4, 7]
	cotinine	0.07	Urinary metabolite of nicotine		[10]
D					
	daidzein	2.5	Phytoestrogen		[13-15]
	demeclocycline	0.7	Tetraciclina	y	[1]
	dehydronifedipine		Nifedipine metabolit (plasma)		[10]
	dehydroabietinal	5.5	Activator of systemic acquired resistance		[8]
	dehydroandrosterone	3.2	Adjuvants, immunologic	y	[12]
	dihydrocholesterol	9.4	Cholesterol derivative	y	[12]
	dihydroprogesterone	4.2	Metabolite of progesterone	y	[12]
	desmethyldiltiazem		Pharmaceutical and personal care products		[10]
	diazepam	2.8	Anxiolytic, tranquilizer	y	[2, 4, 10, 11, 17, 18]
	diclofenac	4.5	Non-steroidal anti-inflammatory	y	[2, 4-6, 19]
	diethylstilbestrol	5.1	Estrogen nonsteroidal		[19]
	Diethyltoluamide (DEET)	2.0	Insect repellent		[10]
	dihexyl phthalate	6.9	Industry		[8]
	digoxin	1.26	Cardiac glycoside	y	[4]
	digoxigenin	1.1	Pharmaceutical and personal care products		[10]
	10.11-dihydro carbamazepine	2.3			[11]
	diisobutyl phthalate	4.1	Industry		[8]
	diisooctyl phthalate	8.3	Industry		[8]
	diltiazem	2.7	Hypertensive, calcium blocker	y	[4, 10]
	dimethyl phenazone (antipyrine)	0.4	Analgesic; anti-inflammatory	y	[4]
	diphenhydramine	3.3	Antagonist, hypnotics, sedative. anti-allergic, antiemetic, anaesthetics		[10]
	domperidone	3.9	Antidopaminergic	y	[4]
	doxycycline	-0.7	Antibiotic	y	[1]
E					
	EDDP (2-ethylidene-1.5-dimethyl-3.3-diphenylpyrrolidine)	5.2	Methadone metabolite	y	[7]
	enalapril	-0.1	Antihypertensive	y	[4, 10]
	erythromycin	3.1	Anti-bacterial agents; gastrointestinal agents	y	[5, 6, 10]
	17-β-estradiol	4.01	Estrogen	y	[4, 5, 12-15, 19]
	17-α-ethynylestradiol	3.67	Estrogen	y	[4, 5, 13-15, 19]
	etofenamate	4.7	Non-steroidal anti-inflammatory	y	[4]
	escitalopram	3.2	Antidepressant	y	[4]
	estriol	2.45	Estrogen	y	[5, 12, 19]

	estrone	3.43	Estrogen	y	[4, 5, 12-15, 19]
	ethylparaben	2.47	Pharmaceutical and personal care products		[9]
	ecstasy (extasy)	2.2	Psychoactive drug	y	[4]
F					
	fenofibric acid	3.9	Lipid regulating agent		[17, 18]
	fentanyl	4.0	Adjuvants, anaesthesia, analgesics, opioid, anaesthetics, intravenous, narcotic	y	[7]
	fentiazac	5.2	Non-steroidal anti-inflammatory	y	[4]
	fluoxetine	4	Antidepressant	y	[2, 4, 18]
	flurbiprofen	4.2	Non-steroidal anti-inflammatory	y	[4]
	fluticasone	3.2	Glucocorticosteroid (asthma)	y	[4]
	furosemide	2.0	Loop diuretic	y	[2, 4]
G					
	galaxolide	5.9	Musk	y	[4-6, 8]
	gemfibrozil	4.8	Lipid-regulating agent that	y	[2, 5, 6, 10]
	genistein	2.8	Antineoplastic and antitumor Agent		[13-15]
	glibenclamide	4.8	Diabetes type II treatment	y	[4, 11]
	α-Gurjunene	4.1			[8]
	γ-Gurjunene	5.3			[8]
H					
	heroin	1.58	Analgesics. opioid, narcotics	y	[7]
	hydrochlorothiazide	-0.1	Thiazide diuretic		[2]
	hydrocodone	2.2	Narcotic analgesic		[10]
	hydroxyzine	2.4	Antihistamine	y	[4]
	10-hydroxy-amitriptyline		Metabolite		[10]
	11-hydroxy androsterone	2.5	Steroid	y	[12]
	16-hydroxydehydro-androsterone	2.7	Steroid	y	[12]
	19-hydroxy androstenedione	1.5	Steroid	y	[12]
	17-hydroxy pregnenolone	3.1	Steroid	y	[12]
I					
	ibuprofen	3.9	Non-steroidal anti-inflammatory	y	[2-6, 10, 16]
	indapamide	2.9	Antihypertensive	y	[2, 4]
	indomethacin	4.3	Non-steroidal anti-inflammatory	y	[4]
K					
	ketoprofen	3.1	Non-steroidal anti-inflammatory	y	[2, 3, 5]
L					
	latanoprost	4.3	Ocular hypertension (glaucoma)	y	[4]
	ledane	5.5			[8]
	levonorgestrel	3.5	Synthetic progestational hormone		[19]
	lincomycin	0.2	Antibiotic	y	[1]
	lorazepam	2.4	Ansiolitic	y	[2]
	lovastatin	4.3	Antideslipidemic	y	[4]
M					
	meclocycline	0.9	Anti-bacterial agents	y	[1]
	mefenamic acid	5.1	Anti-inflammatory agents. Non-steroidal. Cyclooxygenase inhibitors	y	[3, 5, 6]
	meprobamate	0.7	Anti-anxiety		[10]

	mestranol	4.6	Estrogen		[19]
	methadone	3.93	Analgesics. Opioid. Antitussive agents. Narcotics	y	[7]
	methylparaben	2.0	Pharmaceutical and personal care products		[9]
	methyl dehydroabietate	5.9			[8]
	metropolol	1.9	B-Blocker	y	[5, 6]
	mexazolam	3.7	Anxiolytic, tranquilizer	y	[4]
	mirtazepine	3.3	Antidepressant	y	[4]
	morphine	0.89	Analgesics. Opioid. Narcotics	y	[7]
N					
	naproxen	3.2	Non-steroidal anti-inflammatory	y	[2-6, 10]
	norcodeine	0.7	Codeine derivate	y	[7]
	nifedipine	2.2	Calcium blocker	y	[4]
	nimesulide	2.6	Non-steroidal anti-inflammatory	y	[2, 4]
	norethindrone	2.97	Progestational hormone		[19]
	normorphine	0.3	Morphine derivate	y	[7]
	4-nonylphenol	5.8	Pharmaceutical and personal care products		[9, 10, 13-15]
	4-nonylphenol monoethoxylates	4.17	Pharmaceutical and personal care products		[10]
	4-nonylphenol diethoxylates	4.2	Pharmaceutical and personal care products		[10]
O					
	4-octylphenol	5.3	Pharmaceutical and personal care products		[9, 13-15]
	omeprazol	2.2	Proton pump inhibitor	y	[2, 11]
	oxazepam	2.2	Anxiolytic	y	[4]
	oxybenzone	3.8	Sun-screening agent	y	[5, 6]
	oxyphenbutazone	2.7	Non-steroidal anti-inflammatory		[11]
	oxytetracycline	-0.90	Anti-bacterial agents	y	[1]
P					
	paroxetine	2.1	Antidepressant	y	[2, 4]
	penincillin G	1.83	Antibiotic	y	[4]
	phantolide	4.8	Musk	y	[4]
	phenazone	0.4	Non-steroidal anti-inflammatory	y	[4]
	phenylbutazone	3.16	Non-steroidal anti-inflammatory		[11]
	phenylphenol	3.1-3.2	Pharmaceutical and personal care products		[9]
	piroxicam	3.1	Non-steroidal anti-inflammatory	y	[4]
	progesterone	3.87	Steroid contraceptive hormone	y	[4, 19]
	propranolol	3	β-blocker	y	[4, 17, 18]
	propoxyphene	4.18	Analgesics. Opioid		[10]
	propylparaben	3.04	Pharmaceutical and personal care products		[9]
	propyphenazone	1.7	Non-steroidal anti-inflammatory		[11]
	pyrene	4.9	Fluorescent dyes		[8]
R					
	ramipril	1.4	Congestive heart failure	y	[4]
	ranitidine	0.3	Histamine H2 receptor antagonist	y	[4, 10]
	reserpine	4	Antiadrenergic agent	y	[4]
	retene	6.5	Polycyclic aromatic hydrocarbons		[8]
S					

	salbutamol (Albuterol)	0.64	B2-adrenergic receptor Antagonist	y	[4, 10]
	salicilic acid	2.3	Analgesic	y	[3-5]
	sertraline	4.8	Antidepressant	y	[4, 10]
	silenane		Oil compound		[8]
	simvastatin	4.7	Anticholesteremic agents		[2]
	sulfadiazine	-0.1	Anti-Infective agents	y	[1]
	sulfamerazine	0.1	Antibacterial agent	y	[1]
	sulfamethazine	0.14	Anti-infective agent	y	[1]
	sulfamethoxazole	0.89	Antibacterial agent	y	[1, 5, 6, 10, 17, 18]
T					
	telmitarsen		Angiotensive, hypertension	y	[4]
	tetracycline	-1.4	Antibiotic	y	[1]
	tetrahydrocannabinol (THC)	6.97	Psychoactive drug	y	[4, 7]
	THCCOOH (11-nor-carboxy-Δ9- tetrahydrocannabinol)	6.3	Analgesics, non-narcotic, cannabinoid receptor agonists, hallucinogens, psychotropic Drugs	y	[7]
	thiabendazole	2.47	Anthelmintic		[10]
	tiaprofencic acid	3.3	Non-steroidal anti-inflammatory	y	[4]
	tonalide	5.7	Musk	y	[4, 6, 8]
	tramadol	1.4	Opioid centrally action	y	[4]
	traseolide	5.1	Musk	y	[4]
	triamterene	0.98	Diuretic, epithelial sodium Channel Blockers		[10]
	triclocarban	4.9	Anti-Infective agents		[10]
	triclosan	5	Anti-infective agents	y	[5, 6, 20]
	trimethoprim	0.91	Anti-Infective agents, antimalarial	y	[5, 6, 10, 17, 18]
	triprolidine	3.9	Antihistaminic	y	[4]
	tylosin	1.6	Anti-bacterial agents	y	[1]
V					
	valerian		Anxiolytic, tranquilizer	y	[4]
W					
	warfarin	2.7	Anticoagulant	y	[4]
Z					
	zolpidem	2.5	Insomnia treatment	y	[2, 4]

[a] Detected in a WWTP: y = yes

[1] P. Gao, Y. Ding, H. Li, I. Xagoraraki, Occurrence of pharmaceuticals in a municipal wastewater treatment plant: mass balance and removal processes., Chemosphere, 88 (2012) 1-24.

[2] C.M.O. Gonçalves, M.A.D. Sousa, M.d.F.P.S.P.M. Alpendurada, Analysis of acidic, basic and neutral pharmaceuticals in river waters: clean-up by 1°, 2° amino anion exchange and enrichment using an hydrophilic adsorbent, International Journal of Environmental Analytical Chemistry, 93 (2012) 1-22.

[3] P. Lacina, L. Mravcová, M. Vávrová, Application of comprehensive two-dimensional gas chromatography with mass spectrometric detection for the analysis of selected drug residues in wastewater and surface water, Journal of Environmental Sciences, 25 (2013) 204-212.

[4] R. Salgado, R. Marques, J.P. Noronha, J.T. Mexia, G. Carvalho, A. Oehmen, M.A. Reis, Assessing the diurnal variability of pharmaceutical and personal care products in a full-scale activated sludge plant., Environmental Pollution, 159 (2011) 2359-2367.

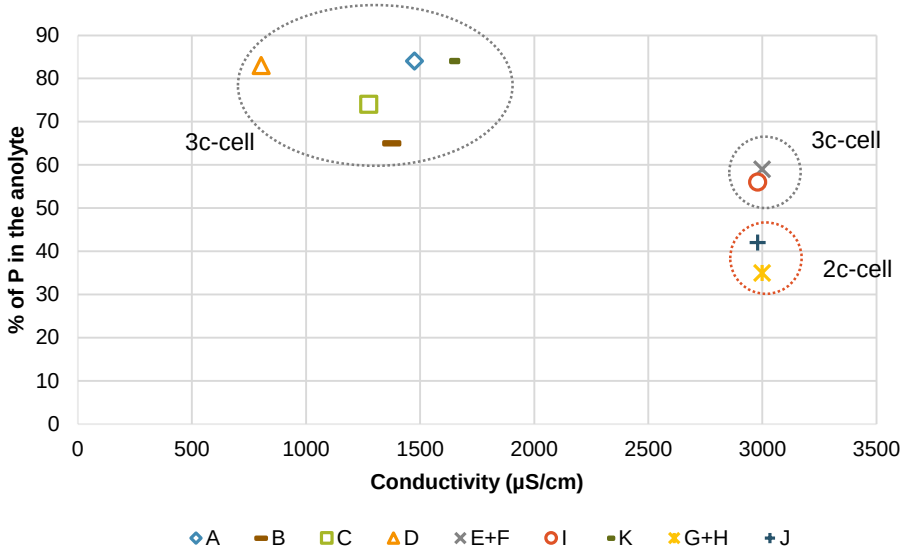
[5] S.K. Behera, H.W. Kim, J.-E. Oh, H.-S. Park, Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea, Science of The Total Environment, 409 (2011) 4351-4360.

[6] J.L. Santos, I. Aparicio, M. Callejón, E. Alonso, Occurrence of pharmaceutically active compounds during 1-year period in wastewaters from four wastewater treatment plants in Seville (Spain), Journal of Hazardous Materials, 164 (2009) 1509-1516.

[7] M.R. Boleda, M.T. Galceran, F. Ventura, Monitoring of opiates, cannabinoids and their metabolites in wastewater, surface water and finished water in Catalonia, Spain, Water Research, 43 (2009) 1126-1136.

[8] S. Chamorro, V. Hernández, V. Matamoros, C. Domínguez, J. Becerra, G. Vidal, B. Piña, J.M. Bayona, Chemical characterization of organic microcontaminant sources and biological effects in riverine sediments impacted by urban sewage and pulp mill discharges, Chemosphere, 90 (2013) 611-619.
[9] N. Jonkers, A. Sousa, S. Galante-Oliveira, C. Barroso, H.-P. Kohler, W. Giger, Occurrence and sources of selected phenolic endocrine disruptors in Ria de Aveiro, Portugal, Environmental Science and Pollution Research, 17 (2010) 834-843.
[10] S.L. Klosterhaus, R. Grace, M.C. Hamilton, D. Yee, Method validation and reconnaissance of pharmaceuticals, personal care products, and alkylphenols in surface waters, sediments, and mussels in an urban estuary, Environment International, 54 (2013) 92-99.
[11] T. Ternes, M. Bonerz, T. Schmidt, Determination of neutral pharmaceuticals in wastewater and rivers by liquid chromatographyelectrospray tandem mass spectrometry, J. Chromatogr., 398 (2001) 175-185.
[12] M. Kopperi, J. Ruiz-Jiménez, J.I. Hukkinen, M.-L. Riekkola, New way to quantify multiple steroidal compounds in wastewater by comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry, Analytica Chimica Acta, 761 (2013) 217-226.
[13] C. Ribeiro, M. Tiritan, E. Rocha, M. Rocha, Seasonal and Spatial Distribution of Several Endocrine-Disrupting Compounds in the Douro River Estuary, Portugal, Archives of Environmental Contamination and Toxicology, 56 (2009) 1-11.
[14] C. Ribeiro, M. Pardal, M. Tiritan, E. Rocha, R. Margalho, M. Rocha, Spatial distribution and quantification of endocrine-disrupting chemicals in Sado River estuary, Portugal, Environmental Monitoring and Assessment, 159 (2009) 415-427.
[15] C. Ribeiro, M. Pardal, F. Martinho, R. Margalho, M. Tiritan, E. Rocha, M. Rocha, Distribution of endocrine disruptors in the Mondego River estuary, Portugal, Environmental Monitoring and Assessment, 149 (2009) 183-193.
[16] J.L. Santos, I. Aparicio, E. Alonso, M. Callejón, Simultaneous determination of pharmaceutically active compounds in wastewater samples by solid phase extraction and high-performance liquid chromatography with diode array and fluorescence detectors, Analytica Chimica Acta, 550 (2005) 116-122.
[17] T.V. Madureira, J.C. Barreiro, M.J. Rocha, E. Rocha, Q.B. Cass, M.E. Tiritan, Spatiotemporal distribution of pharmaceuticals in the Douro River estuary (Portugal), Science of The Total Environment, 408 (2010) 5513-5520.
[18] T.V. Madureira, J.C. Barreiro, M.J. Rocha, Q.B. Cass, M.E. Tiritan, Pharmaceutical trace analysis in aqueous environmental matrices by liquid chromatography–ion trap tandem mass spectrometry, Journal of Chromatography A, 1216 (2009) 7033-7042.
[19] M. Kuster, M. José López de Alda, D. Barceló, Analysis and distribution of estrogens and progestogens in sewage sludge, soils and sediments, TrAC Trends in Analytical Chemistry, 23 (2004) 790-798.
[20] A. Lindström, I.J. Buerge, T. Poiger, P.-A. Bergqvist, M.D. Müller, H.-R. Buser, Occurrence and Environmental Behavior of the Bactericide Triclosan and Its Methyl Derivative in Surface Waters and in Wastewater, Environmental Science & Technology, 36 (2002) 2322-2329.

Appendix 2. Percentage of P recovery in the anolyte as a function of membrane concentrates conductivity.

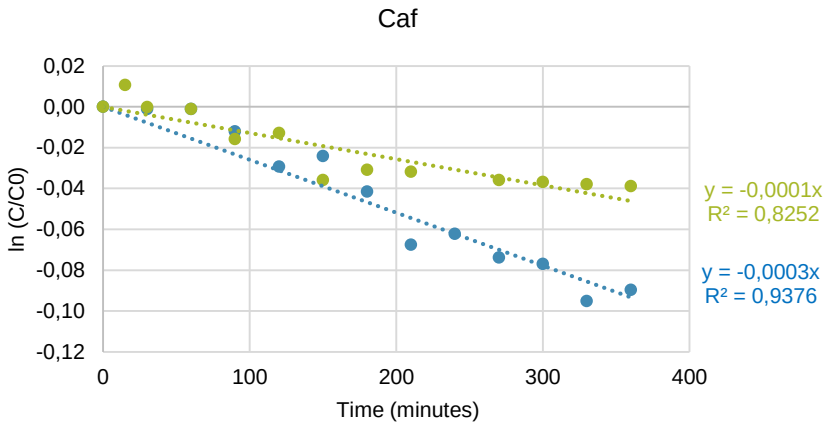


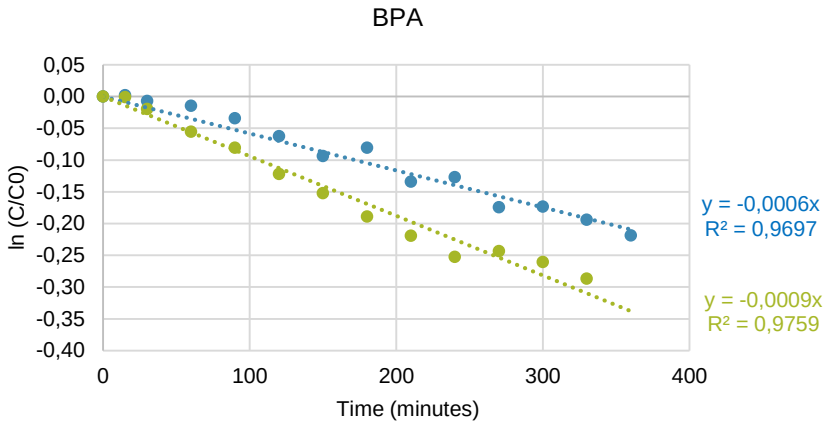
Appendix 3. Standard deviation experiments in percentage of the contaminant detected in the sewage, effluent and electrolyte at the end of the experiments in relation to the initial amount (n=2).

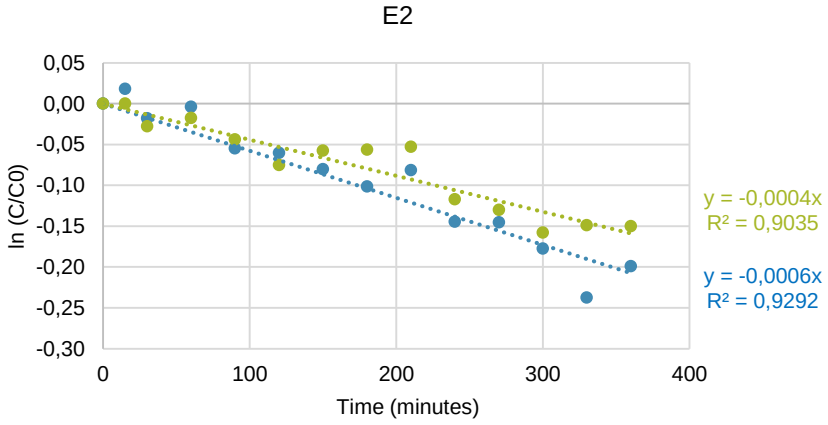
		Compound					
		Caf	**BPA**	**E2**	**EE2**	**IBU**	**MPBh**
Control-1	Sludge	13	4.1	6.0	14	3.4	13
	Effluent	12	5.0	0.77	4.9	2.2	-
	Elect.	13	*	-	7.4	3.1	-
Control-2	Sludge	0.9	0.7	0.2	1.3	1.1	0.6
	Effluent	9.8	4.3	1.2	4.0	*	0.78
	Elect.	1.0	0.02	0.07	0.27	1.9	0.06
Exp-1	Sludge	-	8.2	6.4	6.4	10	8.1
	Effluent	0.50	*	*	*	3.0	*
	Elect.	9.0	-	-	-	-	-
Exp-2	Sludge	13	4.4	5.4	6.5	11	10
	Effluent	*	*	*	*	*	-
	Elect.	4.9	7.2	2.2	3.0	-	-
Exp-3	Sludge	6.0	1.7	2.2	9.8	2.2	0.33
	Effluent	2.0	*	*	*	*	*
	Elect.	1.3	*	-	*	0.46	-
Exp-4	Sludge	2.6	4.7	8.1	8.3	0.42	15
	Effluent	14	*	*	*	*	-
	Elect.	*	15	*	*	1.7	-
Exp-5	Sludge	-	-	-	-	-	12
	Effluent	-	*	*	2.5	0.37	-
	Elect.	4.6	14	*	*	3.8	-

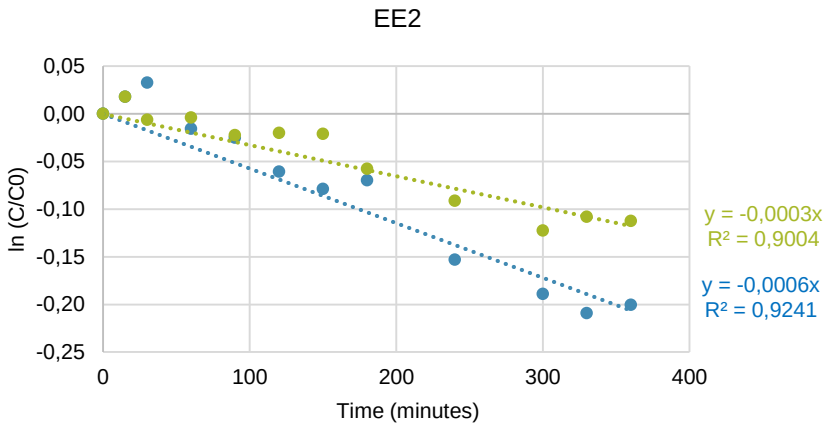
* One of the duplicates presented a value below LQ or LD.

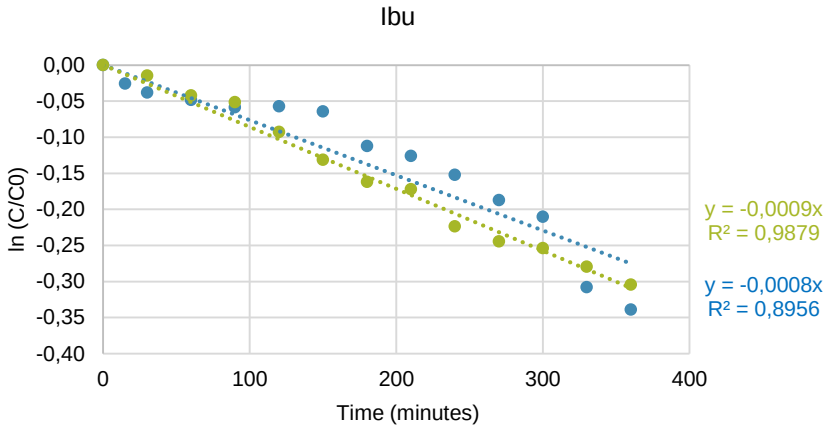
Appendix 4. First-order electrodegradation ($\mathbf{ln}\left(\frac{C}{C0}\right) = -\boldsymbol{kt}$) results obtained in the experiments conducted at the cathode end (green) and anode end (blue), for Caf, BPA E2, EE2, Ibu and MBPh (n=2).

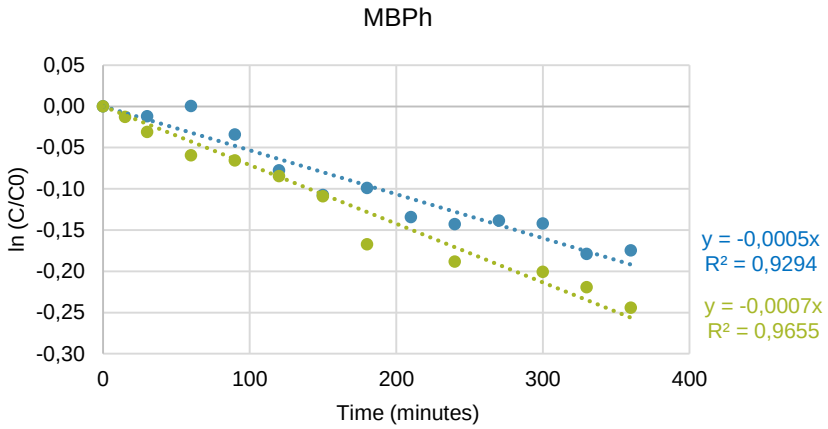







EE2
0,05
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
ln (C/C0)
0
100
200
300
400
Time (minutes)
y = -0,0003x
R² = 0,9004
y = -0,0006x
R² = 0,9241


Ibu
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
-0,30
-0,35
-0,40
ln (C/C0)
0
100
200
300
400
Time (minutes)
y = -0,0009x
R² = 0,9879
y = -0,0008x
R² = 0,8956


MBPh
0,05
0,00
-0,05
-0,10
-0,15
-0,20
-0,25
-0,30
ln (C/C0)
0
100
200
300
400
Time (minutes)
y = -0,0005x
R² = 0,9294
y = -0,0007x
R² = 0,9655

PART II

“No amount of experimentation can ever prove me right;
a single experiment can prove me wrong.”
Albert Einstein
(1879-1955)

PAPER I

INTEGRATED PERSPECTIVES OF A GREENHOUSE STUDY TO UPGRADE AN ANTIMONY AND ARSENIC MINE SOIL – POTENTIAL OF ENHANCED PHYTOTECHNOLOGIES

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Integrated perspectives of a greenhouse study to upgrade an antimony and arsenic mine soil – Potential of enhanced phytotechnologies

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HIGHLIGHTS

- Rehabilitation of a mining area contaminated with As and Sb in a 15-day study.
- Indian mustard showed higher accumulation potential than ryegrass.
- Phosphate and EK had different effectiveness.
- Coupling phosphate, EK and phytoremediation is suitable for rehabilitation.
- Changes in available nutrients and enzymatic activities.

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ABSTRACT

Coupling more than one remediation technology can be an effective option to reduce contamination levels. Phytoremediation, using ryegrass and Indian mustard, was coupled with electrokinetic process (EK) and/or phosphate amendment aiming to remediate a mine soil contaminated with arsenic (As) and antimony (Sb). At the end of 15 days, metalloids uptake, biomass, available soil nutrients and enzymatic activities were assessed. Indian mustard revealed the highest potential to accumulate As and Sb (*approx.* 65% more than ryegrass). But attending to the higher biomass of ryegrass total uptake may be counteracted. Phosphorus amendment was an important factor on the enhancement of metalloids uptake namely for Indian mustard. EK together with P-amendment provided a slight increase in uptake with ryegrass accumulating more 25% of both metalloids and Indian mustard between 30% (Sb) and 48% (As) compared with plant alone. Available soil nutrients and enzymatic activities changed according to the applied treatment but had a similar pattern between plant species. Phytoremediation coupled with EK and/or phosphate amendment can be considered a suitable combination for the upgrade of mine contaminated areas but its efficiency depends on time constraints.

1. Introduction

Soil metal contamination arising from mining operations can be considered a major threat to land use. The rehabilitation of mining areas can be promoted using plants with potential to accumulate the contaminant, e.g., Sb and/or As [10,15,18,23,24,26,29]. Phytoremediation is cost-effective, does not need extensive labour and has an important role in landscape. The rehabilitation of a contaminated site by phytoremediation depends on the adaptation of the plant to environmental conditions (including contaminant toxicity). growth rate and biomass production which may require a long treatment time [5]. Moreover, its effectiveness is linked with the used plant species [2], soil properties and bioavailability of contaminants [5]. The coupling of electrokinetic process (EK) may be an attempt to overcome the limitations of phytoremediation [5]. The electrokinetic remediation relies on the application of electric field in a porous matrix and may enhance metal remediation in different solid matrices [11,13,19,31].

In EK-assisted phytoremediation the removal of metals from soil is performed by the plant with a synergistic effect of a low intensity electric field that increases the bioavailability of contaminant (selective mobilisation and/or enhancement of solubilisation). The hybrid technology increased metal uptake of ryegrass [22] and potato plants [1]. Together with chelating agents, the technique also improved soil removal of Cu/Zn by ryegrass [32] and Pb remediation with Indian mustard [20]. But the presence of a direct current (DC) electric field can affect soil parameters,

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available nutrients and/or microbial population and enzymatic activities [7,8,6,9,17,16,30]. Nevertheless, the effect of the electric field may be counteracted by plant [5,8].

Remediation also depends on metals retention by soil that is usually electrostatic, with cationic and anionic species being associated with negatively and positively charged sites, respectively. Addition of amendments, e.g. phosphate, can influence metal uptake as it can lead, for example, to the enhanced release of Sb due to anion competition for sorption sites. Phosphate-mediated desorption of Sb occurs in both soil and mineral phase where cationic and anionic contaminants coexist in soil matrix [12,27]. The same effect can be expected for As as it is a related chemical to Sb, displaying similar characteristics in the environment [23].

The potential and applicability of phytoremediation enhanced by EK and/or phosphate amendment is here discussed, regarding rehabilitation of mine areas contaminated with As and Sb. The soil was collected from a mining area located in southern Hunan Province (China). The effect of Indian mustard and ryegrass was evaluated in the presence of a low level DC field, with and without phosphate addition. The impact of the applied technologies on biomass, metalloid uptake, available soil nutrients and enzymatic activities were assessed.

2. Experimental

2.1. Soil

An As and Sb contaminated sandy clay loam soil was sampled from a mine area located in southern Hunan Province, China. The clay, silt and sand content of soil are 32.8%, 9.1% and 58.1%. Soil pH was 6.58, electric conductivity (EC) of 0.376 mS cm^{-1}, cation exchange capacity (CEC) 14.5 cmol kg^{-1}, soil organic carbon (SOC) 45.1 g kg^{-1}. The concentration of As, Sb and P in the soil was 65.8 ± 0.8 mg kg^{-1}, 547 ± 0.8 mg kg^{-1}, 668 ± 9.7 mg kg^{-1}, respectively.

2.2. Experimental design

Soil was air-dried and passed through a 10 mm sieve. Rectangular plastic boxes (26.5 cm × 17.5 cm × 8 cm) were filled with 3 kg of soil and fertilised with a solution of 0.99 g urea and 0.96 g KH_2PO_4. Experimental boxes were divided into three compartments (cathode:central:anode) using a vertical nylon mesh (Fig. 1). In the cathode and anode regions 900 g of soil were used whereas 1200 g were in the central compartment. Graphite rods (length 15 cm, diameter 6 mm) were used as working electrodes as they are low cost and inert. Four rods (2 plus 2) were vertically inserted into the soil in opposite sides. Before the experiment, soil was incubated with 70% of its water holding capacity for 7 days. Pregerminated seedlings of Indian mustard (*Brassica juncea*) and ryegrass (*Lolium perenne*) were transplanted to experimental boxes and grew for 10 days. After this period a proportion of 12:16:12 exemplars were left in each box and the remaining scarified and grown for more 35 days.

There were eight treatments in this trial: plant alone (ryegrass or Indian mustard) (T1); plant (ryegrass or Indian mustard) and phosphate amendment (T2); plant (ryegrass or Indian mustard) and EK process – 20 V (T3); plant (ryegrass or Indian mustard), phosphate amendment and EK process – 20 V (T4). Phosphate amendment was applied in a concentration of 0.5 M of PO_4^{2-} (as KH_2PO_4). Each treatment was carried out in triplicate.

Pot experiments were performed in a glass greenhouse. Moisture content was kept at 70% of soil water holding capacity throughout the study. DC current was applied 8 h *per* day for 15 days.

Values of electric current were monitored throughout the experiment. At the end of the experimental period, soils were collected for analysing their As and Sb concentrations, available nutrients and enzymatic activities, pH and EC. Plants were divided in roots and shoots and As and Sb determined in both tissues.

2.3. Analytical methodologies

Soil samples were sieved through a 100-mesh nylon sieve for physico-chemical analysis. Soil pH, conductivity and clay content were determined by conventional methods [21]. CEC was analysed by ammonium acetate extraction method and SOC by dichromate oxidation method. For the determination of total P, As and Sb levels, soil was digested with HNO_3 and HCl (1:3 (v/v)) and analysed

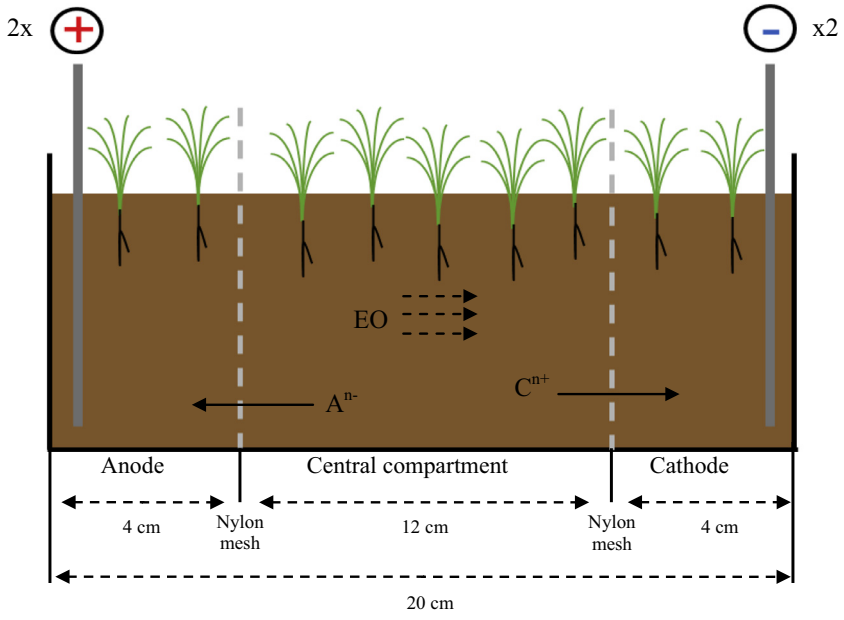

Fig. 1. Experimental scheme of the electrokinetic-assisted phytoremediation set-up.

by inductively coupled plasma atomic emission spectrometry (ICP-AES). Whereas for Sb and As determination in plant tissues, vegetal material was digested in 1:5 (v/v) of $HClO_4$:HNO_3 followed by atomic fluorescence spectroscopy (AFS). Plant reference materials (GBW10010 and GBW10015) were used for analytical control.

Available nutrients and enzymatic activities were carried out using the methodologies described elsewhere [21]. In brief, P was extracted with 0.5 mol L^{-1} $NaHCO_3$ and determined using the molybdenum blue method, K was extracted with 1 mol L^{-1} CH_3COONH_4 and determined by flame photometry (Shanghai FP 640 model, China) and inorganic N was extracted with 2.0 mol L^{-1} KCl in a 1:10 soil to solution ratio (1 h) followed by determination using an automatic procedure (Skalar San + segmented flow analyser, Netherlands). For soil invertase (INV) activity, 5 g of soil were incubated (24 h; 37 °C) with 15 mL of 8% sucrose as substrate, 0.5 mL of toluene and 5 mL of phosphate buffer (pH 5.5) and the produced glucose determined by 3,5-dinitrosalicylic acid colorimetric method (DNS method) at 508 nm. For urease (URE) activity, 5 g of soil were mixed with 0.5 mL of toluene, 20 mL of citrate buffer (pH 6.7), 10 mL of 10% urea followed by incubation (37 °C; 24 h) and the released ammonium determined by Indophenol Blue Method (578 nm). For soil neutral phosphatase (NPH), 5.0 g of soil and 20 mL of 0.5% disodium phenyl phosphate of citrate buffer (neutral pH) were incubated (37 °C; 2 h) and then the produced phenol was extracted and oxidised by potassium hexacyanoferrate in alkaline conditions. The oxidation products were determined by 4-aminoantipyrine colorimetric method (510 nm). Controls were performed wherever needed.

2.4. Statistics

Biomass, pH, metalloids concentration in plant tissues and total uptake per pot, available nutrients, enzymatic activities were comparatively examined. Statistically significant differences among samples for 5% level of significance were evaluated through ANOVA tests using GraphPad Prism software and Tukey pairwise comparisons.

3. Results and discussion

3.1. Variation in electric current, pH and conductivity

Electric current did not vary significantly throughout the experiment (data not shown). After the 15-day period, soil pH did not change in cells without DC electric field (T1 and T2) (*ca.* 6.50) but the application of electric field (T3 and T4) slightly decreased pH in the anode compartment (between 5.94 and 6.35) and increased in the cathode compartment (between 6.95 and 7.49) (Fig. 2). Central compartment presented a similar pH along the study (between 6.50 and 6.65). The treatments in the presence of a DC electric field (T3 and T4) with Indian mustard had the clearest pattern of pH changes. The pH decrease in the anode and increase in the cathode compartment has been reported in other EK-assisted phytoremediation studies [1,7,22] and is explained by water electrolysis and consequent generation of H^+ and OH^- ions in anode and cathode compartment, respectively.

The treatment with ryegrass alone presented a higher EC value than that with Indian mustard (data not shown). The application of DC electric field also influenced EC in the different cell compartments. In general, conductivity was lower in the cathode being followed by central and anode compartments. Acidification or alkalization may enhance soil conductivity due to the presence of increased ion concentration in soil solution. In other way, the decrease of conductivity in soil compartments may be due to the migration of soluble ions towards the electrodes of opposite charge. Treatment with P-amendment (T2) presented an increased conductivity due to the input of ions in soil solution.

3.2. Biomass of plants

Assuming that the presence of plant alone presented an average biomass of 100% a comparison was carried out between applied treatments (Table 1).

At the end of the experimental period, the biomass of ryegrass was 48% higher than the one observed for Indian mustard. The P-amendment (T2) may act as fertilizer but its positive effect was only observed in Indian mustard root being statistically higher than the control in central compartment. EK treatment (T3) enhanced Indian mustard belowground biomass, namely at central compartment but lower effects were observed in ryegrass. Coupling P-amendment and EK (T4) resulted in a general increase of shoot and root biomass in ryegrass (namely in central compartment) and a more pronounced increase in Indian mustard root biomass. The increased concentration of elements in soil solution, due to the presence of DC electric field, makes them bioavailable to plants resulting in a positive effect on the growth of both species. Due to the slightly pH changes found in this work no deleterious effect was observed in plant biomass due to pH changes, e.g. opposite to other reports [22] where plant growth was affected due to acidification in anode compartment. Higher applied voltages (2 and 4 V cm^{-1}) had also been reported as decreasing root biomass but a lower voltage (1 V cm^{-1}) had a positive effect on plant growth [7], as happened in this study.

3.3. Concentration of As and Sb in ryegrass and Indian mustard

Ryegrass alone (T1), with P-amendment (T2) and with EK treatment (T3) presented similar root concentrations (Fig. 3). The most effective treatment for ryegrass was the couple of both treatments (T4) where Sb and As root concentrations were enhanced (*ca.* 143 μg g^{-1} and *ca.* 104 μg g^{-1}, respectively). The concentration of

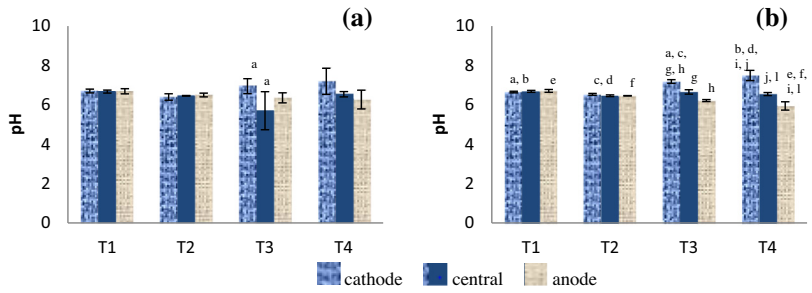

Fig. 2. Soil pH after different treatments with (a) ryegrass and (b) Indian mustard. Mean and standard deviation (error bars) are shown (n = 3). Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend*: box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK.

Table 1
Biomass of ryegrass and Indian mustard at the end of the experiments [% assuming control (T1 treatment) as 100%]. Mean and standard deviation are shown (n = 3).

		Ryegrass (%)			Indian mustard (%)		
		Cathode	Central	Anode	Cathode	Central	Anode
T1	Shoot	100 ± 2	100 ± 24 [a]	100 ± 2	100 ± 6	100 ± 3	100 ± 1
	Root	100 ± 20	100 ± 19	100 ± 37	100 ± 72	100 ± 2 [c, d, e]	100 ± 14
T2	Shoot	94 ± 1	110 ± 25	85 ± 19	116 ± 22	84 ± 3 [g]	95 ± 15
	Root	116 ± 18	68 ± 17 [o]	93 ± 43	179 ± 64[h]	301 ± 108 [o, c, g, h]	189 ± 48
T3	Shoot	100 ± 10	158 ± 8	143 ± 36	126 ± 29	116 ± 16[i]	105 ± 32
	Root	125 ± 14	120 ± 11	99 ± 14	125 ± 18	240 ± 45 [d, i, f, k]	104 ± 27 [f]
T4	Shoot	97 ± 41 [b]	218 ± 27 [a, b]	131 ± 29	114 ± 12	113 ± 19 [j]	94 ± 9 [l]
	Root	151 ± 56	154 ± 8 [p]	113 ± 28	195 ± 57 [m]	363 ± 55 [p, e, j, k, m, n]	213 ± 60 [l, n]

Same letters indicate statistically significant differences among treatments, plant tissues or cell compartments ($p < 0.05$).
Legend: box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK

Table 2
Total As and Sb levels (calculated using metalloids concentration and biomass values of each plant tissue) in ryegrass and Indian mustard after different treatments (μg pot^{-1}). Mean and standard deviation are shown (n = 3).

Treatment	Ryegrass				Indian mustard			
	As		Sb		As		Sb	
	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
T1	1.2 ± 0.6	85.7 ± 14.9	1.3 ± 0.6 [a]	118.1 ± 9.2 [a]	0.9 ± 0.4	78.4 ± 8.1 [i, j]	3.2 ± 1.2	108.2 ± 15.1 [k, l]
T2	1.8 ± 1.0	94.6 ± 52.0 [b]	1.3 ± 0.6 [c]	123.1 ± 53.9 [c, d]	2.0 ± 0.6 [m]	287.7 ± 32.9 [b, i, m, n, o]	2.3 ± 1.1 [p]	404.4 ± 99.5 [d, k, n, p, q]
T3	1.8 ± 0.4	94.9 ± 4.7	1.5 ± 0.6 [e]	118.6 ± 9.3 [e]	1.1 ± 0.7 [r]	174.9 ± 72.8 [o, r, s]	5.0 ± 2.5 [t]	197.4 ± 22.1 [q, t, u]
T4	1.2 ± 0.2 [f]	142.5 ± 13.9 [f, g]	1.2 ± 0.2	195.0 ± 16.8 [h]	1.9 ± 0.5 [v]	333.7 ± 63.7 [g, j, s, v, w]	2.6 ± 0.8 [x]	440.6 ± 84.2 [h, l, u, w, x]

Same letters indicate statistically significant differences among treatments, metalloids or plant tissues ($p < 0.05$).
Legend: box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK.

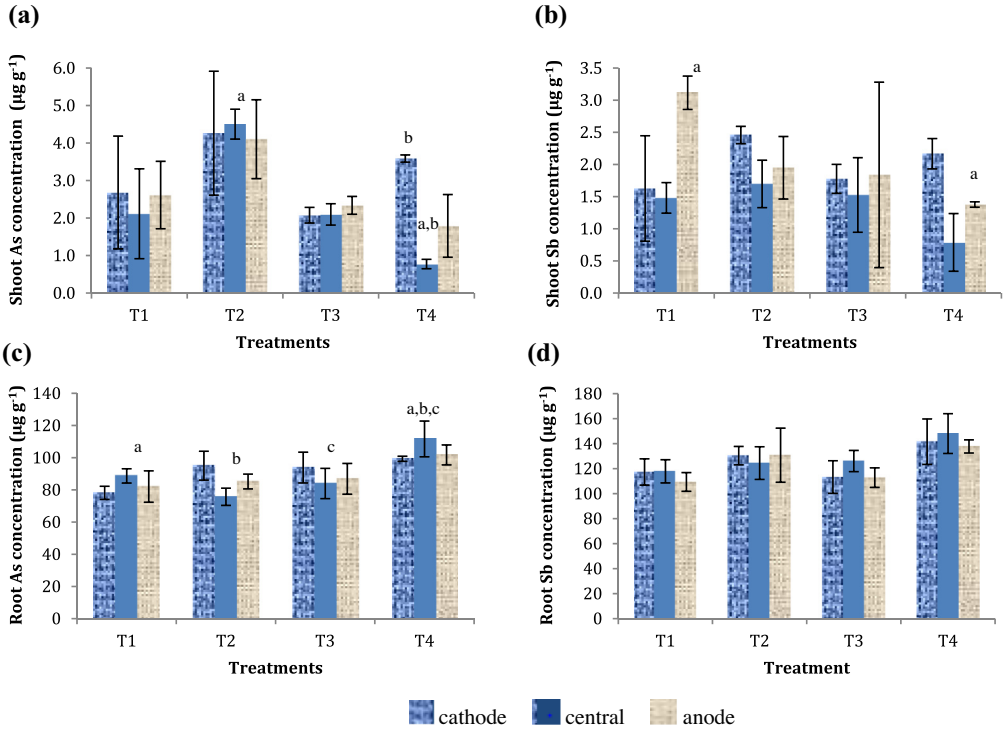

Fig. 3. Ryegrass accumulation in shoot (a, b) and root (c, d). Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend:* box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK.

As and Sb in ryegrass shoot was not significantly enhanced by any applied treatment but P-amendment (T2) suggests a positive effect on As levels. The presence of DC field and P-amendment (T4) provided a redistribution of soil metalloids in shoot tissues with

higher metalloids concentration in those from the cathode compartment section. In soil, metal redistribution was not expressive, an opposite result than the one reported e.g. by [7] where a significant redistribution in soil between anode and cathode was observed due to electromigration towards the electrode of opposite charge. This might be explained by the applied voltage together with soil characteristics.

The concentration of Sb and As in Indian mustard root was similar with and without EK process but the presence of P-amendment suggests a rising in Sb and As uptake (Fig. 4). Phosphate solution may act as mobility-enhancing agents as observed in mine tailings electrokinetically treated where 48% of As was removed in the section near the anode [14]. Phosphate ions influence As uptake by competing for As adsorption by soil particles and As uptake by plant roots [4]. In Indian mustard shoot, As concentration was enhanced by P-amendment and/or EK, whereas Sb concentration increased in the presence of EK process comparing with plant alone. The effect of a DC electric field led to a re-distribution of Sb and As in shoot tissues with higher concentration in electrode compartments.

In general, the concentration of As and Sb in Indian mustard shoot and root tissues was higher than the one observed in ryegrass. Comparing with ryegrass, Indian mustard accumulated more 62% As and 68% Sb, with P-amendment more 87% and 84%, with EK process more 72% and 59% and with the coupled technology (P-amendment and EK process) more 94% and 77%, respectively. It has been reported that the effectiveness of accumulation depends on soil and plant species (i.e., Sb [26], As [3]) but also from the metal/metalloid under study [7,25]. However, taking into consideration total biomass at the end of the experiments, the total uptake of Indian mustard (T1) per pot achieved less 9% of As and 7% of Sb than ryegrass (Table 2). But in the other treatments (T2 to T4) Indian mustard still presented higher uptake per pot than ryegrass. Indian mustard total uptake per pot increased in all applied treatments compared with plant alone. Soil metal concentrations decreased after the applied treatments although higher treatment time may have provided a more extensive remediation.

3.4. Nutrients in Indian mustard and ryegrass set up

The effect of tested parameters on available soil nutrient contents is shown in Figs. 5 and 6

Available P and K levels were higher in treatment with inorganic nutrient amendment (T2 and T4), due to the initial addition of KH_2PO_4 in both sets of plant species. Other study [8] reported that P migrated towards the anode at the high applied voltages (2 or 4 V cm^{-1}) whereas there was no significant redistribution in the presence of lower voltage (1 V cm^{-1}) or plant alone. At a pH of 6–7 phosphate is in the forms of $H_2PO_4^-/HPO_4^{2-}$, anions that would preferentially migrate towards the anode compartment. Probably due to the applied voltage and time to perform this study it was not possible to observe increased P concentration in anode compartment.

Available potassium concentration was higher in phosphate amendment with (T4) or without EK (T2) due to the simultaneous addition of K. In T4, the DC electric field promoted potassium electromigration towards the electrode of opposite charge, the cathode compartment. Available nitrate and ammonium were similar in treatments with plant alone (T1) or with P-amendment (T2). In the presence of EK, with (T4) or without P-amendment (T3), available nitrate concentration was generally lower with a redistribution between soil compartments. In other works, the change and distribution of nitrate content have been attributed to hydrolysis and transport of nitrogen compounds [9]. Nevertheless, it was reported [8] that only the high applied voltage (4 V cm^{-1}) in EK assisted phytoremediation or 2 V cm^{-1} in EK increased soil nitrate content and distribution near anode, but in the presence of only plant or lower voltages there was no redistribution.

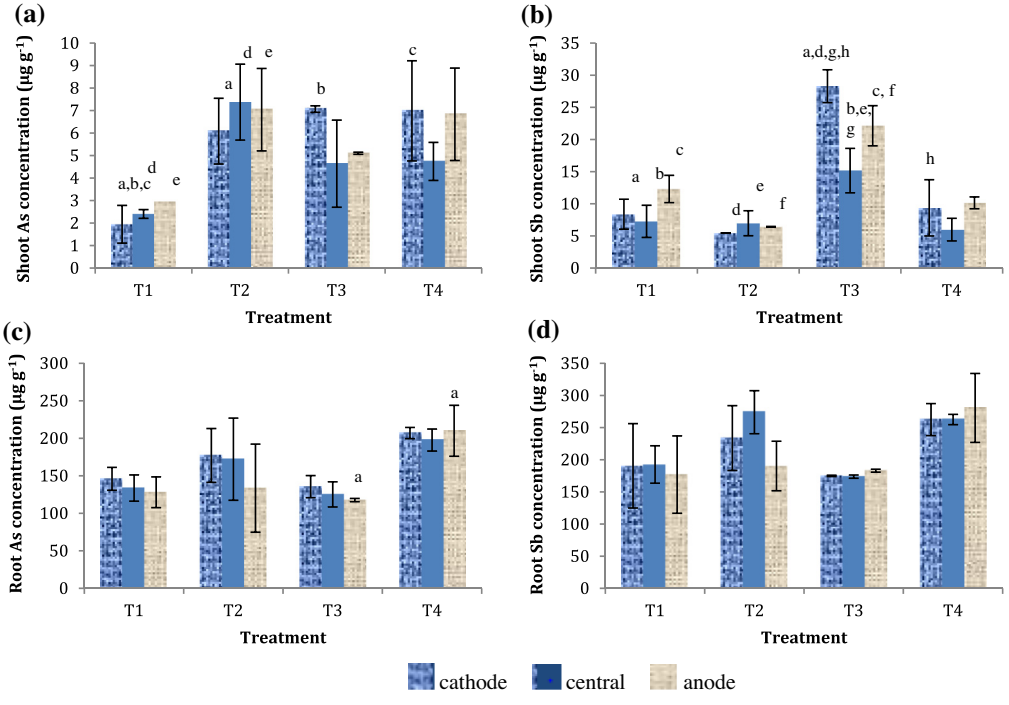

Fig. 4. Indian mustard uptake in shoot (a, b) and root (c, d). Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend:* box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK.

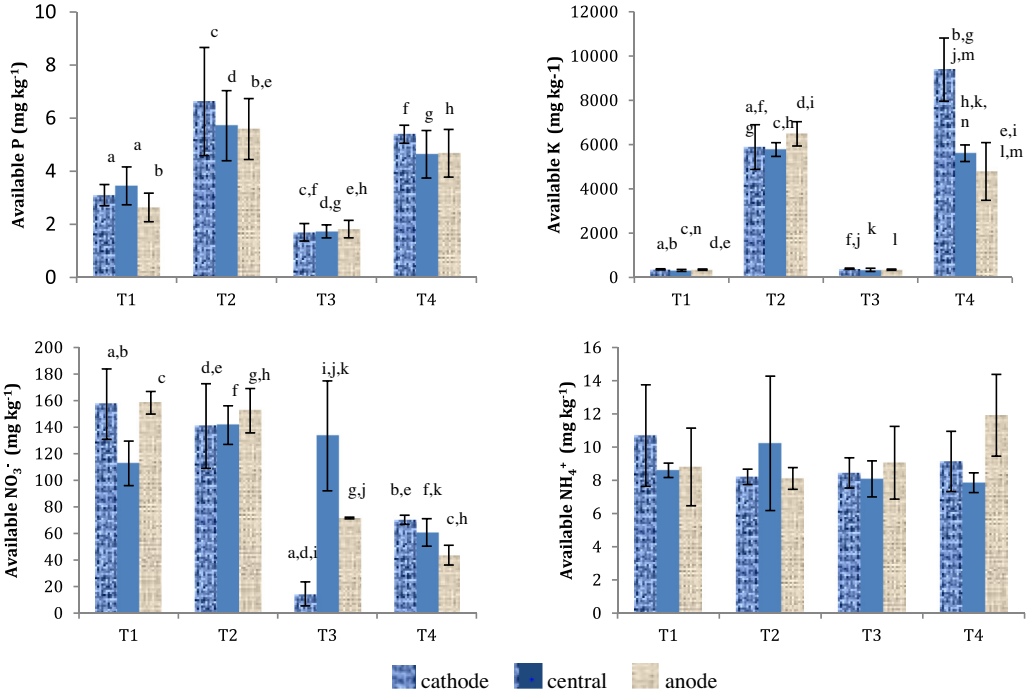

Fig. 5. Available nutrients in ryegrass set. Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend:* box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK. *Initial soil values:* available phosphate 0.4 ± 0.1 mg kg^{-1}; available NO_3^- 24 ± 2 mg kg^{-1}; available NH_4^+ 5.3 ± 0.3 mg kg^{-1}; available K: 244 ± 21 mg kg^{-1}.

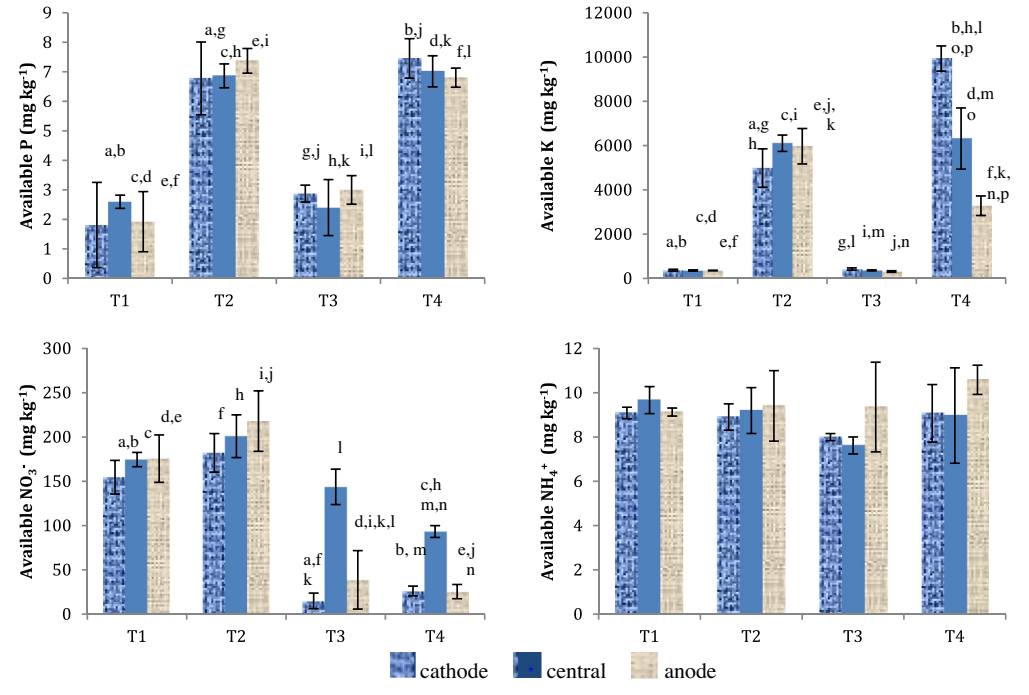

Fig. 6. Available nutrients in Indian mustard set. Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend:* box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK. *Initial soil values:* available phosphate 0.4 ± 0.1 mg kg^{-1}; available NO_3^- 24 ± 2 mg kg^{-1}; available NH_4^+ 5.3 ± 0.3 mg kg^{-1}; available K: 244 ± 21 mg kg^{-1}.

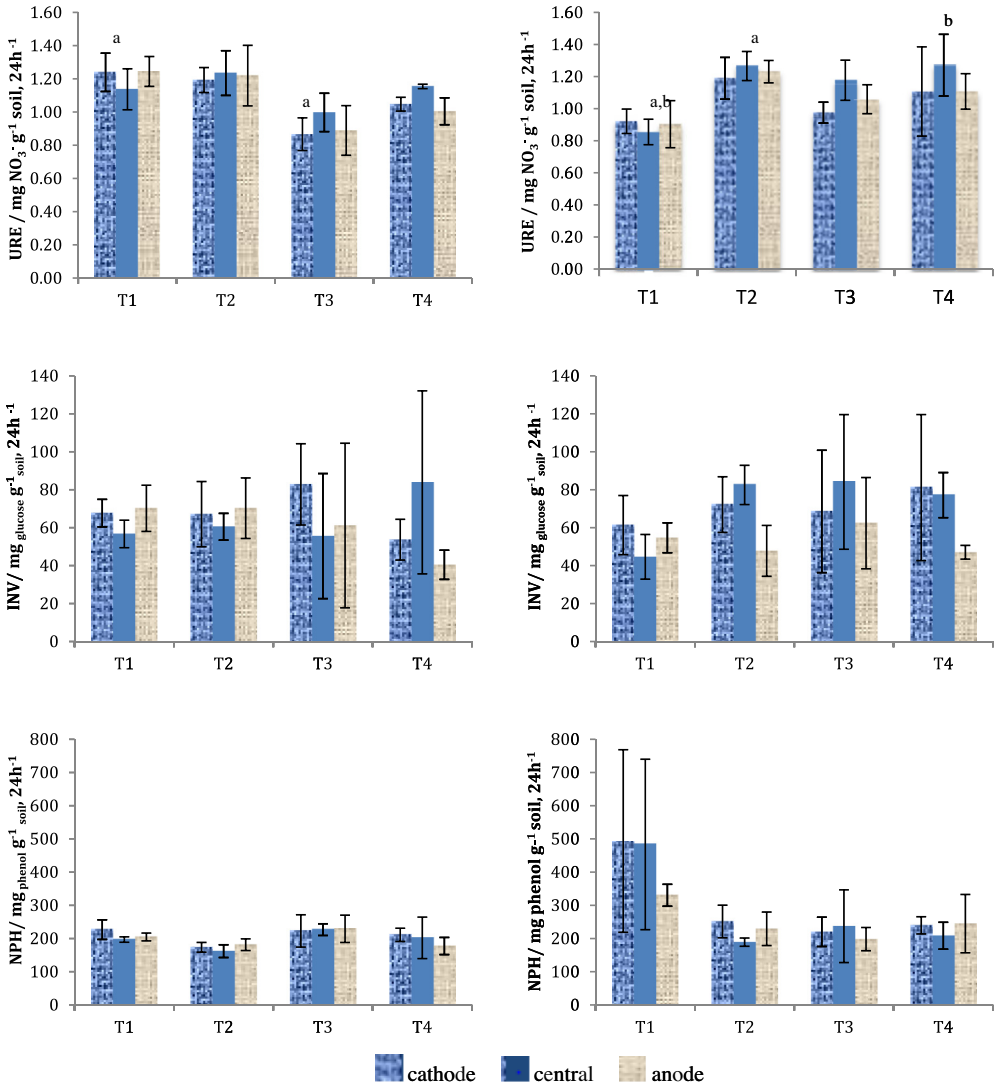

Fig. 7. Urease, invertase and soil neutral phosphatase activities in ryegrass (at left) and Indian mustard (at right). Same letters indicate statistically significant differences among treatments or cell compartments ($p < 0.05$). *Legend:* box with contaminated soil and (T1) plant; (T2) plant and phosphate amendment; (T3) plant and EK; (T4) plant, phosphate amendment and EK. *Initial soil values:* urease 1.3 ± 0.1 mg NO_3^- g^{-1} soil; invertase 65 ± 24 $mg_{glucose}$ g^{-1}_{soil} g 24 h^{-1}; neutral phosphatase 472 ± 69 mg phenol g^{-1} soil, 24 h^{-1}.

Ammonium levels were similar in all tested conditions. In Indian mustard set, there was a similar pattern of nutrients distribution as that found for ryegrass treatment set. This suggests that the used plant species did not directly affect available nutrients pattern whereas the application of a DC field did it for some nutrients. In fact, there was an average increase in nutrients compared with the initial soil values as reported for other EK assisted phytoremediation study in the presence of Indian mustard [8].

3.5. Soil enzymatic activities

Soil enzymes drive the metabolic process of the soil being important in nutrient cycling and detoxification of pollutants [28]. The change in enzymatic activities after the applied treatments is shown in Fig. 7.

Invertase activity showed no tendency between different treatments for both plants, except a slight decrease in anode compartment in the treatment of coupled technologies (T4) compared with plant alone (T1) (Fig. 7). For ryegrass, urease activity was higher in the presence of plant alone and P-amendment and slightly decreased in the presence of EK. For Indian mustard it increased in the presence of P-amendment. Urease catalyzes the hydrolysis of urea into ammonia or ammonium. It was reported that electric current was significantly correlated with urease and invertase, restraining their activities [8]. In the same study [8], their activities were also correlated with nitrate and available potassium levels. There were no statistical differences for neutral phosphatase activity in both plants between the applied treatments. In fact, it was reported [8] that neutral phosphatase activity was less related with EK-assisted phytoremediation and change in soil parameters than with invertase activity. Phosphatase plays an important role in transforming organic phosphorus into inorganic form, suitable for plant uptake [6].

4. Conclusions

Indian mustard revealed the highest potential to accumulate As and Sb. Phosphorus amendment was the main factor on the enhancement of metalloids uptake and its effectiveness was

expressive for Indian mustard. EK together with P-amendment presented a slight improve in total metal uptake with ryegrass accumulating more 25% of As and Sb, and Indian mustard 48% of As and 30% of Sb, comparing to the effect of plant alone. In general, the soil nutrient status and enzymatic activities followed a similar pattern between plant species with or without the application of a low level DC electric field and/or inorganic nutrient amendment. The applied voltage did not present severe limitations for the tested EK-assisted phytoremediation scheme but, in some cases, it slightly decreased enzymatic activities or promoted the electromigration of nutrients towards electrode compartments.

Although at different extents, both coupled technologies showed potential for the remediation of mining areas contaminated with As and Sb. Still, 15 days were not enough to perform an effective reduction of contaminants as the matrix used was collected from an highly contaminated mine area.

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References

[1] H. Aboughalma, R. Bi, M. Schlaak, Electrokinetic enhancement on phytoremediation in Zn, Pb, Cu and Cd contaminated soil using potato plants, J. Environ. Sci. Health Part A 43 (2008) 926–933.
[2] J. Bech, I. Corrales, P. Tume, J. Barceló, P. Duran, N. Roca, C. Poschenrieder, Accumulation of antimony and other potentially toxic elements in plants around a former antimony mine located in the Ribes Valley (Eastern Pyrenees), J. Geochem. Explor. 113 (2012) 100–105.
[3] C. Bergqvist, R. Herbert, I. Persson, M. Greger, Plants influence on arsenic availability and speciation in the rhizosphere, roots and shoots of three different vegetables, Environ. Pollut. 184 (2014) 540–546.
[4] N. Bolan, S. Mahimairaja, A. Kunhikrishnan, G. Choppala, Phosphorus–arsenic interactions in variable-charge soils in relation to arsenic mobility and bioavailability, Sci. Total Environ. 463–464 (2013) 1154–1162.
[5] C. Cameselle, R.A. Chirakkara, K.R. Reddy, Electrokinetic-enhanced phytoremediation of soils: status and opportunities, Chemosphere 93 (2013) 626–636.
[6] L. Cang, D.-M. Zhou, Q.-Y. Wang, D.-Y. Wu, Effects of electrokinetic treatment of a heavy metal contaminated soil on soil enzyme activities, J. Hazard. Mater. 172 (2009) 1602–1607.
[7] L. Cang, Q.Y. Wang, D.M. Zhou, H. Xu, Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard, Sep. Purif. Technol. 79 (2011) 246–253.
[8] L. Cang, D.-M. Zhou, Q.-Y. Wang, G.-P. Fan, Impact of electrokinetic-assisted phytoremediation of heavy metal contaminated soil on its physicochemical properties, enzymatic and microbial activities, Electrochim. Acta 86 (2012) 41–48.
[9] X. Chen, Z. Shen, Y. Lei, S. Zheng, B. Ju, W. Wang, Effects of electrokinetics on bioavailability of soil nutrients, Soil Sci. 171 (2006) 638–647.
[10] R. Feng, C. Wei, S. Tu, S. Tang, F. Wu, Simultaneous hyperaccumulation of arsenic and antimony in Cretan brake fern: evidence of plant uptake and subcellular distributions, Microchem. J. 97 (2011) 38–43.
[11] J. Gao, Q. Luo, C. Zhang, B. Li, L. Meng, Enhanced electrokinetic removal of cadmium from sludge using a coupled catholyte circulation system with multilayer of anion exchange resin, Chem. Eng. J. 234 (2013) 1–8.
[12] C.S. Griggs, W.A. Martin, S.L. Larson, G. O'Connnor, G. Fabian, G. Zynda, D. Mackie, The effect of phosphate application on the mobility of antimony in firing range soils, Sci. Total Environ. 409 (2011) 2397–2403.
[13] P. Guedes, N. Couto, L.M. Ottosen, A.B. Ribeiro, Phosphorus recovery from sewage sludge ash through an electrodialytic process, Waste Manage. 34 (2014) 886–892.
[14] P. Isosaari, M. Sillanpää, Effects of oxalate and phosphate on electrokinetic removal of arsenic from mine tailings, Sep. Purif. Technol. 86 (2012) 26–34.
[15] U. Jana, V. Chassany, G. Bertrand, M. Castrec-Rouelle, E. Aubry, S. Boudsocq, D. Laffray, A. Repellin, Analysis of arsenic and antimony distribution within plants growing at an old mine site in Ouche (Cantal, France) and identification of species suitable for site revegetation, J. Environ. Manage. 110 (2012) 188–193.
[16] G. Lear, M.J. Harbottle, C.J. van der Gast, S.A. Jackman, C.J. Knowles, G. Sills, I.P. Thompson, The effect of electrokinetics on soil microbial communities, Soil Biol. Biochem. 36 (2004) 1751–1760.
[17] G. Lear, M.J. Harbottle, G. Sills, C.J. Knowles, K.T. Semple, I.P. Thompson, Impact of electrokinetic remediation on microbial communities within PCP contaminated soil, Environ. Pollut. 146 (2007) 139–146.
[18] G. Levresse, G. Lopez, J. Tritlla, E.C. López, A.C. Chavez, E.M. Salvador, A. Soler, M. Corbella, L.G.H. Sandoval, R. Corona-Esquivel, Phytoavailability of antimony and heavy metals in arid regions: the case of the Wadley Sb district (San Luis, Potosí, Mexico), Sci. Total Environ. 427–428 (2012) 115–125.
[19] D. Li, X.-Y. Tan, X.-D. Wu, C. Pan, P. Xu, Effects of electrolyte characteristics on soil conductivity and current in electrokinetic remediation of lead-contaminated soil, Sep. Purif. Technol. 135 (2014) 14–21.
[20] J.-M. Lim, A.L. Salido, D.J. Butcher, Phytoremediation of lead using Indian mustard (*Brassica juncea*) with EDTA and electrodics, Microchem. J. 76 (2004) 3–9.
[21] R.K. Lu, Analysis Methods of Soil Agricultural Chemistry, China Agricultural Science Press, Beijing, 2000. pp. 12–28, pp. 106–107, pp. 477–490 (in chinese).
[22] C.S. O'Connor, N.W. Lepp, R. Edwards, G. Sunderland, The combined use of electrokinetic remediation and phytoremediation to decontaminate metal-polluted soils: a laboratory-scale feasibility study, Environ. Monit. Assess. 84 (2003) 141–158.
[23] C. Pérez-Sirvent, M.J. Martínez-Sánchez, S. Martínez-López, J. Bech, N. Bolan, Distribution and bioaccumulation of arsenic and antimony in *Dittrichia viscosa* growing in mining-affected semiarid soils in southeast Spain, J. Geochem. Explor. 123 (2012) 128–135.
[24] J. Pratas, M.N.V. Prasad, H. Freitas, L. Conde, Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation, J. Geochem. Explor. 85 (2005) 99–107.
[25] R.S. Putra, Y. Ohkawa, S. Tanaka, Application of EAPR system on the removal of lead from sandy soil and uptake by *Kentucky bluegrass* (*Poa pratensis* L.), Sep. Purif. Technol. 102 (2013) 34–42.
[26] C. Qi, F. Wu, Q. Deng, G. Liu, C. Mo, B. Liu, J. Zhu, Distribution and accumulation of antimony in plants in the super-large Sb deposit areas, China, Microchem. J. 97 (2011) 44–51.
[27] C. Spuller, H. Weigand, C. Marb, Trace metal stabilisation in a shooting range soil: mobility and phytotoxicity, J. Hazard. Mater. 141 (2007) 378–387.
[28] I. Tahmasbian, A. Nasrazadani, Soil electrokinetic remediation and its effects on soil microbial activity – a review, Afr. J. Microbiol. Res. 6 (2012) 2233–2238.
[29] M. Vaculík, Ľ. Jurkovič, P. Matejkovič, M. Molnárová, A. Lux, Potential risk of arsenic and antimony accumulation by medicinal plants naturally growing on old mining sites, Water Air Soil Pollut. 224 (2013) 1–16.
[30] Q.-Y. Wang, D.-M. Zhou, L. Cang, T.-R. Sun, Application of bioassays to evaluate a copper contaminated soil before and after a pilot-scale electrokinetic remediation, Environ. Pollut. 157 (2009) 410–416.
[31] J.-S. Yang, M.J. Kwon, J. Choi, K. Baek, E.J. O'Loughlin, The transport behavior of As, Cu, Pb, and Zn during electrokinetic remediation of a contaminated soil using electrolyte conditioning, Chemosphere 117 (2014) 79–86.
[32] D.-M. Zhou, H.-F. Chen, L. Cang, Y.-J. Wang, Ryegrass uptake of soil Cu/Zn induced by EDTA/EDDS together with a vertical direct-current electrical field, Chemosphere 67 (2007) 1671–1676.

PAPER II

ELECTROKINETIC REMEDIATION OF SIX EMERGING ORGANIC CONTAMINANTS FROM SOIL

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Electrokinetic remediation of six emerging organic contaminants from soil

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HIGHLIGHTS

- Electrokinetic remediation is a viable method for organic contaminants removal.
- Between 50% and 80% of the contaminants were remediated after four days.
- Electroosmosis was the main mechanism responsible for contaminants mobilization.
- Electrodegradation should also be taken into account in this remediation process.

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ABSTRACT

Some organic contaminants can accumulate in organisms and cause irreversible damages in biological systems through direct or indirect toxic effects. In this study the feasibility of the electrokinetic (EK) process for the remediation of 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS) in soils was studied in a stationary laboratory cell. The experiments were conducted using a silty loam soil (S2) at 0, 10 and 20 mA and a sandy soil (S3) at 0 and 10 mA. A pH control in the anolyte reservoir (pH > 13) at 10 mA was carried out using S2, too. Photo and electrodegradation experiments were also fulfilled. Results showed that EK is a viable method for the remediation of these contaminants, both through mobilization by electroosmotic flow (EOF) and electrodegradation. As EOF is very sensible to soil pH, the control in the anolyte increased EOF rate, consequently enhancing contaminants mobilization towards the cathode end. The extent of the mobilization towards the electrode end was mainly dependent on compounds solubility and octanol-water partition coefficient. In the last 24 h of experiments, BPA presented the highest mobilization rate (ca. 4 μg min^{-1}) with NP not being detected in the catholyte. At the end of all experiments the percentage of contaminants that remained in the soil ranged between 17 and 50 for S2, and between 27 and 48 for S3, with no statistical differences between treatments. The mass balance performed showed that the amount of contaminant not detected in the cell is similar to the quantity that potentially may suffer photo and electrodegradation.

1. Introduction

Over the past years, adverse effects including endocrine disruption and antibiotic resistance of some compounds, defined as 'emerging' have been observed in humans, animals and other organisms (Lapworth et al., 2012) and some can display a biological response even at very low concentrations. These, emerging organic contaminants comprise a wide array of different compounds (as well as metabolites and transformation products) including: pharmaceuticals and personal care products, pesticides, veterinary products, industrial compounds/by-products, food additives, as well as engineered nanomaterials (Clarke and Smith, 2011).

The main transfer pathway for organic contaminants (OCs) to enter the environment is via wastewater treatment plants (Kuster et al., 2005; Boleda et al., 2009; Madureira et al., 2010). Several OCs have been detected in effluents of urban wastewater treatment plants (Golet et al., 2002), ground and river water (Golet et al., 2001), sewage sludge (Göbel et al., 2005), as well as soil and manure (due to veterinary use) (Golet et al., 2003).

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The land application of municipal biosolids (typically to agricultural fields) is one potential route of soil exposure to OCs. The long-term risks associated with land application of biosolids are poorly characterized and, in some cases, difficult to accurately quantify (NRC, 2002). The OCs, once in soils, can be translocated to crop plants, and thus potentially enter in the food chain (Wu et al., 2012). In fact, the consumption of these plants might increase both human and livestock exposure to OCs (Zohair et al., 2006). For example, triclocarban (3,4,4′-trichlorocarbanilide) and triclosan (5-chloro-2-(2,4-dichlorophenoxy)-phenol), that are toxic, lipophilic and persistent, were found in vegetables tissues of pumpkin and zucchini (Aryal and Reinhold, 2011). In a laboratory study, carbamazepine, diphenhydramine, and triclocarban were also detected in plants (pepper, tomato, collard, lettuce and radish) that were grown in biosolids-treated soils (Wu et al., 2012).

Electrokinetic (EK) process is a remediation method for contaminated matrices (Virkutyte et al., 2002). This method aims to remove contaminants from low permeability contaminated soils under the influence of an applied low level direct current (DC), via electroosmosis, electromigration and electrophoresis (Acar et al., 1993). EK was already tested for some OCs namely for the soil removal of herbicides (Ribeiro et al., 2005; Ribeiro et al., 2011), hydrocarbons (Alcántara et al., 2012; Méndez et al., 2012) and simultaneous removal of OCs and heavy metals (Maturi and Reddy, 2006; Li et al., 2010; Alcántara et al., 2012; Cang et al., 2013).

The aim of this work is to assess the potential of EK for the remediation of soils contaminated with organic compounds and how they are mobilized. Six OCs, classified emerging, were selected to the study: two estrogenic steroid hormones, three industrial reagents and one antimicrobial agent. The target compounds were 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), nonylphenol (NP), octylphenol (OP) and triclosan (TCS). All these compounds are known to be endocrine disrupting agents and their chemical properties can be found in Table 1. To the best of our knowledge, EK removal of these emerging organic contaminants has never been reported, and the understanding of their behavior during the treatment can be valuable for the design of further tests.

2. Materials and methods

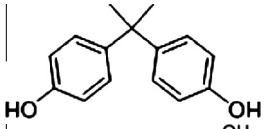
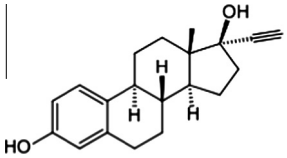
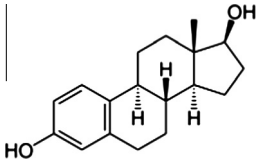
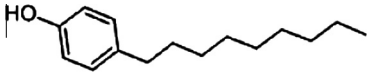
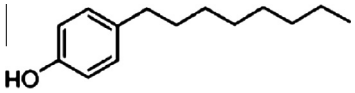
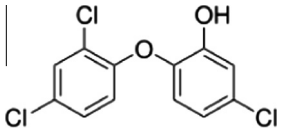
2.1. Chemicals and solvents

Bisphenol A (⩾99%), E2 (⩾97%), EE2 (⩾98%), OP (⩾99%), were purchased from Aldrich (Steinheim, Germany), TCS (Irgasan, ⩾97%) from Sigma–Aldrich (Steinheim, Germany) and NP (⩾90%) from Riedel Haën. All used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). Acetonitrile, methanol and acetone were Gradient Grade. The water (type I) used for analyte extractions and their analytical determinations was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA).

2.2. Organic contaminants analysis

The determination of the residual OCs was performed by high performance liquid chromatography with diode array detection (HPLC–DAD) in the range 200–800 nm.

Table 1
Chemical structure and properties of the 'emerging' organic contaminants.

Compound	Chemical structure	Formula	logK_{ow}[a]	pKa[b]	Solubility in water (mg L^{-1})	CAS-No
Bisphenol A (BPA)		$C_{15}H_{16}O_2$	3.32	9.6-11.3	120 (25 °C)	80-05-7
17α-ethinyloestradiol (EE2)		$C_{20}H_{24}O_2$	3.67	10.3	11.3 (27 °C)	57-63-6
17β-oestradiol (E2)		$C_{18}H_{24}O_2$	4.01	10.7	3.90 (27 °C)	50-28-2
p-Nonylphenol (NP)		$C_{15}H_{24}O$	5.76	10.7	7 (25 °C)	104-40-5
p-Octylphenol (OP)		$C_{14}H_{22}O$	5.30	10.4	19 (22 °C)	1806-26-4
Triclosan (TCS)		$C_{12}H_7Cl_3O_2$	4.76	7.9	10 (20 °C)	3380-34-5

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, www.SigmaAldrich.com.
Notes:
[a] Logarithm of the octanol-water partition coefficient.
[b] Logarithm of acid dissociation constant.

2.2.1. Sample preparation

2.2.1.1. Aqueous samples. The extraction of the analytes present in the electrolyte solutions was performed by solid phase extraction (SPE), using Oasis HLB (200 mg, 6 mL) from Waters (Saint-Quentin En Yvelines Cedex, France). The SPE cartridges were conditioned by washing with 2 × 6 mL of methanol, followed by re-equilibrium with 2 × 6 mL of Milli-Q water. For organic compounds enrichment the samples were acidified to pH 2, using nitric acid, before extraction. The aqueous samples, 200 mL, were passed through the cartridge at a flow-rate of approx. 10 mL min^{-1} by applying a moderate vacuum. After that, the cartridges were dried for approx. 1 min by vacuum. The retained analytes were eluted sequentially with 2 × 2 mL of methanol. All the extracts were collected as one and concentrated under a gentle stream of nitrogen till 2 mL. Samples were transferred to a vial and kept at −20 °C until analysis.

2.2.1.2. Solid samples. Solid samples (soils and passive membranes) were extracted three times by sonication using 50 mL of acetone for 10 min. All the extracts were collected, as one, and concentrated to approx. 10 mL using 250 and 50 mL pear-shaped evaporating flasks on a rota vapor, Büchi RE 111 (40 °C/moderate vacuum). In order to remove the particulate matter, the extracts were filtered through MFV-5 glass microfiber filters (diameter 47 mm, pore size 0.5 μm) from Filter-Lab (Barcelona, Spain).

2.2.2. HPLC-DAD conditions

High-performance liquid chromatography (HPLC) was performed on a Finnigan MAT HPLC system (Thermo Scientific, USA) equipped with a SP P4000 Pump, an AS 3000 auto-sampler, a UV6000LPand a TSP SN 4000 Interface.

Separations were carried out using a Chromolith Performance RP-18e column with 100 mm × 4.6 mm from Merck (Darmstadt, Germany) and Onyx SecurityGuard cartridges (4 mm × 3.0 mm) from Phenomenex (Torrance, CA, USA). The UV wavelength was set to full scan between 200 and 800 nm. Target compounds were measured at 325 nm for BPA, 281 nm for EE2 and 280 nm for E2, OP, NP and TCS, respectively. All HPLC runs were performed at a constant flow rate of 1 mL min^{-1}, in gradient mode. The eluents used were acetonitrile/MiliQ water solutions (solution A: 35/65; solution B: 90/10), adjusted to pH = 2.8 using a formic acid solution (50% in water, Fluka). The gradient run was set at 100% A from 0 to 12 min, then to 75% B until 13 min, where it held until 25 min, then to 100% B until 27 min, where it held until 30 min. The system re-equilibration was performed for 3 min with 100% A. All solvents were filtered before use by Nylon 66 membranes (pore size 0.45 μm; Bellefonte, PA, USA). All operations and data analysis were processed by the Xcalibur software v.1.3. (Thermo Scientific, USA).

The method presents a limit of detection (LOD) of 0.05 mg L^{-1} and quantification limit (LOQ) of 0.10 mg L^{-1}. Method recuperation for both aqueous and solid samples ranged between 84% and 120% for all OCs.

2.3. Soil sampling

Three soils were used in this study: S1, S2 and S3. Their characteristics are presented in Table SM-1 (Supplemental information A). S1 was sampled at Valadares, Vale de Milhaços, Portugal, at 0–15 cm depth, corresponds to an Eutric Regossol (World Reference Base for Soil). Soil S1 presents a sandy texture, low mineral and organic colloids, which lead to a poor cation exchange capacity. It was used in the EK experiments only as a support medium, further on explained (Section 2.5). Soils S2 and S3 were sampled at Paul de Magos, Salvaterra de Magos,Portugal, at 0–20 cm depth, correspond to Fluvisols (World Reference Base for Soil). Soil 2 presents a Silty loam texture (with 53.4% clay), high mineral and organic colloids, which lead to a higher cation exchange capacity, whereas S3 presents a Loamy sand texture (with only 8% of clay) and lower mineral and organic colloids, which conducts to a poor cation exchange capacity. Both soils were used in the EK experiments as spiked matrices.

In order to assess the contaminants mobilization and remediation/degradation by EK (the objective of this study), the soil was spiked with a mixture of the OCs, approximately 500 ppm of each analyte in acetone. This was done to assure that all the contaminants would be detected in all cell compartments (anolyte, catholyte, membranes and soil sections), even in cases of high degradation efficiencies and to test the limits of the technique by using a highly contaminated matrix

2.4. Electrokinetic laboratory cell

The EK experiments were carried out in a laboratorial cell. The cell is divided into three compartments, consisting of two electrode compartments (L = 7.46 cm, internal diameter = 8 cm) and a central one (L = 3 cm, internal diameter = 8 cm), in which the soil, saturated with deionized water, is placed (schematic representation shown in Fig. 1). A set of five cellulose filters, previously tested and known to work as passive membranes (Whatman 42), were used to assure the separation between the electrode compartments and the central one. A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC and the voltage drop was monitored (Kiotto KT 1000H multimeter). The electrodes were platinized titanium bars, with a diameter of 3 mm and a length of 5 cm (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 7, being circulated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions. In each of the electrode compartments of all experiments, the electrolytes were removed to collector flasks. The incoming flows to the electrode compartments were maintained constant (1 mL min^{-1}) but the outlet flows are also dependent on the value of the EOF.

2.5. Electrokinetic experimental conditions

Six different laboratory experiments (A–F) were carried out, according to the experimental conditions presented in Table 2. The central cell compartment of the EK cell was filled with three slices of soils, being the middle slice of soil 2 (S2, silty loam) or soil 3 (S3, loamy sand) that were spiked with the OCs under study, and the outer two slices of soil 1 (S1, sand), for minimizing the OCs diffusion towards the electrode compartments (Fig. 1). The detection and quantification of the contaminants in each soil was carried out before all experiments. Electrolyte samples (catholyte and anolyte) were collected on a daily base during the experiments, for further OCs quantification, and their pH and volume registered. At the end of each experiment, the total soil in the cell was sectioned in three sections ($S1_{anode}$, S2, $S1_{cathode}$) and each sample in three subsamples. Smaller subsamples were also collected for pH and humidity measurements. The OCs contents in the soils, electrolyte solutions and in the passive membranes were analyzed, following the procedures described in Section 2.2. A control experiment for each soil, without applied current, was also carried out (exp. A and E).

2.6. Photo and electrodegradation experiments

Contaminants photo and electrodegradation were also assessed. Degradation experiments were conducted for 6 h (electrolytes estimated residence time in the EK cell) at a constant current of 10 mA. Two containers (not completely closed), one for the cathode and other for the anode, containing 400 mL of electrolyte solution that

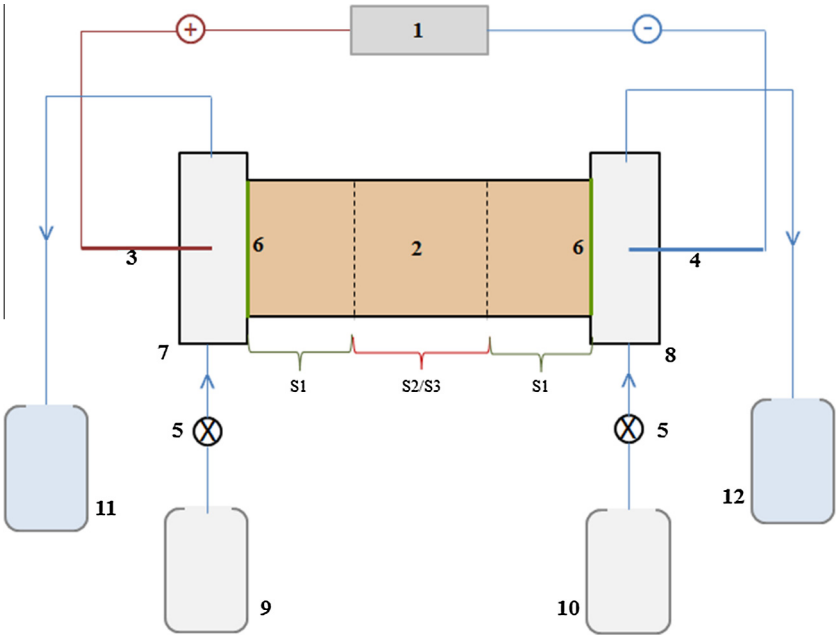


Fig. 1. Schematic view of the electrokinetic cell set-up: (1) DC power supply; (2) soil cell; (3) anode; (4) cathode; (5) peristaltic pump; (6) cellulose filters; (7) anode chamber; (8) cathode chamber; (9) anolyte reservoir; (10) catholyte reservoir; (11) anolyte receiving reservoir; (11) catholyte receiving reservoir; (S1) non-contaminated soil S1; (S2/S3) contaminated soils.

Table 2
Experimental conditions used.

Experiment	Soil (central compartment)	Current (mA)	pH adjustment	Time (h)
A	S2	0	–	96
B	S2	10	–	96
C	S2	20	–	52
D	S2	10	Anolyte pH ≈ 13[a]	96
E	S3	0	–	96
F	S3	10	–	96

[a] pH adjustment was carried out in the anolyte reservoir (number 9 in Fig. 1).

were spiked with the studied OCs (1 mg L^{-1}). A filter paper was used as a saline bridge. The filter paper was submersed in a 1 M KNO_3 solution for 3 s, and then left drying for 30 s in order to remove the excess solution. One end of the filter paper was placed in the cathode end and the other in the anode end. The power supply, electrodes and the filter paper used were the same as the ones used for the EK experiments. Electrolytes pH was not controlled during treatment. The initial and final electrolyte samples and filter paper were collected and analyzed following the procedures described in Section 2.2. Hydrogen peroxide formation was also controlled using Semi-quantitative test strips Quantofix Peroxide 25 (Macherey-Nagel, Germany).

3. Results and discussion

3.1. Photo and electrodegradation

Electrokinetic treatment relies on several interacting mechanisms but the dominant and most important electron transfer reactions that occur at electrodes during the process is the electrolysis of water, Eqs. (1) and (2):

$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- \text{ (anode)} \quad (1)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \text{ (cathode)} \quad (2)$$

Due to water electrolysis, hydroxyl radicals (·OH, redox potential of 2.80 V/SHE) are continuously being generated and these ·OH radicals are the most powerful reactive oxygen species that can oxidize OCs unselectively at a diffusion-controlled rate (Yuan et al., 2013). Also, due to water electrolysis, at the end of the experiments pH was 11.72 ± 0.06 and 2.31 ± 0.08 in the cathode and anode end, respectively. Solution pH in the cathode end is higher than OCs p*Ka* meaning that they will be mainly in their ionized form.

Along the experiment the differences found in the degradation percentages could be mainly related to their chemical structures (Table 1), the reactivity and mechanisms previously studied by different authors. The phenolic ring of TCS can be activated by the two O-containing groups and may be attacked by ·OH radicals, with production of hydroxylated TCS (Yuan et al., 2013). Bisphenol A has only one electron-donating group (–OH) linked with the benzene ring (Yuan et al., 2013). This can result in an electrophilic attack of the carbon in the aromatic ring by ·OH radicals. Both NP and OP can also suffer an attack on the group (–OH) linked with the benzene ring. The E2 can be oxidized mainly by the addition of ·OH radicals through two possible ways: abstraction of hydrogen bonded with the C6 atom in the aliphatic ring (that links to the aromatic ring) or oxidation of its hydroxyl group (Xu et al., 2013). Finally, EE2 should present a similar behavior to E2 although the presence of the ethinyl group in EE2 may stabilize the phenolic ring and improve its resistance to an attack by reactive ·OH radicals (Xu et al., 2013). Besides the possible reactions with the ·OH radical, all studied compounds contain a phenolic functional group, which makes them susceptible to photodegradation. Consequently, all compounds are assumed to suffer photo and electrodegradation with estimated percentages of 52 ± 23% for BPA, 66 ± 7% for E2, 65 ± 12% for EE2, 68 ± 14% for TCS, 64 ± 9% for OP and 60 ± 7% for NP. Hydrogen peroxide was below detection limit (0.5 mg L^{-1} H_2O_2).

The formation of new peaks correspondent to new or related compounds was not detected in the analysis performed by HPLC-DAD (scan from 200 to 800 nm). Still, in other experiments using electro-Fenton process with Ti/MMO cathode, all the intermediates

of BPA and TCS disappeared after 60 min degradation suggesting the breakage of conjugate structures such as benzene ring (Yuan et al., 2013). Electro-Fenton process with a carbon felt cathode and platinum anode were also tested for the study of E2 degradation in aqueous-acetonitrile mixture, and after 40 min, depending on the initial concentration, a complete degradation was observed (Naimi and Bellakhal, 2012). This suggests that in the conditions here presented, 6 h at 10 mA, a complete degradation of the intermediates may have occurred.

3.2. Electrokinetic experiments

3.2.1. Electric current

When no pH adjustment was performed, the experiment conducted with 10 mA (exp. B) presented lower voltage than the experiment with 20 mA (exp. C), for S2. This was expected as, according to Ohm's law, when the resistance in the medium is the same, the voltage increases with an increasing current. As the experiments kept running, the resistance in the soil starts to increase due to the depletion of ions from the soil. As the current is higher in experiment C the resistance increases faster comparatively to experiment B, and, consequently, voltage increases steeply after 20 h. After 40 h, the voltage reached its maximum (57.9 V), the current intensity started to decrease and the experiment was stopped after 52 h. In experiment B, voltage increased more slowly due to the lower applied current. When pH was adjusted in the anolyte (exp. D) the voltage at the beginning of the experiment was higher comparatively to the other experiments, probably due to a higher resistance in the medium. Then, the voltage starts to decrease and after 20 h it is very similar to experiment B that was also carried out with 10 mA. For the experiments conducted with S3 and 10 mA, voltage started to increase after 45 h, and became steady at approximately 53 V between 57 and 96 h. As soil S3 presents 4.5 times higher sand content comparatively to S2 the depletion of the ions is faster and consequently the resistance in the medium also increases faster.

3.2.2. Electroosmotic flow, electrolyte and soil pH

The electrolytes and soil pH of the experiments varied as expected (Table 3). All the catholytes of the three experiments presented predominantly an alkaline pH. The anolytes of the experiments presented an acid pH which varied between 2.2 and 2.5 for experiments without pH adjustment, and approximately 2.5 for the experiment with pH adjustment in the anolyte (exp. D). As the pH measurements were carried out at the anolyte receiving reservoir (element 11 in Fig. 2) and the pH adjustment was done in the anolyte reservoir (element 9 in Fig. 2), the measured pH was acidic contrasting to the initial pH of 13. This was mainly due to fast formation of H^+ and the low velocity of the anolyte entering and exiting of the chamber. Still, the soil pH near the anode chamber ($S1_{anode}$) was 7.54 meaning that the pH control to 13 in the anolyte was indeed increasing soil pH near it as expected.

The electrolysis reaction at the anode caused pH decrease in the anode compartment of experiment B and F, as the acid front generated was transported into the soil towards the cathode via electromigration and electroosmosis (Acar et al., 1995). The OH^- ions generated at the cathode electromigrated towards the anode, in the opposite direction of the EOF, causing a pH increase near the cathode in all experiments, especially in experiment D. When the EOF is lower, the OH^- ions are capable of electromigrating further and having a greater effect on the pH near the anode. The lower mobility of the OH^- ions compared to H^+ also needs to be taken into account (Acar et al., 1995). For the experiment conducted with S3 and 10 mA (exp. F) pH decrease of the soil in section $S1_{anode}$ is more expressive than in exp. B (10 mA, S2). This is probably due to an easier mobility of the H^+ ions towards the cathode end due to soil characteristics (loamy sand) and EOF. Due to the pH control in the anolyte of experiment D, the soil along the cell presented pH above 7.5 for $S1_{anode}$ and S2, and pH 11 for $S1_{cathode}$. Experiment C took 52 h, and pH changes along the soil column were not as expressive as in the others. Still, pH of S2 and both S1 sections suffered slight changes.

The higher volume of fluid found in the catholytes at the end of the experiments suggests that the EOF developed towards the cathode in all the tests (Table 3), except in experiment F, but the magnitude of its flow rate was different due to the effect of electric field intensity (10 and 20 mA) and pH. The movement of fluid resulting from head differences is not considered to influence the differences in volume between catholyte and anolyte, as the experimental cells were horizontally placed (level ruler) in order to avoid hydraulic gradients.

According to the Helmholtz–Smoluchowski theory, the EOF rate is mainly proportional to the zeta potential and the electric-field strength. Therefore, if the current intensity of the EK process is low, the EOF will be negligible. On the other hand, the zeta potential, which depends on the nature and properties of the soil (Asadi et al., 2009), determines the direction of the EOF. In most cases, at low pH values, the zeta potential is positive and the EOF direction is towards the anode chamber (Asadi et al., 2009). When S3 was used, initially EOF was slightly higher towards the cathode end, but, after 72 h it moved towards the anode, due to the low soil pH.

The proportion of fine-grained sediments with net surface charge in a geological matrix will also determine the extent of EOF. Electroosmosis requires a net charge on the surface of sediment and soil grains, consequently clays and silts have the highest electroosmotic permeability due to a high surface charge density (Acar et al., 1995). A high EOF associated to the silty loam soil (S2) was not observed in the experiments. For the same EK conditions and the different soils used (exp. B and F), it can be observed that when loamy sand (S3) was used higher accumulated volumes were collected in the when comparing to exp. B where silty loam (S2) was used. This result may be explained by the differences observed in soil pH (explained above). The presence of S1 as a support medium in the middle compartment that presents a texture

Table 3
Soil sections and electrolytes pH means; accumulated volume for the electrokinetic experiments.

	Cell section	Initial	A	B	C	D	E	F
pH	Anolyte	7.00 ± 0.09	5.03 ± 0.35	2.34 ± 0.18	2.27 ± 0.12	2.57 ± 0.37	5.68 ± 0.58	2.50 ± 0.14
	$S1_{anode}$	6.00 ± 0.21	5.89 ± 0.07	4.15 ± 0.12	6.59 ± 0.20	7.54 ± 0.73	5.71 ± 0.74	3.95 ± 0.11
	S2	5.81 ± 0.13	5.94 ± 0.05	4.78 ± 0.14	5.39 ± 0.32	7.88 ± 1.28	–	–
	S3	5.12 ± 0.10	–	–	–	–	5.12 ± 0.08	3.65 ± 0.13
	$S1_{cathode}$	6.00 ± 0.21	6.36 ± 0.26	7.65 ± 0.06	6.94 ± 0.06	9.36 ± 0.07	5.73 ± 0.19	5.07 ± 0.15
	Catholyte	7.00 ± 0.09	5.73 ± 0.42	11.38 ± 0.26	11.65 ± 0.14	11.57 ± 0.19	5.32 ± 0.78	10.43 ± 0.19
Accumulated volume[a] (mL)	Anolyte	–	5382	4791	2520	5935	5571	5368
	Catholyte	–	5435	4992	2612	6628	5634	5263

Note: Soil sections pH was measured at the end of the experiments whereas the electrolytes were measured along the time.
[a] Total amount of electrolyte collected at the end of the experiments in the anode and cathode receiving reservoir.

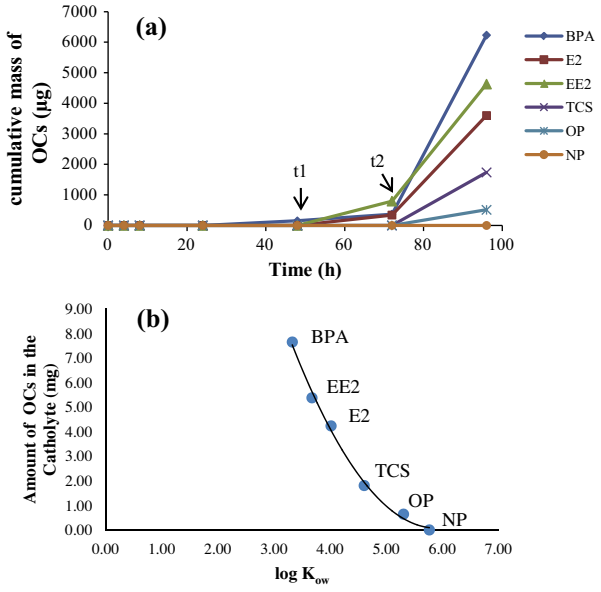


Fig. 2. Experiment D (a) cumulative mass of organic contaminants found in the catholyte and (b) relation between the amount of organic contaminants found in the catholyte and the logarithm of octanol-water partition coefficient.

more similar to S3 than S2 (Table SM-1), may have also influenced the EOF results.

As the electrokinetic movement of OCs is mainly due to the EOF, it was necessary to increase its rate in order to obtain a more effective pollutant removal. By adjusting the pH in the anolyte to 13 (exp. D), the EOF towards the cathode increased of magnitude. In total, at the end of the experiment, more 693 mL were found in the cathode end.

3.2.3. Organic contaminants remediation

The percentage of OCs removed (cathode and anode end), remaining in the contaminated soil and degraded by EK can be seen in Table 4 (as experiments A and E were conducted without the application of electric current, the results are not shown in the table). In the control experiments (A and E) all studied compounds were detected in S1 soil sections (initial non-contaminated soil) meaning that diffusion is one of the movements present in the cell. Using soil S2, between 0 and 2% of the OCs were detected in soil sections near the anode and cathode but slightly higher maximum amounts were detected in the control experiment using soil S3, between 0% and 6%.

When 10 mA were applied to the cell with S2 (exp. B), only BPA was removed (3% to the cathode and 2% to the anode end). In the experiment using S3 and 10 mA (exp. F) 2% and 0.4% of BPA were detected in the cathode and anode end, respectively.

The increase of current intensity applied to S2, from 10 to 20 mA (experiment B and C, respectively) did not improve OCs removal to the electrolytes by EK. However, it must be noted that experiment C only lasted 52 h, in contrast to the 96 h of experiment B. The analysis of the soil section near the anode and cathode ($S1_{anode}$ and $S1_{cathode}$) for both experiments showed that all the OCs were mobilized during the EK treatment although at different extents. In experiment B, 3% of E2 and EE2 and 10% of BPA were detected in $S1_{cathode}$, whereas in experiment C 1% of E2, OP and NP, 2% of EE2 and 9% on BPA were detected in $S1_{cathode}$.

Controlling the pH in experiment D allowed increasing OCs removal mainly towards the cathode end at the end of the 96 h. As the best EK removal efficiencies were obtained in these conditions this experiment will be discussed later in more detail (Section 3.2.4).

At the end of all experiments, the mass balance performed showed that the percentage of OCs not detected in the cell is similar to the percentage that potentially may suffer photo and electrodegradation (see Section 3.1). Mass losses inherent to analysis method also need to be taken into account.

At the end of all experiments the percentage of contaminants that remained in the soil ranged between 17% and 50% for S2 and between 27% and 48% for S3, with no statistical differences between treatments.

Steroids presented slightly different behaviors. When 10 mA were applied 39% of E2 and 50% of EE2 remained in S2.When 20 mA were applied the degradation is more intense and only 30% and 35% of EE2 and E2, respectively remained in S2. As EE2 is more soluble than E2, when the EOF increased (exp. D), EE2 mobilization also increased to $S1_{cathode}$ comparatively to E2 (Table 5). For the plasticisers, the degradation order is BPA > OP $\gg$ NP mainly due to NP presenting low solubility and high log K_{OW}. Between 26% and 28% of TCS remained in the contaminated soil, S2 and S3, of all experiments.

3.2.4. EK mobilization

In experiment D OCs removal was higher due to the increased EOF flow towards the cathode, comparing to the other experiments. As it can be seen in Fig. 2a the OCs mobilization due to EK along the experiment was not constant. Contaminants removal was low during the first 48 h (Fig. 2a, point t1), after which it increases for the following 24 h (Fig. 2a, point t2), and mobilization rate (v) is presented in Table 5. The best mobilization was achieved for BPA (ca.4.07 µg min^{-1}) that presents the highest solubility (120 mg L^{-1}) and the lowest logK_{ow} and, as the EOF towards the cathode keeps its rate, the mobilization of BPA is also kept constant. Compound EE2 (ca. 2.66 µg min^{-1}) is more easily mobilized than E2 (ca. 2.26 µg min^{-1}). NP and OP were the compounds more

Table 4
Percentage of each organic contaminant remaining, removed and degraded from the soil through the electrokinetic process.

Compound	% OC											
	B			C			D			F		
	S2[a]	Removed[b]	Degraded[c]	S2[a]	Removed[b]	Degraded[c]	S2[a]	Removed[b]	Degraded[c]	S3[a]	Removed[b]	Degraded[c]
BPA	21	1	68	18	n.d.	73	17	16	63	27	2	61
E2	39	n.d.	58	30	n.d.	69	45	9	45	41	n.d.	57
EE2	50	n.d.	46	35	n.d.	62	35	11	44	47	n.d.	46
TCS	26	n.d.	74	33	n.d.	66	31	4	64	28	n.d.	68
OP	24	n.d.	74	24	n.d.	74	24	1	73	36	n.d.	63
NP	50	n.d.	50	44	n.d.	54	49	n.d.	48	48	n.d.	51

n.d.: not detected, below LOD.
[a] % OC in S2 or S3 = [(mass of OC detected in the S2 or S3 soil fraction)/(mass of OC added to the soil)]*100.
[b] % OC removed = [$\sum$(mass of OC detected in the cathode and anode end)/(mass of OC added to the soil)]*100.
[c] % OC degraded = [1 − $\sum$(mass of OC detected in all cell compartments)/(mass of OC added to the soil)]*100.

Table 5
Mass of organic contaminants found in the different parts of the cell at the end of electrokinetic process for experiment D and mobilization rate.

Compound	μg					μg min^{-1}	
	Anode end	$S1_{anode}$	S2	$S1_{cathode}$	Cathode end	v_{t1}	v_{t2}
BPA	n.d.	528	8307	1506	7649	0.15	4.07
E2	n.d.	95	21521	730	4235	0.24	2.26
EE2	n.d.	242	17250	4610	5379	0.55	2.66
TCS	n.d.	n.d.	15393	535	1807	0.00	1.21
OP	n.d.	76	12095	749	642	0.00	0.36
NP	n.d.	n.d.	23924	1270	0	0.00	0.00

v: mobilization ratio; t1: between 48 and 72 h; t2: between 72 and 96 h.
n.d.: not detected, below LOD.

difficult to mobilize as both present very high $\log K_{ow}$, with OP presenting a ratio of ca. 0.36 μg min^{-1} due to its higher solubility comparing to NP. Soil analysis corroborate these results as higher amounts of OCs were detected in the cathode end (catholyte plus cathode membranes) as well as in the soil section near the cathode ($S1_{cathode}$) (Table 5). The octanol–water distribution of TCS depends on the pH of the environmental matrix to which it is exposed, and, as the hydroxyl groups (–OH) in the molecule are capable of deprotonation it promotes its water solubility. Triclosan has a pKa of 7.9 and at pH 9.36, soil near the cathode, it will be predominantly in its ionized form resulting in a higher solubility and faster mobilization to the cathode end.

As presented in Fig. 2b, there is a direct correlation (polynomial regression, $y = 1.1374x^2 - 13.376x + 3.405$, $r^2 = 0.9961$) between the amount of OCs that were mobilized to the catholyte and the logarithm of octanol-water partition coefficient. The compounds that presented a $\log K_{ow} \geqslant 4$ are more tightly sorbed to the soil particles, being more difficult to solubilize and consequently were more difficult to remove. Some OCs where also detected in the $S1_{anode}$, but not in the anode end. This suggests that the contaminants may be moving towards the anode end due to diffusion and electromigration.

4. Conclusion

The present study demonstrated the possibility to handle the studied organic contaminants (BPA, E2, EE2, OP, NP, TCS) in soils when submitted to an electric field, as well as the applicability of EK process to remove them from soil solution. The experimental results showed that the highest quantities of contaminants moved towards the catholyte, particularly when the EOF was kept constant, allowing contaminants mobilization towards it. The pH control in the anolyte increased EOF rate consequently enhancing contaminants mobilization towards the cathode end. The extent of mobilization towards the cathode end was mainly dependent on compounds solubility and octanol-water partition coefficient. In the last 24 h of experiment, BPA presented the highest mobilization rate with NP not being detected in the catholyte. At the end of all experiments the percentage of compounds that remained in the contaminated soil ranged between 17% and 50% for S2 and between 27% and 48% for S3, with no statistical differences between treatments. The mass balance performed showed that the percentage of OC not detected in the cell is similar to the percentage that potentially may suffer photo and electrodegradation, with all contaminants presenting a degradation percentage between 52% and 66%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.06.017.

References

Acar, Y.B., Alshawabkeh, A.N., Gale, R.J., 1993. Fundamentals of extracting species from soils by electrokinetics. Waste Manage. 13, 141–151.
Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppala, S., Bricka, M., Parker, R., 1995. Electrokinetic remediation: basics and technology status. J. Hazard. Mater. 40, 117–137.
Alcántara, M.T., Gómez, J., Pazos, M., Sanromán, M.A., 2012. Electrokinetic remediation of lead and phenanthrene polluted soils. Geoderma 173–174, 128–133.
Aryal, N., Reinhold, D.M., 2011. Phytoaccumulation of antimicrobials from biosolids: impacts on environmental fate and relevance to human exposure. Water Res. 45, 5545–5552.
Asadi, A., Huat, B.B.K., Hassim, M.M., Mohamed, T.A.M., Hanafi, M.M., Shariatmadari, N., 2009. Electroosmotic phenomena in organic soils. Am. J. Environ. Sci. 5, 310–314.
Boleda, M.R., Galceran, M.T., Ventura, F., 2009. Monitoring of opiates, cannabinoids and their metabolites in wastewater, surface water and finished water in Catalonia. Spain Water Res. 43, 1126–1136.
Cang, L., Fan, G.-P., Zhou, D.-M., Wang, Q.-Y., 2013. Enhanced-electrokinetic remediation of copper–pyrene co-contaminated soil with different oxidants and pH control. Chemosphere. 90, 2326–2331.
Clarke, B.O., Smith, S.R., 2011. Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ. Int. 37, 226–247.
Göbel, A., Thomsen, A., McArdell, C.S., Alder, A.C., Giger, W., Theiß, N., Löffler, D., Ternes, T.A., 2005. Extraction and determination of sulfonamides, macrolides, and trimethoprim in sewage sludge. J. Chromatogr. A 1085, 179–189.
Golet, E.M., Alder, A.C., Hartmann, A., Ternes, T.A., Giger, W., 2001. Trace determination of fluoroquinoloneantibacterial agents in urban wastewater by solid-phase extraction and liquid chromatography with fluorescence detection. Anal. Chem. 73, 3632–3638.
Golet, E.M., Strehler, A., Alder, A.C., Giger, W., 2002. Determination of fluoroquinolone antibacterial agents in sewage sludge and sludge-treated soil using accelerated solvent extraction followed by solid-phase extraction. Anal. Chem. 74, 5455–5462.
Golet, E.M., Xifra, I., Siegrist, H., Alder, A.C., Giger, W., 2003. Environmental exposure assessment of fluoroquinolone antibacterial agents from sewage to soil. Environ. Sci. Technol. 37, 3243–3249.
Kuster, M., López de Alda, M.J., Barceló, D., 2005. Estrogens and Progestogens in Wastewater, Sediments, and Soil, In: Barceló, D. (Ed.), The Handbook of Environmental Chemistry, Springer, Berlin, Germany, vol. 5, pp.1–24.
Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S., 2012. Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. 163, 287–303.
Li, T., Yuan, S., Wan, J., Lu, X., 2010. Hydroxypropyl-β-cyclodextrin enhanced electrokinetic remediation of sediment contaminated with HCB and heavy metals. J. Hazard. Mater. 176, 306–312.
Madureira, T.V., Barreiro, J.C., Rocha, M.J., Rocha, E., Cass, Q.B., Tiritan, M.E., 2010. Spatiotemporal distribution of pharmaceuticals in the Douro River estuary (Portugal). Sci. Total Environ. 408, 5513–5520.
Maturi, K., Reddy, K.R., 2006. Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin. Chemosphere 63, 1022–1031.
Méndez, E., Pérez, M., Romero, O., Beltrán, E.D., Castro, S., Corona, J.L., Corona, A., Cuevas, M.C., Bustos, E., 2012. Effects of electrode material on the efficiency of

hydrocarbon removal by an electrokinetic remediation process. Electrochim. Acta. 86, 148–156.
Naimi, I., Bellakhal, N., 2012. Removal of 17β-estradiol by electro-fenton process. Mater. Sci. Appl. 3, 880–886.
NRC, 2002, Biosolids applied to land: advancing standards and practices, National Research Council (Eds.), National Academy Press, Washington, DC, p. 368.
Ribeiro, A.B., Rodríguez-Maroto, J.M., Mateus, E.P., Gomes, H., 2005. Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine: experimental and modeling. Chemosphere 59, 1229–1239.
Ribeiro, A.B., Mateus, E.P., Rodríguez-Maroto, J.-M., 2011. Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Exp. Model. Sep. Purif. Technol. 79, 193–203.
Virkutyte, J., Sillanpää, M., Latostenmaa, P., 2002. Electrokinetic soil remediation — critical overview. Sci. Total Environ. 289, 97–121.
Wu, C., Spongberg, A.L., Witter, J.D., Sridhar, B.B.M., 2012. Transfer of wastewater associated pharmaceuticals and personal care products to crop plants from biosolids treated soil. Ecotox. Environ. Safe. 85, 104–109.
Xu, N., Zhang, Y., Tao, H., Zhou, S., Zeng, Y., 2013. Bio-electro-Fenton system for enhanced estrogens degradation. Bioresource Technol. 138, 136–140.
Yuan, S., Gou, N., Alshawabkeh, A.N., Gu, A.Z., 2013. Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode. Chemosphere 93, 2796–2804.
Zohair, A., Salim, A.-B., Soyibo, A.A., Beck, A.J., 2006. Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables. Chemosphere 63, 541–553.

PAPER III

PHOSPHORUS RECOVERY FROM A WATER RESERVOIR - POTENTIAL OF NANOFILTRATION COUPLED TO ELECTRODIALYTIC PROCESS

Waste Biomass Valor
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ORIGINAL PAPER

Phosphorus Recovery from a Water Reservoir–Potential of Nanofiltration Coupled to Electrodialytic Process

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Abstract Worldwide waste streams can represent an environmental problem if they are considered "deleterious material". These streams may also be a source of secondary resources when enclosing compounds with potential to be recovered. Phosphorus (P) is one of those, with an increasing interest, as it is essential for life but its non-renewable reserves are expected to last about one century. Nanofiltration (NF) and electrodialytic process (ED) were applied to a stream from a Water Treatment Plant (WTP). Water from Funcho Dam Reservoir, Portugal, was subject of NF treatment followed by ED process for P recovery. The feed concentration of P for ED process was between 1,429 and 1,845 μg/L. Optimization studies were carried out in laboratory cells. Almost complete P removal out of the central compartment of the ED cell was observed under the action of an applied electric field. Experiments lasted between ca. 7 and 42 h experimental-period, depending on concentrate parameters. In less than 7 h of ED, 72 % of P was recovered in the anolyte and thereby separated from the concentrate stream. Nanofiltration coupled to ED can be considered a promising and sustainable technology to upgrade waste streams, recovering P and avoiding the intensive mining of phosphate rock.

Keywords Phosphorus · Electrokinetic recovery · Nanofiltration · Membrane concentrate · Waste valorisation

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Introduction

Phosphorus (P) is an element of supreme environmental importance as it is essential for all living cells. It can be used for animal feed additions and industrial uses (such as detergents, fire safety, chemicals industry or pharmaceuticals) but its dominant use is as soil fertilizer [1]. Phosphate rock reserves are limited (expected to last ca. one century [2]) being a non-renewable resource. The price of P is already reflecting its scarcity, as the prices for phosphate rock increased 700 % in 2007–2008 [3]. Between 2001 and 2008, world prices for P fertilizers increased more than world prices for rice, wheat and maize [4]. For this reason, securing sufficient P will become critical in food production and efficient technologies to recover it from several matrices have to continue to be developed.

The attempt to remove/recover P from wastewater treatment plants has had increasingly attention in the last few years. Chemical precipitation, biological processes or adsorption are examples of applied technologies [5, 6]. Nevertheless, there is scarce knowledge about P removal from water treatment plants (WTP). In fact, and despite the

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essential need to use fertilizers in order to increase crops production efficiency, large amounts of P drawn from agricultural soils end up in the sewer systems of cities [6] and, more or less 40 % stay in agricultural soil as excess. This resulting excess of P in agricultural lands can be leached [7] and, consequently, promote eutrophication in water reservoirs. To overcome health problems, e.g. those associated with cyanobacteria blooms, WTP use different techniques to clean drinking water. Nanofiltration (NF) is a membrane technology based on pressure-driven filtration, that can be used to guarantee safe levels of contaminants in water as, due to lower pore diameters comparing with ultrafiltration (<2 nm), it retains organic compounds with lower molecular weight which is an advantage to restrain contaminants such as toxins, pesticides and endocrine disruptors [8–10]. Additionally, it is also effective in removing multivalent ions as well as natural organic matter (NOM). Nanofiltration is a type of membrane with characteristics between reverse osmosis and ultrafiltration and presents as advantages lower pressure operation, high flow, high quantity of salt removal, low investment and low operation costs [11]. In this way, NF membrane acts as a physical barrier, allowing the separation of water from the suspended solids and dissolved materials, depending on its type and operational conditions [11]. The recovery of P using NF for wastewaters have been studied [12–14] and all achieved good recoveries, which means that NF is efficient in concentrating P of these streams.

The electrodialytic process (ED) is induced by application of a low level direct current (DC), which causes the transport of species towards one of the electrode compartments, where they concentrate and from where they may be removed. The movement of water, charges and charged particles are associated with electroosmosis, electromigration and electrophoresis, respectively. The use of ion exchange membranes as separators, between processing solutions surrounding the electrodes and the particulate material, adds electrodialysis to the process. Potentialities of ED were shown in the removal of inorganic [15–18] contaminants from several matrices, proving that this is an efficient remediation tool with a large scope of application. In fact, metals were removed from solid waste products [17] such wastewater sludge and bio-ahes [15] and impregnated wood waste [16] but, as far as we could ascertain, P removal from membrane concentrate was never reported using ED technology. Contrary to most heavy metals, phosphate in the pore water exists as anionic species unless the pH is strongly acidic. Thus, when DC current is applied to a water saturated matrix, phosphate, among other anions may selectively accumulate in the anolyte compartment.

This work aimed to optimize conditions to treat a waste, membrane concentrate, resulting from NF in order to recover P for further re-use. The NF will concentrate and remove P and other compounds existing in a waste stream followed by P recover by ED, without the presence of contaminants. In fact, concepts to recover P from water treatment schemes are particularly attractive, if they promise to obtain a product that is "ready-to-use" and of high quality as a fertiliser [19]. Presented results intend to give an overview of P dynamics and preferential movement in an ED cell.

Materials and Methods

Production of Membrane Concentrates

Nanofiltration experiments were carried out using a plate-and-frame unit, Lab-unit M20 from Danish Separation Systems, as described in Ribau Teixeira and Rosa [20]. A NF90 membrane was used. This is a thin film composite NF/RO membrane of polyamide membranes (kindly supplied by DowFilmtec) with an hydraulic permeability of 82.2 kg/ (h.m^2.bar) at 21 °C ($r^2 = 0.997$), and a membrane molecular weight cut-off of ca. 114 Da (using the method proposed by Rosa and de Pinho [21]). In this study the membrane area tested was 0.0720 m^2. All experiments consisted of concentration runs, for it was intended to simulate the industrial NF operation at different water recovery rates, defined as the ratio between the permeate and the initial feed volumes. The NF feed water was a surface water from Funcho Dam reservoir (200 km^2 and 43.4 hm^3, Algarve, southern of Portugal). Since no increase of P occurred in Funcho Dam during the experimental period, 2.2 mg/L of KH_2PO_4 was added to the water.

The membrane processes are characterized by the fact that the feed stream is divided in two streams, the concentrate and the permeate streams. This implies that the concentrate or the permeate stream is the product. In this case, the membrane concentrate is the product stream. NF treatment resulted in the production of a slurry enriched in P that was subsequently used in the ED experiments.

Electrodialytic Laboratory Cell

The ED experiments were carried out in a laboratory cell (Fig. 1), using a set-up developed at the Technical University of Denmark and described in detail elsewhere [22]. The ED laboratory cell is divided into three compartments, consisting of two electrode compartments and a central one (L = 1.5 cm, i.d. = 8 cm), in which the membrane concentrate was placed. The three compartments were separated by ion exchange membranes (cation exchange membrane, CAT, IC1-61CZL386, and anion exchange membrane, AN, IA1-204SXZL386, from Ionics Inc.,

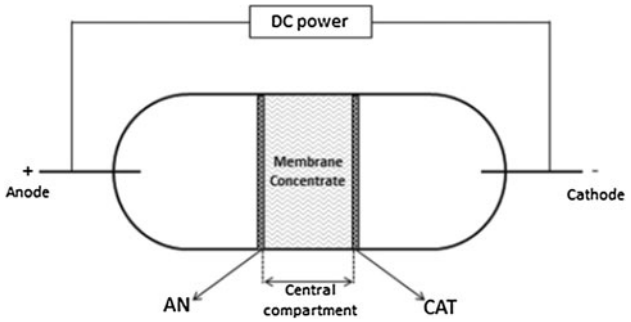

Fig. 1 Schematic representation of the electrodialytic laboratory cell used in the experiments. AN anion exchange membrane, CAT cation exchange membrane

Table 1 Experimental conditions of the electrodialytic process

Membrane concentrate	Current (mA)	ED experiment	Duration (h)
C1	10	E1	48.5
	20	E2	21.0
C2	20	E3	6.5

Massachusetts, USA) that assured the separation between the electrode compartments and the central one. Each electrode compartment contained 1 L of electrolyte solution (10^{-2} M $NaNO_3$; pH 7) and was equipped with a closed circulation system, using a multichannel peristaltic pump (Watson-Marlow 503 U/R, USA). A power supply (Hewlett Packard E3612A) was used to maintain a constant DC current and the voltage was monitored by a multimeter (Kiotto KT1000H). The electrodes were platinized titanium bars, with a diameter of 3 mm and a length of 5 cm (Bergsøe Anti Corrosion A/S, Denmark).

Table 1 presents the conditions of the experiments carried out with membrane concentrates. Membrane concentrate, catholyte and anolyte samples were collected at the beginning and end of each experiment. In the experiment E3, electrolyte samples were collected hourly. All samples were stored at 4 °C until analysis.

Analytical Methodology

Funcho Dam reservoir water and membrane concentrates were analysed for conductivity (Crison GLP32 conductimeter), pH (at 25 °C, using a Whatman WTW pH340 meter), turbidity (HACH 2,100 N turbidity meter of high resolution, 0.001 NTU) and UV 245 nm absorbance (Spectronic Unicam UV300 UV–vis spectrophotometer), using standard methods of analysis. Total P determination was performed using the colorimetric ascorbic acid technique (4500-P E Ascorbic Acid Method) [23]. Table 2 presents the obtained characteristics.

Table 2 Characteristics of the surface water used in NF and membrane concentrates used in ED

Parameter	Water	Membrane concentrate	
		C1	C2
Conductivity (μS/cm)	1,137	4,357 ± 6	2,630 ± 0
pH	8.8	8.4 ± 0.0	8.4 ± 0.0
Turbidity (NTU)	10.5	5.1 ± 0.1	30.0 ± 1.0
UV_{254nm} (1/cm)	0.17	0.63 ± 0.00	0.39 ± 0.00
P (μg/L)	1,126	1,845 ± 196	1,429 ± 7

The total P present in the samples (electrolytes and membrane concentrate), before and after ED process, was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at 178.229 nm. This wavelength was chosen to achieve a lower detection limit and also to minimize the interference of other elements with closer wavelength values. Calibration was carried out by using a P-standard solution (1,000 mg/L, Fluka TraceSelect, ref. 51474). External calibration was carried out (using an aqueous 5 % HNO_3 to prepare different concentrations), between 0 and 2 mg/L and quantification limit (QL) of 0.05 mg/L. Analytical control was pursuit by analysing a standard reference material (EnviroMAT Drinking Water, High (EP-H-3), SCP Science, ref.140-025-032) and blank solutions.

Results and Discussion

Electrodialytic Experiments

Two NF concentrates with different characteristics were produced (Table 2) to test their impact on ED efficiency. NF produces a nutrient rich concentrate stream containing P levels up between 1.3 and 1.6 times higher than the influent water, which is currently discharged as waste. Between the two concentrates, the highest variations are related with conductivity and turbidity: the first between 2,630 and 4,357 μS/cm and the second between 5 and 30 NTU. Also, P content varies between 1,429 and 1,845 μg/L. These concentrates were submitted to ED treatment according to experimental design expressed in Table 1.

Figure 2 presents the results of the voltage between working electrodes during the ED experiments and Table 3 presents the pH measured at the beginning and at the end of the experiments, at the anolytes, catholytes and membrane concentrate. Conductivity changes were also recorded.

The results showed that experiment E2 presented a voltage between working electrodes, during the first 7–10 h of experiments, higher than E1 (12.5 V vs. 7.7 V). According to the Ohm's law (eq. 1).

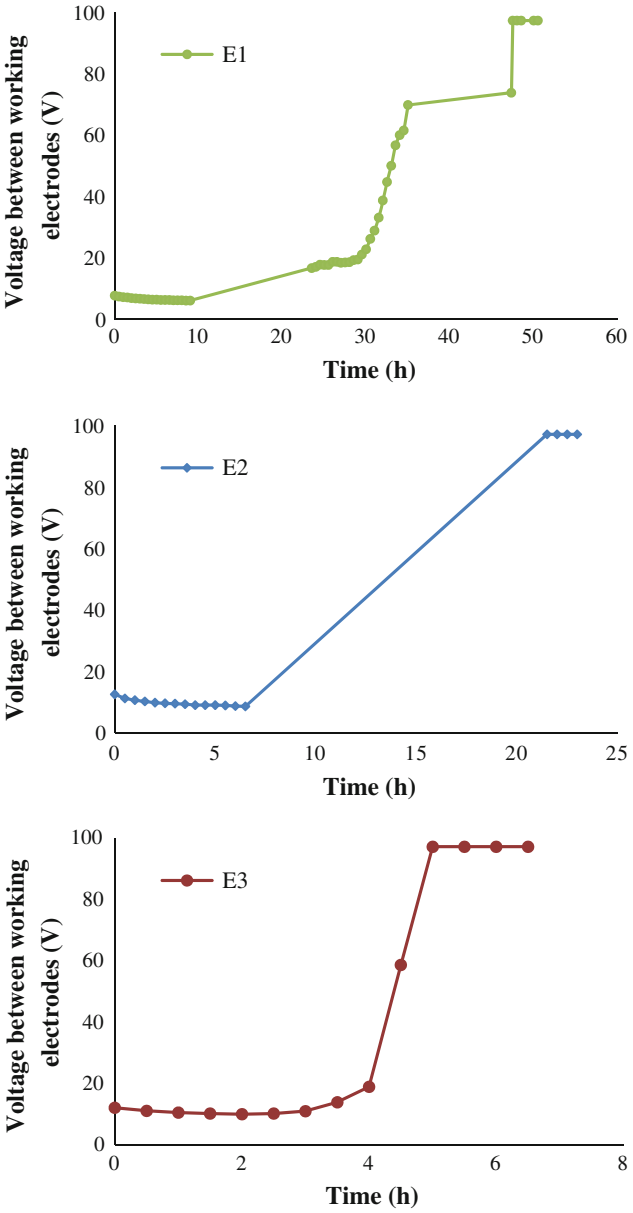

Fig. 2 Voltage drop between working electrodes during the ED experiments

$$V = I \times R \quad (1)$$

where V is the voltage in volts, I the current in amps and R the resistance in ohms, when in the presence of the same resistance (E1 and E2), an increase in current intensity should reflect a raising in voltage, corroborating the obtained results.

Also, E2 took 21 h to finish (when no current was able to pass) while E1 was extended to ca. 48 h. This situation was expected since the current applied in E2 was double of the one applied to E1.

However comparing E2 and E3, where the same current was applied, the time needed until no current was able to pass decreased. This can be due to the lower conductivity observed in C2 concentrate, factor attributed to different concentrate characteristics including less P concentration.

When the DC current was applied between the two electrodes, the ions in the three compartments moved as a result of the action of the electric field.

However this transport is restricted out of the concentrate due to the presence of the ion exchange membranes.

Phosphoric acid molecule (H_3PO_4) can dissociate up to three times, giving up an H^+ each time, which typically combines with a water molecule, H_2O, as shown in the following equations (eq. 2–4).

$$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO^-_{4(aq)} \quad pK_{a1} = 2.12 \quad (2)$$

$$H_2PO^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO^{2-}_{4(aq)} \quad pK_{a2} = 7.21 \quad (3)$$

$$HPO^{2-}_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO^{3-}_{4(aq)} \quad pK_{a3} = 12.67 \quad (4)$$

For each of the dissociation reactions, there is a separate acid dissociation constant (K_a) to which correspond the pK_{a1}, pK_{a2}, and pK_{a3}. At the end of the experiment, pH in the anolyte compartment was strongly acid, final value (ca. 2.15) being very close to change anionic P to its acid form (eq. 2). Nevertheless, in middle compartment, pH was between ca.7 and 9, being known that in pH range between 7.5 and 8.5 the forms $H_2PO_4^-$ (97 g/mol and a Stokes radius of 0.256 nm) and HPO_4^{2-} (96 g/mol; 0.323 nm) are present (eq. 3), with an increase of HPO_4^{2-} fraction with higher pH.

Figure 3 shows total P concentrations at the beginning and the end of the experiments. Phosphorus ED removal

Table 3 pH and conductivity variation in ED experiments

Experiment	pH (initial/final)			Conductivity (μS/cm) (initial/final)
	Anolyte	Catholyte	Membrane concentrate	Membrane concentrate
E1	7.54/2.08	7.53/9.29	8.16/7.70	4,357/23
E2	7.50/2.32	7.52/8.34	8.16/7.81	4,357/24
E3	8.00/2.15	7.50/8.30	8.50/7.00	2,630/7

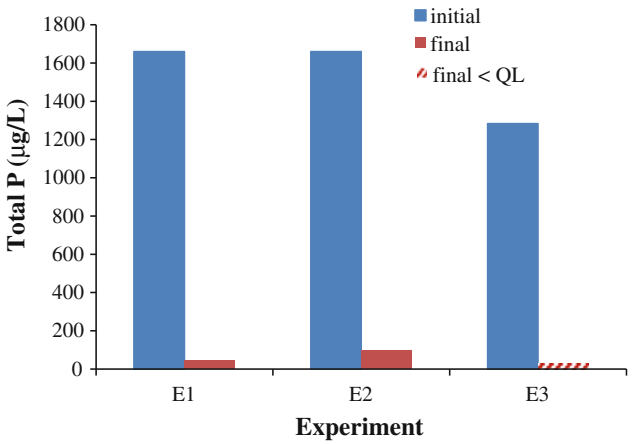

Fig. 3 Total phosphorus present in membrane concentrate at the beginning and at the end of the ED experiments

from the membrane concentrate presented high rates, in one case being even lower than method QL. The same occurred with the catholyte solution. It was also observed that P removal reflected a decrease in conductivity (Table 3), independently of the concentrates characteristics (Table 2) and the current used in ED (Table 1).

As previously stated, P was mainly in its anionic forms ($H_2PO_4^-$/HPO_4^{2-}), implying that its preferential movement from the central cell compartment was towards the anode compartment. High P recoveries were achieved in this part of the ED cell (in general, higher than 70 %).

As similar P removal was observed between E1 and E2 experiments, it was chosen to use the highest current intensity to understand P preferential movement. Additionally a different membrane concentrate was tested (C2) and its results are presented next.

Figure 4 presents the electrolyte pH variations obtained during experiment E3 and Fig. 5 the amount of total P recovered in the electrolyte compartments.

During the first 2 h of experiment E3, almost no movement of P was detected. In fact, the observed lag time period was found to be required for the appearance of P in the anolyte and was related with the time needed to promote the movement of charged particles in these experimental conditions. However in a total of 6.5 h ca. 72 % of P was found in the anolyte, due to electromigration. This mass transport phenomena is considered the main transport mechanism in the system. The movement of fluid resulting from head differences was not considered as experimental cells were carefully placed in order to avoid hydraulic gradients. As no losses were found in the system the remaining 28 % of P should be spread all around, between catholyte and central compartment (in both cases, final values were lower than QL).

As the ED process was applied without conditioning, electrolysis reactions at the electrodes generated an acidic medium (H^+) at the anode due to oxidation and an alkaline

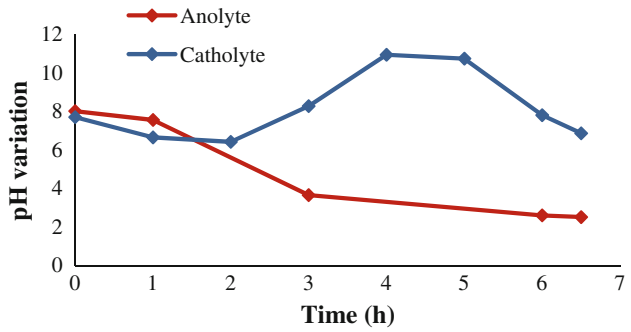

Fig. 4 pH variation in the electrode compartments during experiment E3

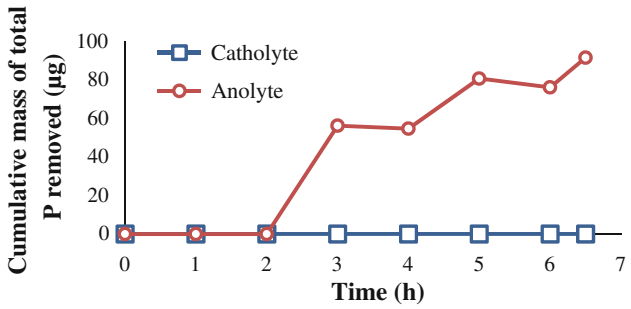

Fig. 5 Total P measured in electrolyte solutions collected during experiment E3 (membrane concentrate: initial value of 126 µg P; final P value lower than QL)

medium (OH^-) at the cathode due to reduction, according to equations (eq. 5–6):

$$\text{Anode: } 2H_2O - 4e^- \rightleftharpoons O_2 + 4H^+, \quad Eo = -1.229V \tag{5}$$

$$\text{Cathode: } 2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-, \quad Eo = -0.828V \tag{6}$$

Therefore, when the anions $H_2PO_4^-$ and HPO_4^{2-} reach the anolyte they react with the hydrogen cations forming phosphoric acid, H_3PO_4 (eq. 7) as pH was near pK_{a1}

$$H_2PO^-_{4(aq)} + HPO^{2-}_{4(aq)} + 3H^+_{(aq.)} \rightleftharpoons 2H_3PO_{4(aq)} \tag{7}$$

In future, ED could be applied in larger scale for concentration of P, as already described in literature for other matrices and compounds of interest [24].

No data exists about recovery of P from membrane concentrate although there are several different approaches for P removal in wastewater treatment plants like precipitation, adsorption, ion exchange and biological methodologies [6]. The removal of P using NF showed good efficiency ratios [12–14] but it can also be coupled with other treatment technologies aiming P recovery, like combination of a low pressure wet oxidation for sewage sludge decomposition and P dissolution plus NF to separate P from heavy metals [12]. In the case of precipitation, di/trivalent metals (e.g. Ca. Mg, Al, and Fe) can be used for P removal. Despite high

efficiencies, P can be strongly bonded to the metal, a situation that will difficult its direct application in agriculture [25]. In other way, struvite precipitation (magnesium ammonium phosphate) can occur when phosphate reaches high concentrations (100–200 mg/L) and ammonium is present [26]. It is considered a high quality slow release fertilizer [27], but in general, it cannot be applicable in water reservoirs due to the low P concentration. In other way, the use of adsorbents, like the iron-based ones [6] followed by removal through sedimentation and filtration can also be an option aiming P removal from waters. Nevertheless it should be taken into account that some of these wastewater treatment techniques were developed for removal of phosphate from municipal wastewaters that can present a wide range of P concentrations, some of them being between 5 and 10 mg/L [6]. However, in case of water reservoirs even lower P concentrations can be removed and further recovered using NF and ED (in the present case a concentration lower than 2 mg/L).

Additionally, all the methods aiming P recovery should account environmental and economical aspects a requirement that seems to be accomplished in this work as this innovative water treatment technology searches for (1) water cleaning, so that in can be consumed, but also (2) P recovery for further reuse. Nonetheless, further tests must be carried out on water from a reservoir that presents eutrophication problems. However, obtained results are a major step towards the understanding and screening of the possibility to use NF plus ED as a P recovery technology.

Conclusions

The electrodialytic process was able to mobilize and remove P from the NF membrane concentrates, towards the anode compartment of the cell, at high rates. The ED experiments showed that after 6.5 h, 72 % of P was recovered at the anode compartment, due to electromigration process, showing that it is a viable technique that can be used to recover this essential macronutrient from membrane concentrates. Obtained results enforce its potential use as a subsequent step of NF, a technique that can be applied in WTP plants.

The coupled techniques seem to be a feasible option to avoid the so intensive mining of phosphate rock, an increasingly scarce natural resource. However, further research is required to determine the most sustainable way for P recovery from waste streams, taking into account energy consumption, availability, resource use and pollution, in order the make the process economically viable. Environmental and social costs should also be addressed.

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References

1. Heffer, P., et al.: Phosphorus Fertilization Issues and Outlook, Proceedings no 586, p. 32. International Fertilizer Society, York UK (2006)
2. Cordell, D., Drangert, J.-O., White, S.: The story of phosphorus: global food security and food for thought. Global Environmental Change **19**(2), 292–305 (2009)
3. Elser, J.J., Phosphorus: a limiting nutrient for humanity? Current opinion in biotechnology, 2012(0)
4. Nations, F.a.A.O.o.t.U., The state of food insecurity in the world. (2011)
5. Cornel, P. and Schaum, C., Phosphorus recovery from wastewater: Needs, technologies and costs. (2009). p. 1069–1076
6. Rittmann, B.E., et al.: Capturing the lost phosphorus. Chemosphere **84**(6), 846–853 (2011)
7. Carpenter, S.R. and E.M. Bennett, Reconsideration of the planetary boundary for phosphorus. Environ. Res. Lett. **6**(1), 12pp (2011)
8. Ribau Teixeira, M., Rosa, M.J.: Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration. Water Res. **40**(15), 2837–2846 (2006)
9. Yangali-Quintanilla, V., et al.: Proposing nanofiltration as acceptable barrier for organic contaminants in water reuse. J. Membr. Sci. **362**(1–2), 334–345 (2010)
10. Zhang, Y., et al.: Removal of pesticides by nanofiltration: effect of the water matrix. Sep. Purif. Technol. **38**(2), 163–172 (2004)
11. Mulder, M.: Basic Principles of Membrane Technology. Kluwer Academic Publishers, Netherlands (1998)
12. Blöcher, C., Niewersch, C., Melin, T.: Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration. Water Res. **46**(6), 2009–2019 (2012)
13. Leo, C.P., et al.: Phosphorus removal using nanofiltration membranes. Water Sci. Technol. **64**(1), 199–205 (2011)
14. Niewersch, C., et al.: Selectivity of polyamide nanofiltration membranes for cations and phosphoric acid. Desalination **250**(3), 1021–1024 (2010)
15. Ottosen, L.M., et al.: Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method. Electrochim. Acta. **52**(10), 3420–3426 (2007)
16. Ribeiro, A.B., et al.: Electrodialytic removal of Cu, Cr, and As from chromated copper arsenate-treated timber waste. Environ. Sci. Technol. **34**(5), 784–788 (2000)
17. Ottosen, L.M., et al.: Electrodialytic removal of heavy metals from different solid waste products. Sep. Sci. Technol. **38**(6), 1269–1289 (2003)
18. Ferreira, C., et al.: Removal of selected heavy metals from MSW fly ash by the electrodialytic process. Eng. Geol. **77**(3–4), 339–347 (2005)
19. Cordell, D., et al.: Towards global phosphorus security: a systems framework for phosphorus recovery and reuse options. Chemosphere **84**(6), 747–758 (2011)

20. Ribau Teixeira, M., Rosa, M.J.: Microcystins removal by nanofiltration membranes. Sep. Purif. Technol. **46**(3), 192–201 (2005)
21. Rosa, M.J., de Pinho, M.N.: Separation of organic solutes by membrane pressure-driven processes. J. Membr. Sci. **89**(3), 235–243 (1994)
22. Ribeiro, A.B., Use of electrodialytic remediation technique for removal of selected heavy metals and metalloids from soils, Ph.D. Thesis. Technical University of Denmark, Denmark (1998)
23. Clesceri, L.S., Greenberg, A.E., Steelink, C.: Stantard Methods for the Examination of Water and Wastewater. American Pubblic Health Association, American Water Works Association and Water Environment Federation, Washington, DC (1998)
24. Kirkelund, G., et al.: Test of electrodialytic upgrading of MSWI APC residue in pilot scale: focus on reduced metal and salt leaching. J. Appl. Electrochem. **40**(6), 1049–1060 (2010)
25. Morse, G.K., et al.: Review: phosphorus removal and recovery technologies. Sci. Total Environ. **212**(1), 69–81 (1998)
26. Le Corre, K.S., et al.: Phosphorus recovery from wastewater by Struvite crystallization: a review. Crit. Rev. Environ. Sci. Technol. **39**(6), 433–477 (2009)
27. Johnston, A.E., Richards, I.R.: Effectiveness of different precipitated phosphates as phosphorus sources for plants. Soil Use Manag. **19**(1), 45–49 (2003)

PAPER IV

ELECTRODIALYTIC PROCESS OF NANOFILTRATION CONCENTRATES - PHOSPHORUS RECOVERY AND MICROCYSTINS REMOVAL

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ELECTRODIALYTIC PROCESS OF NANOFILTRATION CONCENTRATES – PHOSPHORUS RECOVERY AND MICROCYSTINS REMOVAL

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ABSTRACT

Toxic cyanobacteria blooms are associated with nutrient enrichment of surface waters. Nanofiltration (NF) is a pressure-driven process that can be used in water treatment plants, to effectively remove particulate matter and organic contaminants, including cyanobacteria toxins, and nutrients. NF produces a nutrient and toxin-enriched stream, e.g. with microcystin-LR (MC-LR), that has to be safely disposed of.

The suitability of the electrodialytic (ED) process for phosphorus recovery and decrease of MC-LR concentrations from NF waste stream was assessed. In ED experiments running between 5 and 12 h, phosphorus electromigrated towards the anode compartment promoting an isolated clean phosphorus product. The maximum obtained phosphorus recovery was 84%, varying with the NF waste stream (membrane concentrate) characteristics, cell design and treatment time. After the application of the ED process the concentration of MC-LR was also reduced. These results encourage further tests, aiming the inclusion of this hybrid technology (NF followed by ED) in water treatment plants, contributing not only for the phosphorus recovery, but also for the decrease in the toxicity of the NF concentrate, lowering the costs and promoting safe disposal.

1. INTRODUCTION

The increase fluxes of nutrients arriving to water bodies, namely phosphorus and nitrogen, due to agricultural runoff/sewage treatment plants/other anthropogenic sources is one of the main factors to promote the existence of cyanobacterial blooms [1].

Microcystins are hepatotoxic cyclic peptide toxins (Fig. 1) released by freshwater cyanobacteria. Microcystin-LR (MC-LR) is the most common and toxic variant [2]. The contamination in freshwater sources may have severe health effects, leading the World Health Organization (WHO) to recommend a guideline value of 1 μg/L for MC-LR in drinking water [3].

The review of Corbel et al. [1] states the high concentrations of MC-LR in countries worldwide. It was also reported [1] that cyanobacterial blooms are used as organic fertilizer in some countries which, together with spray irrigation with contaminated water, can add more sources of health hazard as toxins, like MC-LR, may enter in the food chain. The removal of MC-LR from water may be carried out by oxidation using chlorine, ozone and permanganate as oxidants [2,5]. However, some undesired by-products may be formed, e.g. chlorine may react with certain types of naturally occurring organic compounds in water forming trihalomethanes and haloacetic acids [2]. Photolysis and advance oxidation processes (AOPs) such as UV/H_2O_2 process, Fenton reagent, sulfate radical based AOPs, radiolysis, ultrasonic degradation, TiO_2 photocatalysis, ferrate (VI) have also been used [2,6,7]. Physical treatment processes such as membranes are effective in the removal of toxins [8–11] guaranteeing safe levels in waters. In the membrane concentrate stream, toxins as well as other compounds will be present representing an environmental risk if not adequately treated or disposed.

Electrokinetic and electrodialytic (ED) processes had been used aiming to recover resources, like phosphorus, from matrices such as sewage sludge [12], sewage sludge ashes [13,14] and membrane concentrate [15]. The ED process consists in the application of an electric field to a matrix, causing the movement of its species towards one of the electrode compartments, from where they can

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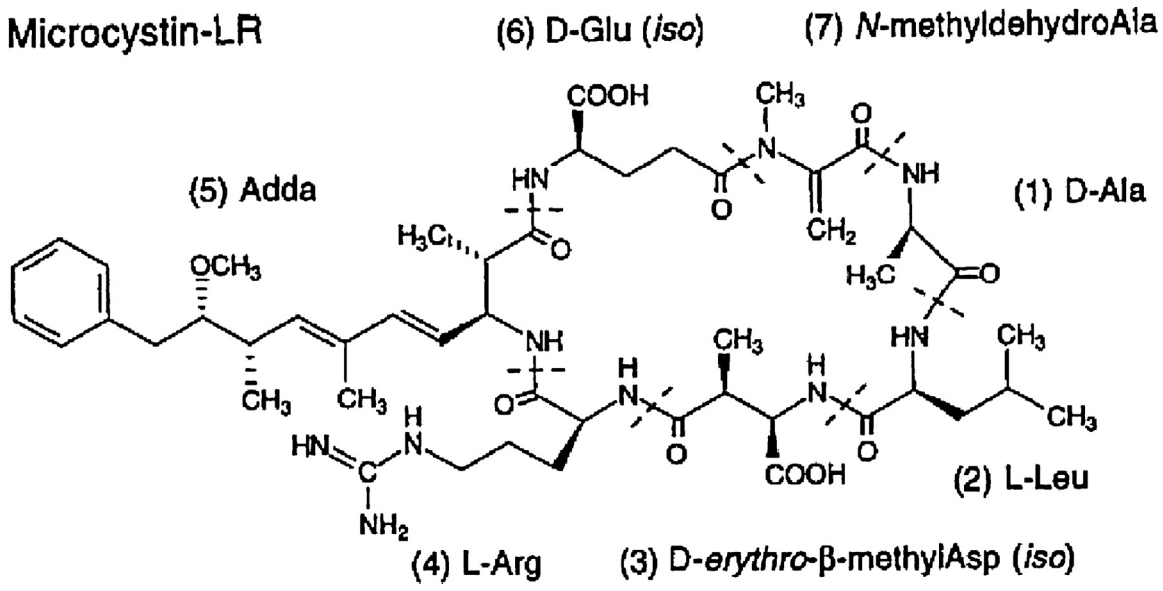

Fig. 1. Structure of MC-LR [4].

be removed. The main mechanisms responsible for the movement are electromigration, electroosmosis and electrophoresis and, in the specific case of the ED process, also electrodialysis.

This work goes forward on phosphorus recovery. It aims to integrate two water treatment processes and recover phosphorus from nanofiltration (NF) concentrates [16]. The ED process was applied to membrane concentrates in order to evaluate the recovery of phosphorus as well as to decrease MC-LR levels.

2. MATERIALS AND METHODS

2.1. Production of membrane concentrates

The production of membrane concentrate was carried out using a plate-and-frame unit (Lab-unit M20) described in detail elsewhere [10]. A thin film composite NF membrane with an hydraulic permeability of 82.2 kg/(h.m^2.bar) at 21 °C and a membrane molecular weight cut-off of *ca.* 114 Da, NF90 (DowFilmtec), was used. The experiments consisted of concentration runs, mimetizing industrial NF operation at different water recovery rates (defined between permeate and initial feed volumes).

The concentrate stream resulting from NF (membrane concentrate) contains cyanotoxins (MC-LR) and phosphorus, as well as natural organic matter. This slurry was used in ED experiments. The NF feed water was a surface water from two Portuguese Dam reservoirs: Amoreiras (101.2 km^2 and 11 hm^3, Alentejo) and Funcho (200 km^2 and 42.8 hm^3, Algarve). Since no occurrence of cyanobacterial blooms was reported in both reservoirs during the experimental period, 2.2 mg/L of KH_2PO_4 and 10 μg/L of microcystins, extracted from cultures of *Microcystis aeruginosa* grown in laboratory (supplied by Pasteur Culture Collection), were added to the surface water. Table 1 presents the characteristics of the produced membrane concentrates.

2.2. Electrodialytic laboratory cells

Two cell designs were used for the ED experiments (Fig. 2a and b). The design in Fig. 2a, described in detail elsewhere [17], is divided into three compartments, consisting of two electrode compartments (each one with an electrode) and a central one, in which the membrane concentrate was placed. The three compartments were separated by ion exchange membranes (cation exchange membrane IC1-61CZL386, and anion exchange membrane, IA1-204SXZL386, both from Ionics Inc. Massachusetts, USA). The design in Fig. 2b, adapted from [18], is divided in two (electrode) compartments, separated by an anion exchange membrane (similar to the previous one). Membrane concentrate was placed in the cathode compartment.

The electrodes were platinized titanium bars, with a 3 mm diameter and a 5 cm length (Bergsøe Anti Corrosion A/S, Denmark). A power supply (Hewlett Packard E3612A) was used to maintain a constant direct current and the voltage was monitored by a multimeter (Kiotto KT1000H). The electrolyte was a 10^{-2} M $NaNO_3$ with pH 7 being circulated using a multichannel peristaltic pump (Watson-Marlow 503 U/R, UK) in a closed circulation system.

Table 2 presents the experimental conditions used with the membrane concentrates. Summing-up, the table is divided in control experiments (C1 to C3), experiments to study phosphorus migration (A to H) and experiments to study phosphorus migration

Table 1
Characteristics of the membrane concentrates used in the experiments.

Memb Conc.	Dam	Cond (μS/cm)	pH	Turbidity (NTU)	DOC (mg C/L)	UV254nm (1/cm)	P (μg/L)	MC-LR (μg/L)
1		1635	8.5	33.0	28.8	0.25	876.2	16.5
2	Amoreiras	2980	8.3	281	42.8	0.51	1442	21.1
3		3000	8.4	300	54.1	0.48	1250	–
4		1476	8.3	188	32.0	0.36	1495	–
5	Funcho	1276	8.3	146	26.2	0.31	1245	42.9
6		804	8.2	80.7	31.0	0.20	900.5	36.7

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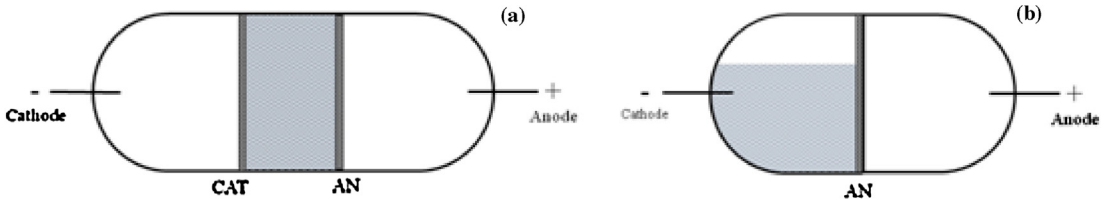

Fig. 2. Electrodialytic cell designs used: (a) three compartments (control C1 and experiments A to F, I and K) and (b) two compartments (control C2 and experiments G to H and J).

and MC-LR degradation (I to K). All the experiments were carried out in dark conditions. The cell design with three compartments (Fig. 2a) was used in the first set of experiments with membrane concentrates #4 to #6 (experiments A to D). The cell design with two compartments (Fig. 2b) was also used to assess if a different and simpler design would improve phosphorus recovery in the anode compartment. The comparison between cell designs for phosphorus removal was carried out in experiments G and H for two compartments and E and F for three compartments. Membrane concentrate #3 was used in both cases.

In the second set of experiments, the membrane concentrates #1 (controls C1 and C2 and experiment K) and #2 (control C3 and experiments I and J) were used. The controls C1 and C2 were conducted to mimetize, respectively, the three and two compartment cell designs without the application of electric current. A control experiment to assess MC-LR electrodegradation (C3; membrane concentrate #2) was also carried out.

Experiments A-D run between 5 and 8 h (depending on membrane concentrate characteristics) and were considered finished after the steeply voltage increase. The membrane concentrates used for experiments E to H (#3; 3000 μS/cm), I and J (#2; 2980 μS/cm) and K (#1; 1635 μS/cm) presented higher conductivity than those previously tested. In this case, the criteria to stop the experiments was not the abrupt voltage increase but a fixed time interval (12 h) that would allow the monitoring of phosphorus migration.

In the experiments with a cell design with three compartments the application of 10 mA corresponded to a current density of 0.06 mA/cm^2 and 20 mA to 0.12 mA/cm^2. In the cell design with two compartments the current density was also of 0.06 mA/cm^2 for 10 mA.

Table 2
Experimental design.

CODE	Memb. Conc.	Current intensity (mA)			Cell design	
		0	10	20	2C	3C
C1	1	x				x
C2	1	x			x	
C3*	2		x			
A	4		x			x
B	4			x		x
C	5		x			x
D	6		x			x
E	3		x			x
F	3		x			x
G	3		x		x	
H	3		x		x	
I	2		x			x
J	2		x		x	
K	1		x			x

Legend: **C**: control experiments; **A to H**: experiments to study phosphorus migration; **I to K**: experiments to study phosphorus migration and MC-LR removal. **2C**: cell design with two compartments; **3C**: cell design with three compartments.
* experiment performed with beakers (detailed information in text).

For the electrodegradation control (C3), three beakers (not completely closed) were used, where cathode and anode beakers contained 200 mL of electrolyte each, and the third beaker 100 mL of membrane concentrate (Fig. 3). Two filter papers were used as a saline bridge. Papers were submersed in a 1 M KNO_3 solution for 3 s, and then left drying for 30 s in order to remove the excess solution. The power supply and the electrodes were similar to the ones used for the ED experiments. The initial and final electrolytes, membrane concentrate and filter paper were collected and analysed following the procedures described below.

Membrane concentrate and electrolyte samples were collected at the beginning and at the end of each experiment and analysed for phosphorus and MC-LR content. Electrolyte samples were also hourly collected, to follow phosphorus recovery and stored at 4 °C until analysis. MC-LR were analysed immediately after extraction.

2.3. Analytical methodologies

The surface waters and membrane concentrates were analysed for conductivity (Crison GLP32 conductimeter), pH (25 °C, Whatman WTW pH340 meter), turbidity (HACH 2100N turbidity meter of high resolution, 0.001 NTU), dissolved organic carbon (DOC) (Shimadzu TOC 5000A analyser, 50 ppb–4000 ppm) and UV 245 nm absorbance (SpectronicUnicam UV300 UV–vis spectrophotometer), using standard methods of analysis. The total phosphorus present in the samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at 178.229 nm. Calibration was carried out by using a phosphorus standard solution (1000 mg/L, Fluka TraceSelect, ref. 51474). External calibration was carried out (using an aqueous 5% HNO_3 to prepare different concentrations), between 0–2 mg/L and the limit of quantification was of 0.05 mg/L. Analytical control was pursuit by analysing a standard reference material (EnviroMAT Drinking Water, High (EP-H-3), SCP Science, ref.140-025-032) and

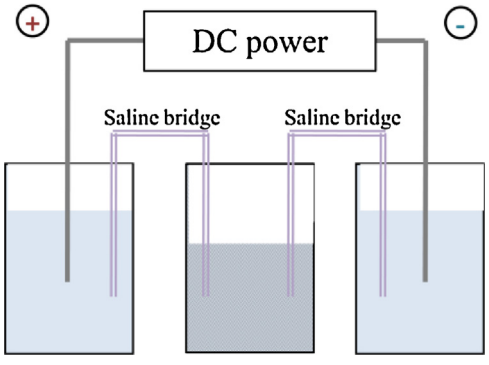

Fig. 3. Scheme of the laboratory cell used for the electrodegradation experiments.

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blank solutions. For all experiments, mass balances were between 80 and 120%, supporting the quality of results.

MC-LR extraction was carried out according to the method described elsewhere [10] and followed the operating procedure developed by Meriluoto and Spoof [19]. Analytes were analysed by liquid chromatography using a high pressure liquid chromatography equipped with a photo-diode array detector (HPLC/PDA; Dionex, ICS-3000). A C18 column was used (Atlantis dC18 3 μm, 4.6 × 30 mm; Waters). The mobile phase used a gradient of Mili-Q water and acetonitrile, both with 0.05% (v/v) of trifluoracetic acid. Chromatograms were analysed between 180 and 900 nm, with a main detection at 238 nm to the typical absorption spectra of MC-LR. Calibration was carried out by using a MC-LR standard solution (10 μg/mL in methanol, analytical standard, Fluka, ref. 33893).

3. RESULTS AND DISCUSSION

3.1. Phosphorus separation from membrane concentrates

Experiments A and B were carried out with the same membrane concentrate (#4; 1476 μS/cm) but different applied currents which led to different durations (7 and 5 h, respectively). Experiment C (10 mA; #5; 1276 μS/cm) had a similar duration as experiment A due to similar characteristics between the membrane concentrates used. Experiments A to C were considered finished when voltage started to be more constant, whereas Experiment D continued for 2 more hours to search for additional phosphorus migration.

In experiments A to K the pH values varied between 2.3 and 2.9 in the anode compartment, between 5.2 and 8.3 in the central compartment and between 10.3 and 12.1 in the cathode compartment. In the controls C1 and C2 the pH did not vary significantly between cell compartments but in control C3 (electrodegradation) it followed the same tendency as in the ED experiments. In the ED process, the use of ion exchange membranes only allows the passage of anions to the anode compartment, and cations to the cathode compartment. Due to the water electrolysis it is expected that anolyte compartment presents an acidic pH (due to the generation of H^+ ions) and catholyte compartment an alkaline pH (due to the generation of OH^- ions). Water splitting at the anion exchange membrane may contribute to a slight pH decrease in the central compartment due to formation of H^+ [20–22].

For phosphorus, four phosphate speciation states need to be considered (H_3PO_4, $H_2PO_4^-$, $HPO_4^{2-}$and PO_4^{3-}) with corresponding acidity constants (pKa, 298 K) of 2.12, 7.2 and 12. At pH below 2.12, phosphoric acid is dominant and has no electric charge being unaffected by the electric field. At pH higher than 2.12, ionic species are dominant. Initial membrane concentrates presented pH around 8, resulting in equilibrium between $H_2PO_4^-$and HPO_4^{2-}, so anions electromigrated towards the anode compartment. Throughout the experiments with three compartments, the pH values in the central compartment (between 5.2 and 8.3), still corresponded to the equilibrium between $H_2PO_4^-$ and HPO_4^{2-} anions. The pH decrease in the anode compartment puts phosphorus in forms H_3PO_4 and $H_2PO_4^-$.

The changes in conductivity at the end of the experiments are shown in Table 3. In experiments A to F and I and K, the conductivity in the central compartment decreased compared with the initial values due to the movement of ions towards the electrode compartments. The higher conductivity in the anode compartment, compared with the cathode compartment, may be due to the amount of phosphate ions and the H^+ produced in the anode [23]. The same is applied for the cell design with two compartments. In the controls there was no significant change in the conductivity.

Table 3
Final values of conductivity (μS/cm) for different experiments.

CODE	Conductivity (μS/cm)			
	Memb. Conc.	An	Central	Cat
C1	1	1370	802	1755
C2	1	1319	–	958
A	4	3266	28	2119
B	4	3594	36	1948
C	5	3007	31	2056
D	6	2450	51	1969
E	3	3382	266	2078
F	3	3982	47	2641
G	3	2652	–	1620
H	3	2699	–	1736
I	2	2910	109	2373
J	2	3035	–	2436
K	1	3352	23	2822

Legend: membrane concentrate in central compartment in controls C1, and experiments A to F, I and K; membrane concentrate in cathode compartment in control C2 and experiments G to H and J.

The cumulative mass of phosphorus observed in the different cell compartments throughout the experiments A-H is shown in Fig. 4a to h. The majority of phosphorus migrated towards the anode compartment, with minor quantities found in the central and/or cathode compartments.

In experiment A, 84% of phosphorus migrated towards the anode compartment. In experiment B, the percentage of electromigration decreased to 65%. The higher applied voltage in experiment B (20 mA) and consequent reduction of time until the experiment can be considered finished seems not to favour a more extensive movement of phosphorus, with 22% still being present in central compartment at the end of 5 hours. In experiment C 74% of phosphorus was recovered in the anode compartment with 11% still in the central compartment. As experiment C was conducted in the same conditions as experiment A, the differences found may be due to the slight variations between membrane concentrates characteristics (#4 and #5). In experiment D, at the end of 7 hours, 83% of phosphorus migrated towards the anode compartment and 5% remained in the central compartment. At the end of 5 hours, 73% of the phosphorus had already migrated towards the anode compartment. In the cell design with two compartments (experiments G and H; Fig. 4 g and h), 38% and 32% of phosphorus was recovered in the anode compartment and a part remained in the anion exchange membrane. In the experiment E, cell design with three compartments, 48% was recovered in the anode compartment but the recovery increased to 70% in the experiment F (Fig. 4e and f). Regarding voltage drop, in experiments E, G and H the voltage remained approximately constant during the 12 hours whereas in experiment F it started to increase after 10 hours. The cell design with three compartments has shown higher phosphorus recovery, in the tested conditions. Between cell designs the membrane concentrate in the cathode compartment changes the phosphorus speciation forms. Membrane concentrate with pH between 10.3 and 12.1 will present HPO_4^{2-} and PO_4^{3-} as anionic forms able to electromigrate. This may have also influenced the electromigration of phosphorus. Even though other matrices present higher phosphorus contents, e.g. sewage sludge (123 mg/L [12]) or sewage sludge ashes (70 - 134 g/kg [13,18]), comparing to membrane concentrate (in this case, approx. between 0.9 and 1.5 mg/L), its recovery is still justified taking into consideration the environmental and socio-economic perspectives. In an economic point of view it is possible to optimize the process by applying the direct current for shorter or longer periods of time, attending to membrane concentrate characteristics and phosphorus migration

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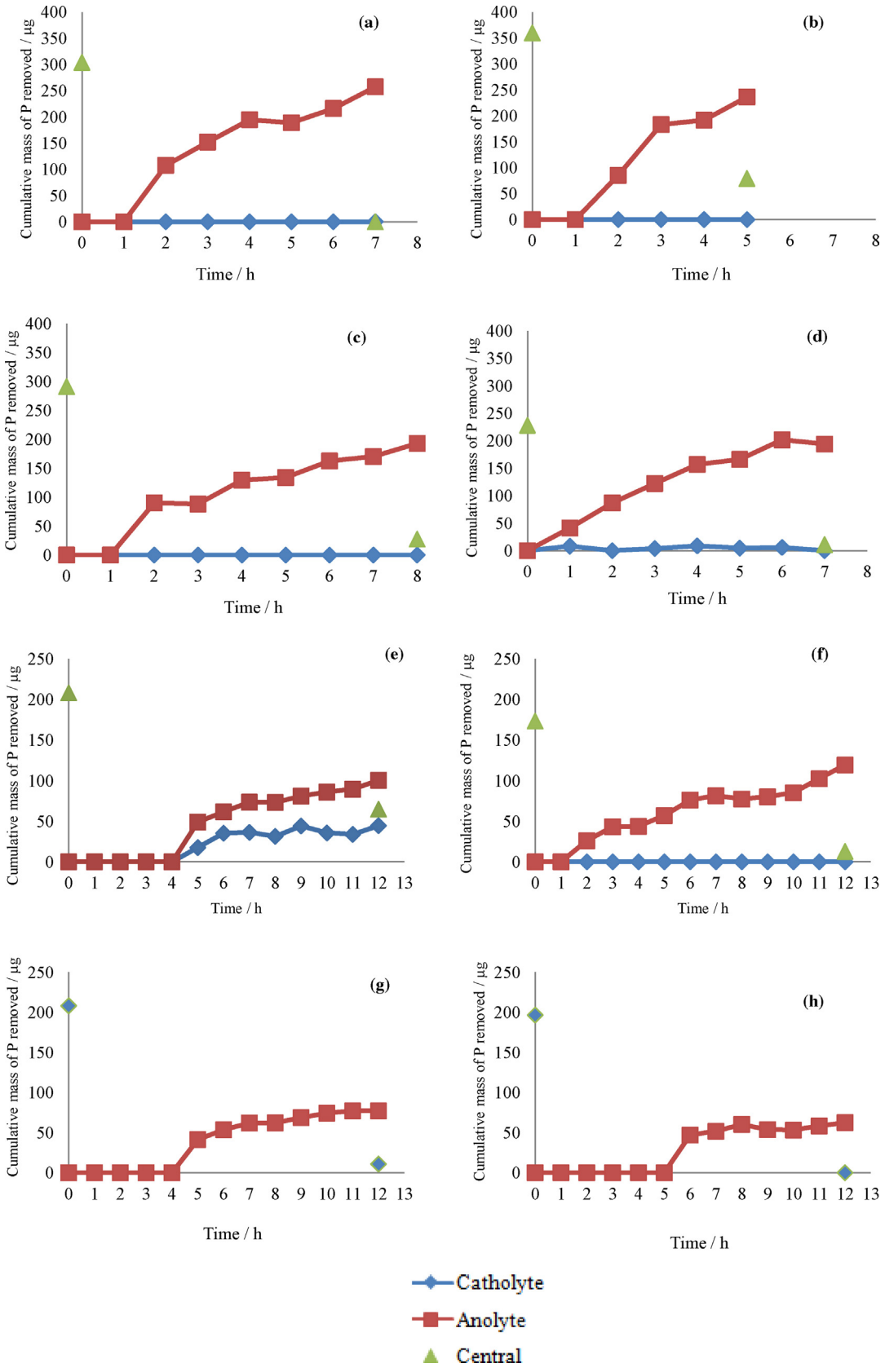

Fig. 4. Cumulative mass of phosphorus in two cell designs: (a) to (f) three compartments (A to F); and (g) and (h) two compartments (G and H), respectively.

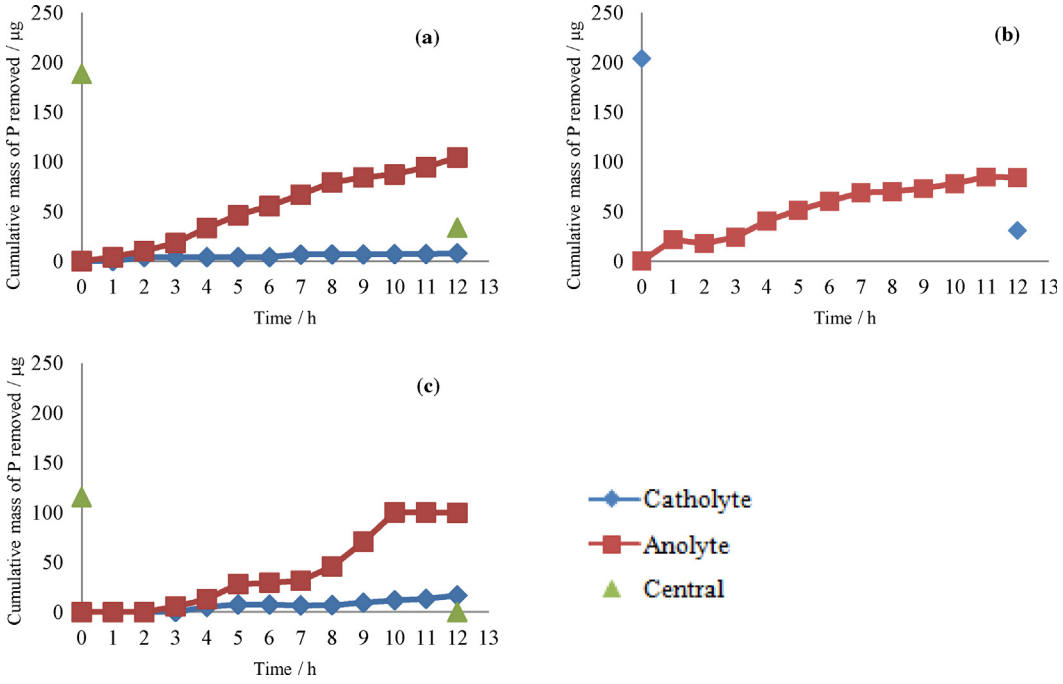

Fig. 5. Cumulative mass of phosphorus in two cell designs: (a) and (c) three compartments (I and K); and (b) two compartments (J), respectively.

behaviour. The migration behaviour in experiments A and B followed the same trend. After 1 hour, phosphorus electromigration towards the anode started following a linear tendency and then stabilized for another 1 hour (between 4th and 5th hours in experiment A and between 3rd and 4th hours in experiment B) followed by a second stage of electromigration. In experiment C, the tendency was quite different with less pronounced phosphorus migration, which explains the decrease in phosphorus recovery in the anode compartment. In the experiment D, phosphorus mobilization started earlier than in the other experiments (within the 1st hour) and it may be due to the lower conductivity of the medium. Most likely this concentrate contained less "competing species" (sulfate, carbonate, chloride, etc.) to phosphorus ions, which would benefit its migration. The migration was linear until the 4th hour and then stabilized for 1 hour followed by 2 hours corresponding to the second stage. In experiments G and H, cell design with two compartments, and in experiment E, cell design with three compartments, the migration started after 4 or 5 hours. In the experiment F, also with three compartments, it started after 1 hour.

In the controls, carried out during 12 hours, phosphorus mobilization was very small compared with ED experiments. In both controls of three (C1) and two compartments (C2), the sum of phosphorus found in the cathode and anode compartments was less than 5% of total phosphorus. In the electrodegradation control (C3), a similar trend was observed. In this case, the low phosphorus migration (inferior to 5%) towards the anode compartment is explained by the used cell design.

In all the ED experiments, electromigration was the main mechanism of phosphorus mobilization towards the electrode of opposite charge (comparing with controls with negligible phosphorus migration).

3.2. Phosphorus and mycrocistin separation

To achieve a complete valorization of the membrane concentrate, the MC-LR concentration should decrease. To the tested conditions, the higher phosphorus recovery was observed in the cell design with three compartments. As so, two different membrane concentrates were used in this cell design to assess the performance of this configuration to remove MC-LR. Additionally, one of the membrane concentrates was also used in the cell design with two compartments.

The cumulative mass of phosphorus recovered in the anode compartment of cell designs with two or three compartments is shown in Fig. 5.

The phosphorus recovery in the anode compartment of experiment I (three compartments) was 56%, 18% remained in the membrane concentrate, and approx. 10% was in the anion exchange membrane. This suggests that if the experiment was carried out for longer (using the previous mentioned criteria of stopping after the abrupt voltage increase) more phosphorus could have migrated to the anode compartment. In experiment J (two compartments), 15% of phosphorus remained in the membrane concentrate, approx. 29% in the anion exchange membrane (almost three times higher than in experiment I), so the phosphorus recovery in the anode compartment was slightly lower (42%) than in experiment I. In experiment K, 84% of phosphorus was recovered in the anolyte compartment. In this experiment, the phosphorus migration was higher than in experiments I due to different characteristics between membrane concentrates. In fact, membrane concentrate #1 presents low conductivity and minor initial phosphorus content in the solution (almost half the concentration). Additionally, in this membrane concentrate it could also be that there were less "competing species" (sulphate, carbonate, chloride, etc.) to phosphorus ions.

The changes observed in the pH and conductivity of experiments I-K are in the range of the previously observed (experiments A-H). Summing-up, in both ED cell designs a decrease of conductivity was observed in membrane concentrate, and an increase in anode compartment due to an increase in phosphate ions and especially due to the formation of H^+ [23].

The final concentration of MC-LR at the end of the experiments is shown in Table 4. The ED process not only promoted phosphorus

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Table 4
Final concentration of MC-LR (μg/L) for different experiments.

CODE	Memb. Conc.	Final MC-LR		
		An	Central	Cat
C1	1	1.37	10.5	1.35
C2	1	1.30	–	11.9
C3	2	nd/pns	nd/pns	nd/pns
I	2	nd/pns	4.67	0.68
J	2	nd/pns	–	0.52
K	1	nd/pns	0.17	0.57

Legend: nd/pns - not detected/peak not solved.

recovery but it also showed potential to decrease MC-LR concentration in the NF concentrate.

In the presence of three compartments (experiment I) the amount of MC-LR in the membrane concentrate decreased (final concentration of 4.67 μg/L) compared with the control C1. In experiment K, the different characteristics of membrane concentrate may explain the lower MC-LR concentration observed after the ED treatment. In fact, in all cell compartments, including the one with membrane concentrate, the MC-LR concentration was lower than the guideline value of 1 μg/L recommended by WHO for drinking water. Most likely, in both cases, MC-LR electromigrated to the anode compartment where it may have degraded. Reactions in the membrane concentrate may have also increased MC-LR removal.

MC-LR presents two ionisable carboxyl groups and one ionisable amino group that are not part of the peptide bonds that make up the cyclic peptide structure. In a pH lower than 2.09 the MC-LR has a cumulative charge of +1 and between 2.09 and 2.19 MC-LR is zero charged. At pH between 2.19 and 12.48, MC-LR has a cumulative charge of -1 and at pH higher than 12.48 is -2 [24].

In the beginning of the experiments, the pH of membrane concentrates was around 8, meaning that MC-LR is in the form of a negatively charged ion that can migrate towards the anode compartment, where it may degrade.

When membrane concentrate was in the cathode compartment (experiment J) the removal of MC-LR was also considerable, presenting concentrations below the guideline value recommended by WHO. Again, the migration towards the anode compartment seems to be important for the MC-LR removal but the use of a cell design with two compartments may have also promoted reactions between MC-LR and other components present in the matrix.

In the cell controls with three (C1) and two (C2) compartments, MC-LR was detected in the lateral compartment, probably due to diffusion. In the electrodegradation control (C3), performed in a different cell design (see Material and Methods section 2.2), MC-LR was not detected in all compartments.

It is important to mention that the performance of phosphorus recovery and MC-LR removal could have been different in the presence of a membrane concentrate prepared from a field "natural" contamination. Nevertheless, the obtained results encourage further research for the application of this hybrid technology.

4. CONCLUSIONS

The suitability of the ED process to recover phosphorus and decrease of MC-LR concentrations from NF concentrate was assessed.

The electromigration of phosphorus towards the anode compartment resulted in recoveries between 32% and 84%, which were mainly dependent on membrane concentrate characteristics, cell design and time of the ED process. The behaviour of phosphorus migration may help a cost-benefit analysis of the best time needed to perform the nutrient recovery.

In the tested conditions, the ED process also promoted a significant decrease of microcystin concentrations in the NF concentrate, in some cases with values below the WHO guideline for MC-LR.

Still, more tests with NF concentrate using natural water are needed to achieve optimum conditions for phosphorus recovery and MC-LR removal.

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References

[1] S. Corbel, C. Mougin, N. Bouaïcha, Cyanobacterial toxins: Modes of actions, fate in aquatic and soil ecosystems, phytotoxicity and bioaccumulation in agricultural crops, Chemosphere 96 (2014) 1–15.
[2] V.K. Sharma, T.M. Triantis, M.G. Antoniou, X. He, M. Pelaez, C. Han, W. Song, K.E. O'shea, A.A. de la Cruz, T. Kaloudis, A. Hiskia, D.D. Dionysiou, Destruction of microcystins by conventional and advanced oxidation processes: A review, Separation and Purification Technology 91 (2012) 3–17.
[3] WHO, third ed., Guidelines for Drinking Water Quality, vol. 1, World Health Organization, Geneva, 2004.
[4] J. Meriluoto, Chromatography of microcystins, Anal. Chim. Acta 352 (1997) 277–298.
[5] J. Chang, Z.-l. Chen, Z. Wang, J.-m Shen, Q. Chen, J. Kang, L. Yang, X.-w. Liu, C.-x. Nie, Ozonation degradation of microcystin-LR in aqueous solution: Intermediates, byproducts and pathways, Water Research 63 (2014) 52–61.
[6] T. Fotiou, T.M. Triantis, T. Kaloudis, A. Hiskia, Evaluation of the photocatalytic activity of TiO2 based catalysts for the degradation and mineralization of cyanobacterial toxins and water off-odor compounds under UV-A, solar and visible light, Chemical Engineering Journal 261 (2015) 17–26.
[7] L.C.V. Jacobs, P. Peralta-Zamora, F.R. Campos, R. Pontarolo, Photocatalytic degradation of microcystin-LR in aqueous solutions, Chemosphere 90 (2013) 1552–1557.
[8] A.J. Gijsbertsen-Abrahamse, W. Schmidt, I. Chorus, S.G.J. Heijman, Removal of cyanotoxins by ultrafiltration and nanofiltration, Journal of Membrane Science 276 (2006) 252–259.
[9] U. Neumann, J. Weckesser, Elimination of microcystin peptide toxins from water by reverse osmosis, Environmental Toxicology and Water Quality 13 (1998) 143–148.
[10] M. Ribau Teixeira, M.J. Rosa, Microcystins removal by nanofiltration membranes, Separation and Purification Technology 46 (2005) 192–201.
[11] M. Ribau Teixeira, M.J. Rosa, Neurotoxic and hepatotoxic cyanotoxins removal by nanofiltration, Water Research 40 (2006) 2837–2846.
[12] P. Guedes, C. Magro, N. Couto, A. Mosca, E.P. Mateus, A. Ribeiro, 2015. Potential of the electrodialytic process for emerging organic contaminants remediation and phosphorus separation from sewage sludge, Electrochimica Acta (2015) , doi:http://dx.doi.org/10.1016/j.electacta.2015.03.167 (in press).
[13] P. Guedes, N. Couto, L.M. Ottosen, A.B. Ribeiro, Phosphorus recovery from sewage sludge ash through an electrodialytic process, Waste Management 34 (2014) 886–892.
[14] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, Electrodialytic Separation of Phosphorus and Heavy Metals from Two Types of Sewage Sludge Ash, Separation Science and Technology 49 (2014) 1910–1920.
[15] N. Couto, P. Guedes, E.P. Mateus, C. Santos, M. Ribau Teixeira, L.M. Nunes, H.K. Hansen, C. Gutierrez, L.M. Ottosen, A.B. Ribeiro, Phosphorus recovery from a water reservoir-potential of nanofiltration coupled to electrodialytic process, Waste Biomass Valor 4 (2013) 675–681.
[16] C. Santos, A. Ribeiro, M. Ribau Teixeira, 2014 Phosphorus recovery from waters using nanofiltration, Desalination and Water Treatment (2014) .

[17] A.B. Ribeiro, Use of electrodialytic remediation technique for removal of selected heavy metals and metalloids from soils, Ph.D. Thesis, Technical University of Denmark, Denmark, 1998.
[18] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, B. Ebbers, Electrodialytic recovery and purification of phosphorous from sewage sludge ash, sewage sludge and wastewater (2014) PCT/EP2014/068956.
[19] J. Meriluoto, L. Spoof, SOP: Solid phase extraction of microcystins in water samples, Abo Akademi University, Finland, 2005.
[20] L.M. Ottosen, H.K. Hansen, C.B. Hansen, Water splitting at ion-exchange membranes and potential differences in soil during electrodialytic soil remediation, Journal of Applied Electrochemistry 30 (2000) 1199–1207.
[21] R. Simons, The origin and elimination of water splitting in ion exchangemembranes during water demineralisation by electrodialysis, Desalination 28 (1979) 41–42.
[22] R. Simons, Electric field effects on proton transfer between ionizable groupsand water in ion exchange membranes, Electrochimica Acta 29 (1984) 151–158.
[23] H. Strathmann, Ion-exchange membrane separation processes, Elsevier, 2004.
[24] P.-J. de Maagd, A. Hendriksb, W. Seinena, D. Sijma, PH-dependent hydrophobicity of the cyanobacteria toxin microcystin-LR, Water Res. 33 (1999) 677–680.

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PAPER V

PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE ASH THROUGH AN ELECTRODIALYTIC PROCESS

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Phosphorus recovery from sewage sludge ash through an electrodialytic process

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ABSTRACT

The electrodialytic separation process (ED) was applied to sewage sludge ash (SSA) aiming at phosphorus (P) recovery. As the SSA may have high heavy metals contents, their removal was also assessed. Two SSA were sampled, one immediately after incineration (SA) and the other from an open deposit (SB). Both samples were ED treated as stirred suspensions in sulphuric acid for 3, 7 and 14 days. After 14 days, phosphorus was mainly mobilized towards the anode end (approx. 60% in the SA and 70% in the SB), whereas heavy metals mainly electromigrated towards the cathode end. The anolyte presented a composition of 98% of P, mainly as orthophosphate, and 2% of heavy metals. The highest heavy metal removal was achieved for Cu (*ca.* 80%) and the lowest for Pb and Fe (between 4% and 6%). The ED showed to be a viable method for phosphorus recovery from SSA, as it promotes the separation of P from the heavy metals.

1. Introduction

Phosphorus (P) has no substitute in food production and the European Union is almost entirely dependent upon imports, with China, Jordan, Morocco, South Africa and USA controlling 85% of global phosphate reserves (Smit et al., 2009). As EU is a phosphate importer it is vulnerable to geopolitical tensions in the countries that export phosphate and to its volatile prices (as demonstrated during the recent 800% spike in the price of phosphate rock in 2008) (Schröder et al., 2010. Phosphorus peak has been estimated to occur by 2035 (Cordell et al., 2009) and published data on the lifetime of the exploitable high quality reserves of phosphate rock vary to a great extent, between one hundred and several hundreds of years (EFMA, 2000; IFDC, 2010; United States Geological Survey, 2012). This makes the development new strategies for P recovery from secondary resources one of the new world challenges.

One potential P resource is sewage sludge from municipal and industrial wastewater treatment plants (WWTP) (Schaum et al., 2009) which potential substitution for primary phosphate imports has been estimated, e.g. 40% for Germany (Cornel and Schaum, 2003). Incineration of sewage sludge is increasing as it presents several advantages when compared to other available disposal routes as it reduces the volume and mass generated by 90% and 70%, respectively (Chen and Yan, 2012; Hjelmar, 1996; Kirby and Rimstidt, 1993; Medici et al., 2000). Also it destroys pathogenic agents, oxidizes organic compounds and generates thermal energy that can be reused (Marani et al., 2003; Porteous, 2005). The obtained SSA can be rich in P but they do not have a direct value as fertilizer, as P is not in a plant available form (Ottosen et al., 2013). In addition, due to the presence of leachable heavy metals, SSA must be treated before the P resource can be reused.

1.1. Electrodialytic process

The electrodialytic process (ED) was developed at the Technical University of Denmark in 1992 and was patented in 1995 (PCT/DK95/00209). This method applies a low level direct current (DC) and proved to be efficient in removing contaminants from soils and other porous matrices (Virkutyte et al., 2002). A basic ED cell can be divided in three compartments. The electrodes are placed in opposite sites where electrolyte solutions circulate and the contaminants are concentrated at the end of the process. To separate the central compartment (with the contaminated matrix) from the electrode ends, ion exchange membranes are used. An anion and cation exchange membranes are used only allowing the passage of anions and cations, respectively.

Electrodialytic treatment relies on several interacting mechanisms but the dominant and most important electron transfer reactions that occur at electrodes during the process is the electrolysis of water (Eqs. (1.1) and (1.2)):

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$$H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- \quad \text{(anode)} \tag{1.1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \quad \text{(cathode)} \tag{1.2}$$

As the anion exchange membrane is not a 100% perfect rectifier some hydrogen ions are still transported from the anode end towards the cathode end, passing through the middle compartment and consequently lowering the pH.

When ED is applied to ashes in stationary cells, there is a decrease of mass and subsequently volume during the process (Hansen et al., 2004; Pedersen, 2003), due to their high percentage of easily soluble particles. This decrease can be a problem during ED in a stationary setup, but it is overcome when a stirrer is introduced in the ED cell (Fig. 1), improving the process efficiency when compared to an unstirred cell (Ottosen et al., 2000).

Several authors studied the ED remediation of fine-grained materials in suspension, using non-stationary set-ups, such as municipal solid waste incineration (MSWI) fly ash (Ferreira et al., 2005; Pedersen, 2002), wood combustion fly ash (Pedersen, 2003), wastewater sludge (Jakobsen et al., 2004), contaminated harbor sediments (Nystroem et al., 2005) and SSA (Pazos et al., 2010).

The advantage of treating SSA is their exclusively inorganic formation, a fact which (in contrast to sewage sludge) facilitates phosphorus recovery (Cornel and Schaum, 2009). During ED the part of P presented in negatively charged species (orthophosphates) will be transported out of the ash suspension towards the anode. Still, during the ED process, other elements present in the ash may also move towards the anode end (e.g., metals of negative standard reduction potential).

This works aims to evaluate the possibility to recover P and separate it from the heavy metals from SSA using the ED process. For this, two SSA samples were collected at a sewage sludge incineration facility and laboratory experiments with ED treatment of the SSAs as stirred suspensions were conducted.

2. Materials and methods

2.1. Sewage sludge ash

Sewage sludge ashes were collected at Lynettefællesskabet, Copenhagen, Denmark, in June 2012. This plant mono-incinerates sewage sludge from about 500,000 PE. In this WWTP, the process of P precipitation is initially done in a Bio-P tank followed by the addition of iron salt. The sludge is incinerated in a fluid bed oven at about 800 °C. The incinerator has an installed capacity of 2.35 t DM h^{-1} and an outgoing flue of 17,000 N m^3 h^{-1} at 59 °C. It produces 1 t DW ash h^{-1} and for that it consumes 3.8 MW h^{-1} in kettle and 2.9 MW h^{-1} in flue gas condensation. After incineration the SSA is stored (until it finds use) in an open air deposit at the site of Lynettefællesskabet close to the sea.

Two SSAs were sampled for this investigation: one immediately after the incineration process (SA) and the other from the deposit (SB). The exact residence time of SB is not known. The samples were stored in closed 5 L plastic containers, at room temperature.

2.2. Analytical

2.2.1. Ash characterization

The water content of the ash was measured as weight loss after 24 h at 105 °C. Ash pH and conductivity were measured in a 1:2.5 (mass:volume) suspension in deionized water, using Radiometer pH and conductivity electrodes. The solubility in water was evaluated by a four times washing procedure in a 1:10 suspension in deionized water, followed by ash drying and weighting at the end of the procedure. Loss on ignition was found after 30 min at 550 °C. Gas production was measured with a volumetric calcimeter flask in a 10% HNO_3 suspension. For pH, conductivity, loss on ignition and gas production five replicates were made, three replicates for water content and two replicates for solubility in water.

2.2.2. Heavy metal and phosphorus content

The concentration of Al, Cd, Cu, Cr, Fe, Ni, P, Pb, and Zn were determined after a pre-treatment of the ash in accordance to DS259 (DS259, 2003): 1.0 g dry ash and 20 mL of HNO_3 (1:1) was heated until 120 °C and 200 kPa for 30 min. The samples were filtered through a 0.45 μm filter and the element contents measured in an Inductively Coupled Plasma–Optical Emission Spectrometer (ICP–OES), Varian 720-ES. All metal concentrations are given on a dry weight basis. Five replicates were made for the initial SSA determinations.

In terms of Fe, the DS259 standard does not give its total concentration and the reason is that there is a small mineral residue that contains insoluble Fe compounds, which is removed before the ICP analysis (Ottosen et al., 2013).

Three replicates of the anolyte solutions collected after 14 days of ED treatment of each SSA sample were analysed by standard colorimetric methods (Standard Methods, 1998) for total phosphorus, inorganic phosphorus and orthophosphate content. Polyphosphates were determined by indirect method (polyphosphates = inorganic P – orthophosphates).

2.2.3. Electrodialytic experiments

The ED laboratory cell (Fig. 1) is divided in three compartments, with a stirrer in the central one to maintain the matrix suspended. The cell was made from Plexiglas with an internal diameter of 8 cm. The ion exchange membranes separating the central compartment from the electrode compartments were commercial membranes from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated electrodes from Permascand were

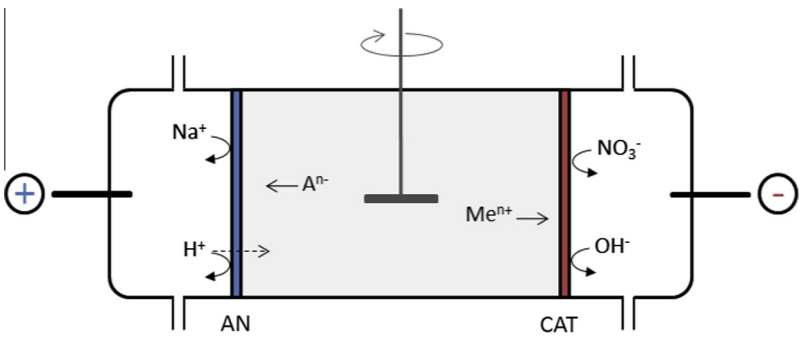

Fig. 1. Schematic electrodialytic stirred cell (AN: anion exchange membrane, CAT: cation exchange membrane).

used as working electrodes and a power supply (Hewlett Packard E3612A) maintained a constant current. The length of the central compartment was 10 cm. Through a hole, the stirrer made of flexible plastic flap fastened to an insulated wire (total length of the flap *ca*. 5 cm and width of 6 mm) was placed approximately in the middle of the compartment, coupled to a HETO motor, with a rotation velocity of 1300 rpm. The SSA was suspended in H_2SO_4 (0.08 M) in the ratio of 1:10 (mass:volume), and 500 mL of 0.01 M $NaNO_3$ was used as anolyte and as catholyte, with pH adjusted to 2 with 1:1 HNO_3.

During the experiments voltage drop, current density, pH in the electrolytes and pH and conductivity in the SSA suspension were measured. The pH of the electrolytes was manually adjusted to pH between 1 and 2 with 1:1 HNO_3 when necessary.

At the beginning and at the end of each experiment, samples were taken from catholyte and anolyte and from the suspension, for phosphorus and heavy metal analyses. At the end of the experiments the ash suspensions were drained through filter paper before drying, to separate the solids from the liquid phase, and water content was measured. Membranes and cathode were soaked in HNO_3 (1 and 5 M, respectively) for 24 h to release metals for further analysis. SSA (three replicates), aqueous phases, electrolytes, membranes and cathode were analysed for phosphorus and heavy metal contents, using the same ICP–OES.

A total of six ED experiments (three experiments for each SSA sample) were carried out, all run at 50 mA, for different periods of time (3, 7 and 14 days).

3. Results and discussion

3.1. Ash characterization and elements content

Characterization of the two SSA is shown in Table 1. The characterization showed no significant differences regarding elements concentration between SA and SB samples. Regarding physico-chemical parameters, differences were observed, namely for the parameters directly influenced by disposal conditioning. For example, the massive difference in water content is clearly related to the disposal conditions and to environmental factors to which SB is subjected. Differences were also observed regarding pH and loss on ignition.

Table 1
Physico-chemical characteristics, phosphorus and heavy metal content in the incinerated sewage sludge ashes (mean ± STD).

Parameter	SA	SB
Physical and chemical characteristics		
pH (H_2O)	12.44 ± 0.01	8.85 ± 0.03
Water content (%)	0.10 ± 0.18	16 ± 0.38
Conductivity (mS cm^{-1})	3.23 ± 0.51	4.81 ± 0.13
Loss on ignition (550 °C;%)	0.15 ± 0.05	0.92 ± 0.08
Solubility in water (%)	1.8 ± 0.1	3.1 ± 0.0
Carbonate content (%)	1.57 ± 0.21	1.34 ± 0.12
Elements concentration		
P (g kg^{-1})	134 ± 1	129 ± 5
Na (g kg^{-1})	5.71 ± 0.03	6.73 ± 0.09
Ca (g kg^{-1})	163 ± 1	152 ± 2
Al (g kg^{-1})	22.6 ± 0.5	21.5 ± 0.7
Fe (g kg^{-1})	60.0 ± 1.4	62.0 ± 2.3
Zn (mg kg^{-1})	3335 ± 77	3157 ± 129
Cu (mg kg^{-1})	758 ± 5	733 ± 9
Pb (mg kg^{-1})	293 ± 4	297 ± 9
Cr (mg kg^{-1})	45.5 ± 0.4	44.9 ± 0.7
Cd (mg kg^{-1})	3.25 ± 0.04	3.14 ± 0.08
Ni (mg kg^{-1})	54.6 ± 0.6	55.7 ± 1.0

STD: standard deviation.

3.2. Electrodialytic experiments

3.2.1. Overall results

Table 2 shows the initial conditions and the changes in pH, conductivity and mass loss resulting from the ED experiments.

As pH of the ash suspension influences the different elements solubility (increasing solubility with decreasing pH), immediately before the experiment the ash was suspended in sulphuric acid. This aimed to convert the precipitated and adsorbed P into mobile ionic forms, able to electromigrate during the ED treatments. The initial pH in the central cell compartment varied between 3.2 and 3.6 for the ashes (Table 2). During the ED experiments, pH in the central compartment decreased, as the remediation periods increase. This is mainly related to the water splitting at the anion exchange membrane that can significantly contribute to the supply of H^+ to the central compartment (Ottosen et al., 2000; Simons, 1979, 1984). The exchange of H^+ ions from the catholyte with other ions from the cation exchange membrane may have also contributed for the acidification (Kirkelund et al., 2013). Some of the acid may also originate from the anolyte, since anion exchange membranes are not 100% ideal.

The dissolution of ash particles during the ED treatment results in a mass loss that can be quite significant (Ottosen et al., 2006). The ash dissolution is directly correlated with the experimental time (Table 2).

Increasing amount of ions present in the suspension was seen as increasing conductivity along the experiments (Fig. 2) except for SA3 and SB3. This is due to a fast mobilization of ions that are present in the medium at the beginning of the experiments and 3 days were not enough to solubilize the elements present in the ash (e.g. metals) what would increase the suspension conductivity.

The voltage drop decreased during all the experiments, except for SA3. This indicates that the resistance in the middle compartment also decreased, showing that the suspension was not depleted of ions, even after the 14-day period. Pedersen et al. (2005) showed that the most efficient remediation is achieved for approximately 14 days of ED treatment, although they used another type of ash and assisting agents.

In experiment SA3, an increase in the voltage was observed, probably explained by an enhanced resistance in the anode compartment, due to the appearance of a white precipitate in this compartment. However, as the current was maintained constant, this was not considered to significantly influence the overall separation results. Together with the referred precipitate, several other factors may have also contributed to the overall cell voltage, like cathodic and anodic over potentials, over the ash compartment and in the ion exchange membranes. The electrical resistance in the electrode compartments is considered low, due to the high ionic strength of the electrolytes and the low polarisation potential at the electrodes, once the electrolytes are recirculated (Pedersen et al., 2005).

3.2.2. Mass balance

Mass balance of an element was defined as the relation between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration. The mass balances for the elements presented high variability for all the experiments. There is an inhomogeneous distribution of metals in the ash and, consequently, imperfect mass balances are expected when working with these type of samples. Finally, even though careful handling of all samples the precipitation of insoluble compounds may occur in e.g. set-up tubing. Mass balance in the different experiments varied between 80% and 120% with no linear tendency. The only exception

Table 2
Parameters measured at the beginning and at the end of the electrodialytic experiments.

Experiment	Current density (mA cm^{-2})	Voltage drop (V)	Suspension pH	Suspension conductivity (mS cm^{-1})	Mass loss (%)
SA3	0.99	19.4–30.4	3.34–2.48	7.77–5.94	23
SA7	0.99	10.8–4.5	3.43–1.83	6.51–11.52	56
SA14	0.99	9.8–8.2	3.56–1.51	7.55–9.17	64
SB3	0.99	9.1–6.1	3.15–2.29	8.01–6.10	29
SB7	0.99	8.7–4.6	3.00–1.89	6.58–10.61	47
SB14	0.99	10.8–6.0	3.31–1.33	8.23–14.97	61

Legend: SA – sample A; SB – sample B; number corresponds to the duration of the treatment in days.

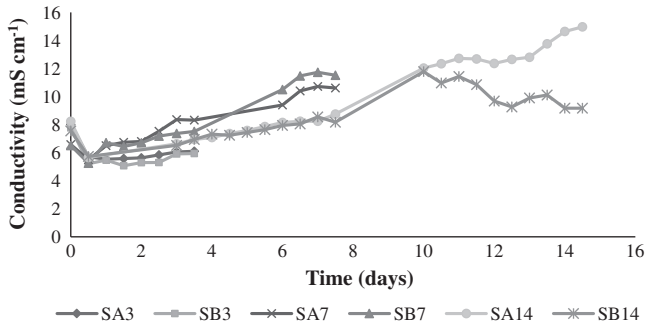

Fig. 2. Conductivity variation in the ash suspensions during the electrodialytic experiments.

was observed for Ni in the 14 days experiment for the new ash, with a value of 131%, so this result was not considered.

3.2.3. Electrodialytic heavy metal removal

The ED removal efficiency is defined as the percentage of the element effectively removed from the ash towards the cathode and anode end. Fig. 3 presents the amount of elements found in the different parts after the ED process, except for Fe and Pb where the removal efficiencies were very low (<5%). Elements found in the solid and liquid phase of the central cell compartment were not considered removed, whereas metals present in the electrolytes, cathode and membranes were considered removed. The removal percentages were calculated dividing the mass of element removed to different parts of the cell (electrodes, electrolyte solutions and membranes) by the initial mass.

The removal efficiencies increased along the ED treatment time for phosphorus and almost all metals studied. This means that the residual amount of elements bound into the ash tend to decrease with time. The species are continuously being released from the ash during the treatment process and transported towards the anode end or cathode end depending on their speciation. Some remain in the liquid phase, either as uncharged species or ionic forms, to be removed as the experiment proceeds. According to the respective Pourbaix diagrams and the suspension pH variation along the experiment, Fe will be mainly present with an ionic charge of +3 and +2; Al +1; Cd, Pb, Ni and Zn as +2; Cu +2 and +1; Cr +3,+2 and −1. Finally, P ionic charge will mainly be −1. Still, complexation occurring between species present in the solution can alter the ion charge from positive to negative and *vice versa*.

In general the fraction of the desorbed metals was mainly transported towards the cathode end showing that they were mostly present in cationic forms, whereas phosphorus was transported towards the anode end, supporting the overall separation objective of P-recover for further reuse.

The highest removal efficiency was obtained for Cu, 79% and 82% in experiments SA14 and SB14, respectively. Good removal rates (*ca.* 50%) were obtained for Al, Zn and Cd for the 14 days experiments. When compared to acid wash with HNO_3 applied to the same SSA (results not shown) the ED process improved the Cu removal efficiency by *ca.* 27% in both SSA samples used. In the case of Zn, the removal rate was not improved by ED, when compared to the achieved ones only with the acid wash (results not shown). The ED removal of Ni was similar between samples, after 7 days the removal was *ca.* 25% and for Cr between 12% and 15% in the SB14 and SA14.

For Fe and Pb the removal towards the electrode compartments were low (*ca.* 6%), indicating that these metals are highly bound to the less soluble SSA particles. Lead also remained in the ash during the ED experiments with other ashes suggesting that it is generally hardly bound into ash (Ottosen et al., 2006; 2007). Pedersen et al. (2005) showed that suspending MSWI fly ash in ammonium citrate in the central cell compartment promoted a higher removal of Pb, after a 70 days ED remediation period. So even if better removal efficiencies can be achieved, this is not an easy task. Copper had similar removal rates in the reported study (Pedersen et al., 2005) and the here presented experiments, but higher removals for this metal (90%) were achieved by Ottosen et al. (2006) when using MSWI suspended in water.

In this work better removal rates were achieved than those obtained by Pazos et al. (2010), who used the same ED cell, for 14 days, although a different SSA, suspended in water in the central cell compartment in the ratio 1:7 (mass:volume) and a current density of 0.8 mA cm^{-2} (vs. H_2SO_4 and 0.9 mA cm^{-2} used in this study). As previous stated, although mobilization is enhanced by the pH changes that are due to the ED process, heavy metal desorption can be promoted by assisting agents, like the one used in this work. These differences (sulphuric acid as assisting agent and a higher current density) increased the heavy metal desorption, and the efficiency of the ED process.

If further use of the ash is intended, the assisting agent should be carefully chosen. For example, the use of H_2SO_4 may cause formation of a high quantity of gypsum crystals in the remaining ash and this must be taken into account when considering ash handling in e.g. construction materials or as an increased volume to be deposited (Ottosen et al., 2013).

3.2.4. Electrodialytic P-recovery

After 7 days, only 20% of total P was recovered in the anode end, with almost 42% of the phosphorus remaining in the liquid phase of the suspension experiments. After 14 days, 59% and 69% P was transported towards the anode, while 17% and 12% P was transported towards the cathode end for the SA and SB, respectively. Phosphorus Pourbaix diagram, suggests that at pH between 3.5 and 1.3 it would be present as $H_2PO_4^-$ and H_3PO_4. Phosphorus could have reacted with some species forming a positively charged compound being mostly found deposited in the electrode. Less than 3% of P remained in the liquid phase of the central compartment (Fig. 3). Thus, after phosphorus solubilisation, its removal towards the anode end is fast.

Iron and P were generally not associated in ash samples as little Fe was extracted in contrast to phosphorus. However, solubilized

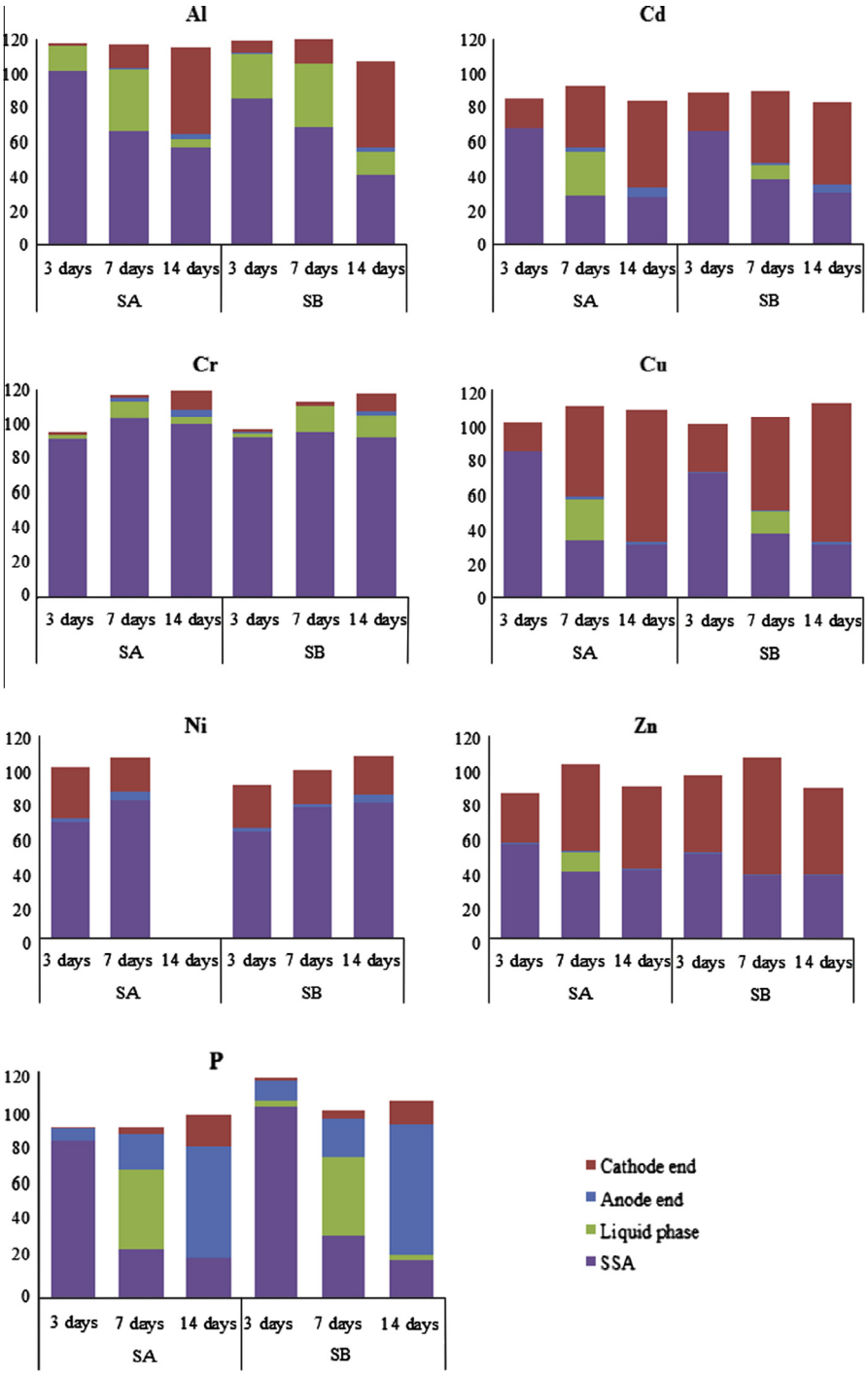

Fig. 3. Percentage of heavy metals and phosphorus in the electrodialytic cell sections at the end of the experiments. The distribution of the elements is based on the amounts found in the cell (SSA, liquid phase, cathode end and anode end) at the end of the experiments, in relation to the amount found in the initial ash sample before the ED treatment.

Fe could have re-precipitated during the ED process (Ottosen et al., 2013).

Sturm et al. (2010) studied feasibility of an electrokinetic P-recovery from sewage sludge ash (P-content ~5 wt%). Packed bed experiments showed that galvanostatic conditions were superior to potentiostatic conditions and acid pre-treatment is preferable over packed bed saturation with water. The use of ion-exchange membranes improved the product quality but increased the energy demand. However, P recovery was below 1% of the initial contents (Sturm et al., 2010), a lower recovery from the one here reported.

A recently conducted study aiming P-recovery through acid extraction of SSA using H_2SO_4 and HNO_3 (Ottosen et al., 2013) reported that, simultaneously to P, heavy metals were also removed to the liquid phase. Consequently, a separation step is needed. Using electrodialytic treatment for 14 days resulted in an anolyte solution rich in P with low heavy metal content (Table 3). The anolyte has in total *ca.* 98% of P in relation to the studied elements (phosphorus plus heavy metals). The electrodialytic separation of phosphorous and heavy metals was thus successful.

Table 3
Concentration of elements present in the anode end after 14 days of electrodialytic treatment (mg kg^{-1}).

Element	SA	SB
P	79,319	89,018
Al	849	498
Fe	883	521
Zn	35.7	26.0
Cu	14.4	9.05
Pb	1.14	1.22
Cr	1.65	1.27
Cd	0.19	0.15
Ni	2.60	–

The analysis performed on the anolyte of SSA samples (Table 3) showed that 91% and 85% of total P was present in its inorganic form, for the SA and SB respectively. In SA anolyte sample, the inorganic P is composed by orthophosphate (92%) and polyphosphate (8%). Once in contact with environmental conditions, the polyphosphates convert to orthophosphate through hydrolysis. In fact, all inorganic phosphorus in the SB anolyte sample was present as orthophosphate, ions that are readily bioavailable for plants (Reynolds and Davies, 2001; Schachtman et al., 1998).

Another factor to take into consideration is the analysis of socio-economical and environmental aspects related with the applied technique aiming P recovery. The energy consumption was recently reported by Sun et al. (2013). The energy distribution analysis showed that most energy was consumed by the transport of ionic species through the soil suspension, followed by membranes and electrolytes. The use of pulse current decreased the energy consumption to different extent depending on the pulse frequency used, being the lowest energy consumption obtained for the highest pulse frequency (96 cycles day^{-1}) for both soils studied (Sun et al., 2013). Although the performed studied was carried out using soil, it gives good indications of how to reduce energy consumption for the overall treatment method.

4. Conclusions

Phosphorus recovery and simultaneous heavy metal removal were achieved by electrodialytic separation during treatment of sewage sludge ash. The separation was equally successful for an ash sample taken directly after the incineration and an ash sample sampled from an open air deposit. Electromigration was responsible for the transport of P towards anode end whereas heavy metals were mainly transported to the cathode end. The highest heavy metal removal efficiency after 14 days was achieved for Cu (*ca.* 80%) and the lowest for Pb and Fe (*ca.* 4% and 5%, respectively) for both ash samples. The relation between heavy metals (incl. Fe and Al) and phosphorus in the anode end were very low (*ca.* 98% P). In total, 79 and 89 g P kg^{-1} were recovered mainly as orthophosphate from the two ashes. The obtained P-product, anolyte solution, can be further reused, in e.g. industries or agriculture, contributing for the sustainable nutrient cycle and waste management strategies.

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References

Chen, T., Yan, B., 2012. Fixation and partitioning of heavy metals in slag after incineration of sewage sludge. Waste Manage. 32, 957–964.
Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: global food security and food for thought. Global Environ. Chang. 19, 292–305.
Cornel, P., Schaum, C., 2003. Rückgewinnung von Phosphor in der Landwirtschaft und aus Abwasser und Abfall. In: Symposium Proceedings, 6-7 February 2003, Berlin, organised by The Federal Environment Agency and the Institute of Environmental Engineering, RWTH Aachen University, Aachen, Germany.
Cornel, P., Schaum, C., 2009. Phosphorus recovery from wastewater: needs, technologies and costs. Water Sci. Technol. 59, 1069–1076.
DS259, 2003. Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry in flame. Dansk Standardiseringsråd (in Danish).
EFMA, 2000. Phosphorus essential element for food production. European Fertilizer Manufacturers Association, Brussels.
Ferreira, C., Jensen, P., Ottosen, L., Ribeiro, A., 2005. Removal of selected heavy metals from MSW fly ash by the electrodialytic process. Eng. Geol. 77, 339–347.
Hansen, H.K., Ottosen, L.M., Villumsen, A., 2004. Electrodialytic removal of cadmium from straw combustion fly ash. J. Chem. Technol. Biotechnol. 79, 789–794.
Hjelmar, O., 1996. Disposal strategies for municipal solid waste incineration residues. J. Hazard. Mater. 47, 345–368.
IFDC, 2010. Sufficient phosphate rock resources available for years. IFDC Report 35.
Jakobsen, M.R., Fritt-Rasmussen, J., Nielsen, S., Ottosen, L.M., 2004. Electrodialytic removal of cadmium from wastewater sludge. J. Hazard. Mater. 106, 127–132.
Kirby, C.S., Rimstidt, J.D., 1993. Mineralogy and surface properties of municipal solid waste ash. Environ. Sci. Technol. 27, 652–660.
Kirkelund, G.M., Jensen, P.E., Ottosen, L.M., 2013. Electrodialytic extraction of heavy metals from Greenlandic MSWI fly ash as a function of remediation time and L/S ratio. In: Jon, E.Z. (Ed.), 10th international symposium on cold regions development, Anchorage, Alaska, pp. 87–96.
Marani, D., Braguglia, C.M., Mininni, G., Maccioni, F., 2003. Behaviour of Cd, Cr, Mn, Ni, Pb, and Zn in sewage sludge incineration by fluidised bed furnace. Waste Manage. 23, 117–124.
Medici, F., Piga, L., Rinaldi, G., 2000. Behaviour of polyaminophenolic additives in the granulation of lime and fly-ash. Waste Manage. 20, 491–498.
Nystroem, G.M., Ottosen, L.M., Villumsen, A., 2005. Electrodialytic removal of Cu, Zn, Pb, and Cd from harbor sediment: influence of changing experimental conditions. Environ. Sci. Technol. 39, 2906–2911.
Ottosen, L.M., Hansen, H.K., Hansen, C.B., 2000. Water splitting at ion-exchange membranes and potential differences in soil during electrodialytic soil remediation. J. Appl. Electrochem. 30, 1199–1207.
Ottosen, L.M., Lima, A.T., Pedersen, A.J., Ribeiro, A.B., 2006. Electrodialytic extraction of Cu, Pb and Cl from municipal solid waste incineration fly ash suspended in water. J. Chem. Technol. Biotechnol. 81, 553–559.
Ottosen, L.M., Pedersen, A.J., Hansen, H.K., Ribeiro, A.B., 2007. Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method. Electrochim. Acta 52, 3420–3426.
Ottosen, L.M., Kirkelund, G.M., Jensen, P.E., 2013. Extracting phosphorous from incinerated sewage sludge ash rich in iron or aluminum. Chemosphere 91, 963–969.
Pazos, M., Kirkelund, G.M., Ottosen, L.M., 2010. Electrodialytic treatment for metal removal from sewage sludge ash from fluidized bed combustion. J. Hazard. Mater. 176, 1073–1078.
Pedersen, A.J., 2002. Evaluation of assisting agents for electrodialytic removal of Cd, Pb, Zn, Cu and Cr from MSWI fly ash. J. Hazard. Mater. 95, 185–198.
Pedersen, A.J., 2003. Characterization and electrodialytic treatment of wood combustion fly ash for the removal of cadmium. Biomass Bioenerg. 25, 447–458.
Pedersen, A.J., Ottosen, L.M., Villumsen, A., 2005. Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent. J. Hazard. Mater. 122, 103–109.
Porteous, A., 2005. Why energy from waste incineration is an essential component of environmentally responsible waste management. Waste Manage. 25, 451–459.
Reynolds, C.S., Davies, P.S., 2001. Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. Biol. Rev. 76, 27–64.
Schachtman, D.P., Reid, R.J., Ayling, S., 1998. Phosphorus uptake by plants: from soil to cell. Plant Physiol. 116, 447–453.
Schaum, C., Cornel, P., Jardin, N., 2009. Phosphorus recovery from sewage sludge ash: possibilities and limitations of wet chemical technologies. Proceedings International Conference on Nutrient Recovery From Wastewater Streams, Vancouver, pp. 659–670.
Schröder, J.J., Cordell, D., Smit, A.L., Rosemarin, A., 2010. Sustainable Use of Phosphorus, EU Tender ENV.B.1/ETU/2009/0025.
Simons, R., 1979. The origin and elimination of water splitting in ion exchange membranes during water demineralisation by electrodialysis. Desalination 28, 41–42.

Simons, R., 1984. Electric field effects on proton transfer between ionizable groups and water in ion exchange membranes. Electrochim. Acta 29, 151–158.
Smit, A.L., Bindraban, P.S., Schröder, J.J., Conjin, J.G., Meer, H.G.v.d., 2009. Phosphorus in agriculture: global resources, trends and developments. Plant Research International B.V., Wageningen Report 282.
Standard Methods, 1998, Standard Methods for the Examination of Water and Wastewater (1998) twentieth ed., APHA – AWWA – WEF, USA.
Sturm, G., Weigand, H., Marb, C., Weiß, W., Huwe, B., 2010. Electrokinetic phosphorus recovery from packed beds of sewage sludge ash: yield and energy demand. J. Appl. Electrochem. 40, 1069–1078.
Sun, T.R., Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., 2013. Effect of pulse current on acidification and removal of Cu, Cd, and As during suspended electrodialytic soil remediation. Electrochim. Acta 107, 187–193.
United States Geological Survey, 2012. Mineral Commodity Summaries – Phosphate rock.
Virkutyte, J., Sillanpää, M., Latostenmaa, P., 2002. Electrokinetic soil remediation – critical overview. Sci. Total Environ. 289, 97–121.

PAPER VI

VALORISATION OF FERRIC SEWAGE SLUDGE ASHES: POTENTIAL AS A PHOSPHORUS SOURCE

Valorisation of ferric sewage sludge ashes: potential as a phosphorus source

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Abstract

Sewage sludge ashes (SSA), although a waste, contain elements with socio-economic and environmental potential that can be recovered. This is the case of phosphorus (P). SSA from two Danish incinerators were collected during two years and characterized. The sampling was done immediately after incineration (fresh SSA) or from an outdoor deposit (deposited SSA). Although morphology and mineral composition were similar, physico-chemical and metal concentration differences were found between incinerator plants and sampling periods. No differences were observed between deposited and fresh SSA, except for the parameters directly influenced by disposal conditioning (e.g. moisture content). All the SSAs had high concentrations of P (up to 16 wt. %), but they all exceeded Danish EPA Cd and Ni thresholds for direct application at agricultural soil.

Fresh and deposited SSA were acid washed aiming P extraction, achieving 50 g P/kg (approx. 37% of total P), but heavy metals were also co-extracted to the liquid phase. To avoid and/or minimize the heavy metals pollution of the extracted P, selective P recovery from the SSA was tested, using the electrodialytic (ED) process. ED laboratory cells, with 3 compartments (3c) and 2 compartments (2c), and two acid concentrations (H_2SO_4, 0.08 M and 0.19 M) were used for 7 days. The most concentrated acid solution increased P solubilization. The 2c-cell combined with the higher acid concentration resulted in higher P recoveries, 125 g of P/kg of SSA in the anolyte. The use of SSA collected after the incineration or from the deposit influenced the total P solubilization in the 2c-cell when 0.08M of sulfuric acid was used. The deposition of the SSA promoted the decrease in the amount of P solubilized, less 24%. Consequently, less 21% of P were recovered in the deposited SSA anolyte.

Keywords: *Electrodialytic process, acid extraction, characterization, phosphorus, heavy metals, recovery*

1. Introduction

Incineration of sewage sludge ash (SSA) is a well-established technology (Werther and Ogada, 1999), being estimated that 300-400 kg of SSA are produced *per* ton of dried sewage sludge (Cyr et al., 2007). During the incineration process, organic contaminants and pathogens are destroyed, while achieving mass reduction, water evaporation and organic matter oxidation to NO_x, SO_x and CO_2. After the incineration in a fluidized bed furnace, exhaust gas fines are collected by electrostatic precipitators or bag filters (Donatello et al., 2010b). Incineration cost is about 210-310 euros *per* ton of dry solids but some controversy arises as this technique promotes potentially hazardous SSA (Smith et al., 2009). In fact, incineration can concentrate up to 13 times the amount of heavy metals when compared to the ones reported in the original matrix (Donatello et al., 2010b; Ottosen et al., 2013).

The SSA are generally considered a waste material to be disposed into landfill (Donatello et al., 2010b), but they can also be reused as adsorbents (Pan et al., 2003), in geotechnical applications (Ferreira et al., 2003) or in construction materials (Al Sayed et al., 1995; Anderson et al., 2002; Lin et al., 2005), since SSA is not considered hazardous waste (Donatello et al., 2010b). Due to the P concentration, typically between 4 and 9% (Biswas et al., 2009; Franz, 2008), fly SSA can be applied at agricultural land, if it complies with the established metal thresholds (e.g. Danish EPA, Miljøstyrelsen). The addition of salts (iron or aluminium) during wastewater treatment results in insoluble phosphate complexes, which decrease the value of SSA as fertilizer, as P is not in a plant available form (Franz, 2008; Ottosen et al., 2014a; Ottosen et al., 2013). The SSA can be treated aiming P extraction (Donatello et al., 2010a; Franz, 2008; Weigand et al., 2012) using different technologies, e.g. thermal (Adam et al., 2009; Mattenberger et al., 2008; Mattenberger et al., 2010; Vogel et al., 2010), wet treatment process (Petzet et al., 2011; Petzet et al., 2012; Stark et al., 2006) or electrodialytic (ED) separation (Ebbers et al.; Guedes et al., 2014a; Ottosen et al., 2014a; Sturm et al., 2010). An experimental screening of ED P recovery and simultaneous heavy metals removal has been conducted with a 3 compartment (3c) cell (Ebbers et al., 2015; Guedes et al., 2014b; Ottosen et al., 2014b), Figure 1a (Jensen and Villumsen, 1995), and 2 compartment (2c) cell (Ebbers et al., 2015; Parés Viader et al.), Figure 1b (Ottosen et al., 2014c). In the 3c cell, the possibility of P extraction from Al-rich and Fe-rich SSA was assessed using acid washing (Ottosen et al., 2013) and the ED process (Ottosen et al., 2014b). Phosphorus separation into the central compartment liquid and the anode compartment ranged between 15-85% for an Al-precipitated SSA and between 45-95% for a Fe-precipitated SSA. The combination of ED process in the 2c-cell and initial acidification of the

stirred suspension with mineral acids showed to be more effective in dissolving P, comparing to the 3c-cell. In the 2c-cell, removals up to 90% (Parés Viader et al.) and 96% (Ebbers et al., 2015) were achieved in 7 days. A previous work reported phosphorus removals up to 70% have been achieved in the anode compartment of a 3c-cell for deposited and fresh Fe-rich SSA of the 3c-cell using 0.08M H_2SO_4 (Guedes et al., 2014b). However, neither the 2c-cell setup nor the influence of acid concentration were evaluated.

This work had two main objectives: (i) to evaluate the major differences between SSA collected in different sampling periods, storage conditions and incinerator plants (Lynettefællesskabet and Avedøre Spildevandscenter, Copenhagen, Denmark), and (ii) to assess P recovery from recently collected (fresh) and deposited SSA. This last objective was tested with SSA, collected in the incinerator at Lynettefællesskabet, using a combined acid washing and ED treatment with a 3c and 2c cell setups.

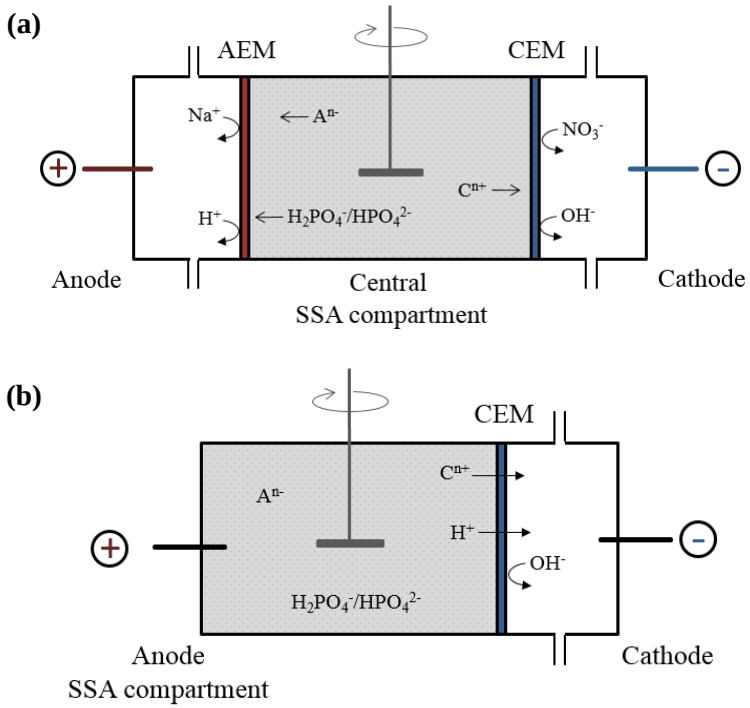

Figure 1. Schematic view of (a) 3-compartment and (b) 2-compartment electrodialytic laboratory cell. (CEM: cation exchange membrane; AEM: anion exchange membrane)

2. Experimental

2.1. Sewage sludge ashes

The SSA samples were collected after incineration by fluidized bed combustion at Avedøre Spildevandscenter and Lynettefællesskabet wastewater treatment plants (WWTP), located in Copenhagen, Denmark. The plants treat waste water annually from 345,000 and 500,000 population equivalent, respectively, with no major industrial discharges, prevailing non-industrial wastewater. At both facilities P in the wastewater is precipitated in a Bio-P tank followed by addition of iron salt. After incineration of the sewage sludge, the SSA is collected in electrofilters and the ferric SSA is disposed of in separate landfills for SSA only. In total, 8 samples of SSA were collected. From Avedøre, two samplings (2012 and 2014) were made directly after the electrofilters (fresh). From Lynetten, six samples (twice in 2012 and once in 2013) were collected from the electrofilters (fresh) and at the disposal site (deposited). The deposited SSA were collected from the top part of the SSA pile in an open air deposit, and the storage time is unknown. After sampling, the SSA was stored in closed plastic containers at room temperature until the experimental work was carried out.

2.2. SSA characterization

Characterization of the SSA and heavy metals extraction were carried out with oven dried SSA (105 ºC). For all characterization procedures five replicates of each type of SSA were used. Water content of the SSA was calculated as weight loss at 105 ºC for 24 h. The pH was measured in a 1:2.5 (mass:volume) suspension in distilled water using a Radiometer pH electrode. Loss on ignition (LOI) was determined in a muffle at 550 ºC for 30 min. The concentrations of different elements were measured after pre-treatment of the SSA in accordance to DS259 (2003), as 1.0 g of SSA and 20.0 mL (1:1) HNO_3 extracted at 200 kPa, 120 ºC for 30 min and then vacuum filtered through a 0.45 μm filter. Phosphorus, Al, Fe, Zn, Cu, Pb, Cr, Cd and Ni were measured by inductively coupled plasma optical emission spectrometry (ICP-OES).

Morphology analysis was performed by scanning electron microscopy supported by energy dispersive spectrometry (SEM-EDX), without pre-treatment of the SSA samples. The accelerating voltage of the SEM was 20-25 kV with large field detector (and X-ray cone). Different areas of the samples were analysed by SEM and the element distribution was examined using EDX. SSA mineralogy was studied by X-ray diffraction (XRD) for the identification of the major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-70 2Θ.

2.3. Relation between pH release of metals and P

To determine the pH dependent extraction of P and metals, 10 g dried SSA were suspended in 50 ml HNO_3 of different concentrations (0.00; 0.01; 0.05; 0.08; 0.10; 0.30; 0.50; 0.70 and 1.0 M). The suspensions were placed at an agitating table for 7 days at room temperature. At the end of the experiment, pH was measured and suspensions were filtered by vacuum using 0.45 µm filters and the concentrations determined by ICP-OES. Each extraction was made in duplicate and reference samples were made using distilled water with the same procedure. pH dependent extractions was carried out for the Lynettefællesskabet SSA (2012, 1st sampling).

2.4. ED treatment of SSA

Two ED laboratory cells were used (Figure 1). The cells were made of plastic with an internal diameter of 8 cm, with a suspension compartment length of 10 cm and the electrode compartment of 5 cm. Electrode compartments were separated from the suspension compartment by an anion-exchange membrane and/or a cation-exchange membrane from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The electrodes were platinum coated titanium from Permascand. A power supply (Hewlett Packard E3612A) was used, maintaining a constant current of 50 mA. The SSA was stirred in the suspension compartment by a flexible plastic flab, coupled to a HETO motor, with a rotation velocity rate of up to 1300 rpm. The SSA was suspended in H_2SO_4 at 0.19 M in the 3c-cell and 0.08 and 0.19 M for the 2c-cell, in the ratio of 1:10 (mass:volume), and 500 mL of 0.01 M $NaNO_3$ was used as electrolyte, with pH adjusted to 2 with 1:1 HNO_3. A total of six ED experiments with SSA from Lynettefællesskabet (2012, 1st sampling), two experiments for each SSA sample (fresh and deposited) were carried out for 7 days with different experimental conditions (Table 1).

During the experiments voltage, current, pH in the electrolytes and pH and conductivity in the SSA suspension were measured. The pH of the electrolytes was manually adjusted to pH between 1 and 2 with 1:1 HNO_3 when necessary.

Table 1. Experimental design for the Lynettefællesskabet SSA (2012, 1st sampling).

Experiment	Lynetten SSA sample	Cell design	SSA compartment	H_2SO_4 (M)
F-3-0.19	Fresh (2012)	3 compartment	central	0.19
D-3-0.19	Deposited (2012)			
F-2-0.08	Fresh (2012)	2 compartment	anode	0.08
D-2-0.08	Deposited (2012)			
F-2-0.19	Fresh (2012)			0.19
D-2-0.19	Deposited (2012)			

At the beginning and at the end of each experiment, samples were taken from electrolytes and from the suspension, for P and heavy metal analyses. At the end of the experiments the SSA suspensions were drained through filter paper before drying, to separate the solids from the liquid phase, and water content was measured. Membranes and cathode were soaked in HNO_3 (1 and 5 M, respectively) for 24 hours to release metals for further analysis. The SSA (three replicates), aqueous phases, electrolytes, membranes and cathode were analysed for P and heavy metal contents, using the same ICP-OES.

2.5 Minteq calculations

MINTEQ was used to gain further insight into the formation of charged phosphorus complexes which could be transported through the AEM and CEM. For the calculations the chemical composition of the solution in experiments after the 7 days, with elements present in SSA with Fe as Fe^{3+} or as Fe^{2+}. The pH was fixed to the final experimental pH and temperature to 25 °C. The Ionic strength was calculated in the program.

2.6. Statistical analysis

Physico-chemical characteristics, element concentrations in all fresh and deposited SSA were subjected to analysis of variance (ANOVA) and then compared by Tuckey multiple range test at $p < 0.05$. A Student t-test was used for comparison of SSA collected in the same incinerator plant.

3. Results and Discussion

3.1. Chemical characterization of different SSA

The characterization of fresh Avedøre SSA (2012 and 2014) and fresh/deposited Lynetten SSA (2012 and 2013) is presented in Table 2.

Regarding physico-chemical characteristics, the changes in pH and conductivity did not follow a specific tendency, differences being attributed to SSA heterogeneity (wastewaters from different urban areas in Denmark but with no major industrial discharges). The high difference in water content between deposited (up to 16%) and fresh (≤ 0.1%) SSA was related to storage (e.g. air humidity, rain). The LOI was generally low (<0.9%), only increasing for one Lynetten sample (2.7%). Both plant facilities have thus shown sufficient incineration conditions.

The concentration of the different elements was in the same range in all studied SSA. The P content was generally high in all SSA (between 7 and 16 wt. %). Differences in P are majorly attributed to population diet (Mihelcic et al., 2011), type of wastewater treatment plant system, and type of detergents used. In general, the Zn concentration was higher in Lynettefællesskabet 2012 SSA than in the other samples. In 2014, Avedøre Spildevandscenter had higher concentrations of Cu and Pb than in 2012 or in Lynetten. Again, these variations can be related to the characteristics of the area covered by the WWTP, which directly influence the heterogenous characteristics of the daily SS flows. Most of the studied Danish SSA were in accordance with reported literature ranges (Donatello et al., 2010a; Ebbers et al.; Franz, 2008; Levlin et al., 2003; Ottosen et al., 2013) (also in Table 2, for comparison purposes), except for some samples with higher Zn, Cu and Pb values or lower Fe and Ni concentrations. In this work, Cr levels were below all the concentrations reported in literature.

The Danish EPA has two set of limiting values for heavy metals when spreading waste at agricultural land. The dry matter related concentrations (see Table 1) met the limiting values except for Cd (2.2-3.5 mg/kg) and Ni (35-62 mg/kg) for all SSA, and Pb for one sampling period in Lynetten and Avedøre (Table 2). As previously discussed, to be spread at agricultural land, a pre-treatment of the SSA is also needed to get plant available P.

***Table 2**- Characteristics of the studied Danish SSA including heavy metal concentrations in relation to the total dry mass (mean ± STD) and limiting values for spreading at agricultural land. Values reported in literature were also used for comparison.*

		Lynetten						***Avedøre***		**Limiting values (mg/kg) [a]**	***Literature [b]***
		2012 (1st sampling)		***2012 (2nd sampling)***		***2013***		***2012***	***2014***		
	Parameter	***Fresh* (1)**	***Deposited* (1)**	***Fresh***	***Deposited***	***Fresh***	***Deposited***	***Fresh***	***Fresh***		
Physical and chemical characterization	pH (H_2O)	12.44 ± 0.01 *#	8.85 ± 0.03 *	12.4 ± 0.05 *#	8.3 ± 0.03 *	12.6 ± 0.02 #	12.6 ± 0.01 #	10.4 ± 0.0 *	9.6 ± 0.10 *		
	Water content (%)	0.10 ± 0.18 *	16 ± 0.38 *	0.09 ± 0.03	14.4 ± 0.09	3.70 ± 0.04 #	3.93 ± 0.07 #	-	0.16 ± 0.01		
	Conductivity (mS/cm)	3.23 ± 0.51 *	4.81 ± 0.13 *#	7.81 ± 0.02 *	5.59 ± 0.11 *#	10.54 ± 0.21 #	9.97 ± 0.82 #	2.12 ± 0.02 *#	2.52 ± 0.14 *#		
	Loss on ignition (550 ºC; %)	0.15 ± 0.05 *#	0.92 ± 0.08 *	0.25 ± 0.05 *#	0.16 ± 0.00 *	2.58 ± 0.01 *	0.47 ± 0.04 *	0.3 ± 0.1 *#	0.57 ± 0.07 *		
	Solubility in water (%)	1.8 ± 0.1 *	3.1 ± 0.0 *	5.12	0.84	5.3 ± 0.0	5.6 ± 0.79	-	29.5		
	Gas production (mL gas/g)	1.6 ± 0.1	1.9 ± 0.2	-	-	-	-	-	-		
Elements	P (g/kg)	134 ± 1	130 ± 5	161 ± 12	-	72.5 ± 0.01 *	68.3 ± 1.5 *	112 ± 2 #	105.4 ± 3.8 #		39-123
	Al (g/kg)	22.6 ± 0.5 *	21.5 ± 0.7 *	21.2	19.5	14.2 ± 0.0	-	20.3 ± 0.5 *	22.1 ± 0.6 *		19.7-218
	Fe (g/kg)	60.0 ± 1.4	62.0 ± 2.3	44.0	-	36.3 ± 0.1	-	78.2 ± 2.9 *	53.2 ± 1.5 *		47-200
	Zn (mg/kg)	3335 ± 77 *#	3157 ± 128 *	3060 ± 222 #	2810 ± 117	2414 ± 10 *#	2270 ± 66.7 *#	2160 ± 60 *#	2410 ± 72 *#	***4000***	448-2737
	Cu (mg/kg)	758 ± 4.9 *	733 ± 9 *	711 ± 5.65 *	694 ± 6.49 *	512 ± 4 #	507 ± 7.58 #	550 ± 10 *	815 ± 18 *	***1000***	417-690
	Pb (mg/kg)	293 ± 44 #	297 ± 9	102 ± 2.15 #	99.5 ± 1.08 #	102 ± 2 #	98.8 ± 5.44 #	90 ± 1 #	253 ± 181 #	***120***	18-158
	Cr (mg/kg)	45.5 ± 0.4 #	44.9 ± 0.7 #	29.7 ± 0.66	28.6 ± 0.61	45.0 ± 0.5 #	44.9 ± 0.40 #	80 ± 2 *	47 ± 1 *#	***100***	102-136
	Cd (mg/kg)	3.25 ± 0.04 #	3.14 ± 0.08	2.21 ± 0.05	2.16 ± 0.09 #	2.2 ± 0.1 #	2.2± 0.1 #	3.4 ± 0.1 #	3.54 ± 0.35 #	***0.8***	0.4-3.9
	Ni (mg/kg)	54.6 ± 0.6	55.7 ± 1.0	35.2 ± 0.72	35.4 ± 0.58	38.9 ± 0.6	37.8 ± 0.14	60 ± 1	62 ± 1.6	***30***	50-93

NOTES:
* indicate statistically significant differences among pairs (columns with some colour) ($p < 0.05$) – t-test
# indicate the absence of statistically significant differences inside the group of non-deposited and deposited SSA ($p < 0.05$) – ANOVA
[a] Danish EPA (Miljøstyrelsen)
[b] [5, 12, 14, 24, 28]
(1) samples used in the experiments aiming P-recovery (acid washing and ED process).

3.2. Study of SSA from Lynettefællesskabet *(2012)*

Deposited and fresh Lynettefællesskabet SSA from the first 2012 sampling (Table 2) were further analysed, including morphology, mineral composition and potential of acid washing to remove P. These SSA were chosen to deepen the comparison between fresh and deposited SSA.

3.2.1. Morphology and mineral composition

SEM analysis show that the SSA particles generally had irregular shaped (Figure 2) and no major differences were found between fresh and deposited samples. Additionally, SEM/EDX analysis revealed that O, P, Fe, Al, K, Na, Mg, Si, S, and Ca were distributed all over the particle surfaces in both SSA.

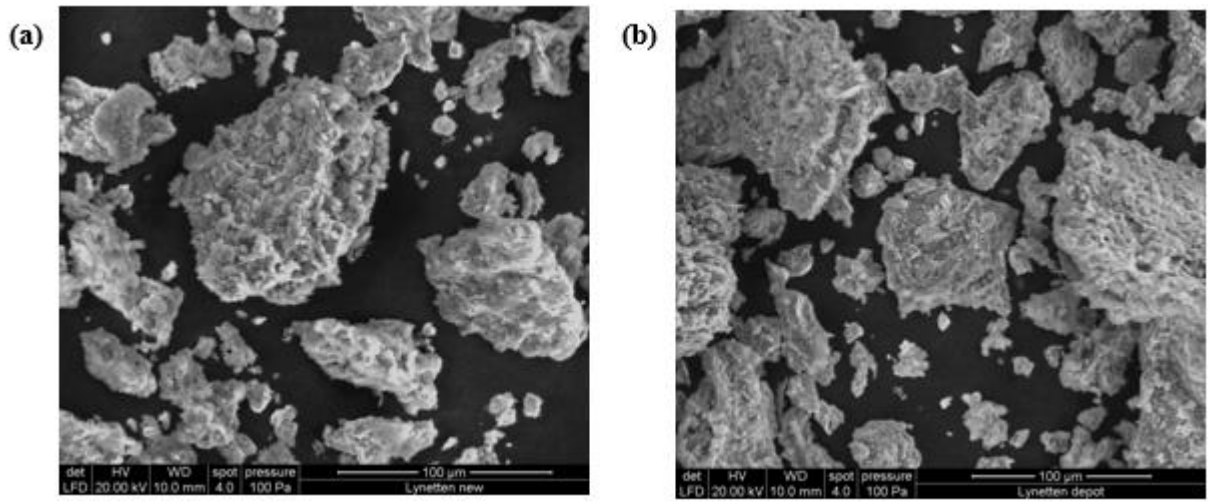

Figure 2. SEM micrographs of (a) fresh and (b) deposited Lynettefællesskabet SSA 2012 1st sampling.

The mineralogy of fly SSA generally represents an assemblage of crystalline and amorphous phases (Bayuseno and Schmahl, 2011). The major mineral phases identified by XRD are presented in Figure 3 and show differences between deposited and fresh SSA. Silicon oxide in the form of quartz (SiO_2) was identified in both SSA, agreeing with published data for other SSA (Cyr et al., 2007) where Si is likely to be present in its crystalline or amorphous phase. Phosphates on both SSA were indicated as calcium phosphates, but the only chemical formula clearly identified was as whitlockite [$Ca_9(MgFe)(PO_4)_6PO_3OH$]. Hematite (Fe_2O_3) was also identified, being the iron oxide a consequence of SS incineration (800-900 ºC) in excess air which promotes the existence of metals as oxides (Donatello et al., 2010b).

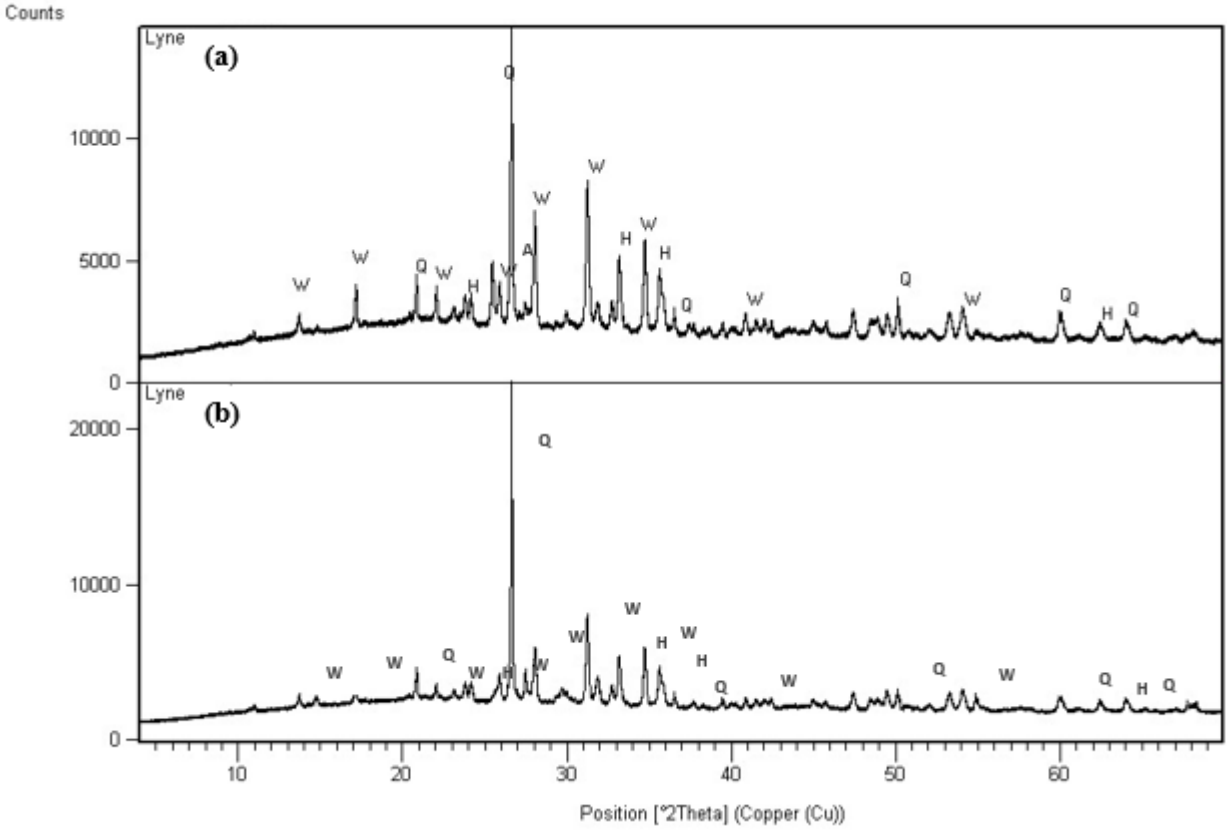

Figure 3. XRD diffractograms of (a) fresh and (b) deposited Lynettefællesskabet SSA 2012 1st sampling (Q - Quartz, W- Whitlockite, H – Hematite, A – Anhydrite).

There was $CaSO_4$ in both samples, however difficult to completely identify. In the fresh sample, it is likely present as anhydrite ($CaSO_4$) and in the deposited, it was not clear, although not anhydrite nor gypsum ($CaSO_4 \cdot 2H_2O$). However, anhydrite can be present in SSA when they are fresh but as a result of "hydration" of the SSA, gypsum may start to form (Bayuseno and Schmahl, 2011), though this was not confirmed by XRD in the present work. In SEM/EDX a S rich region was observed and can belong to i) an amorphous $CaSO_4$ or ii) $Na_2SO_4/K_2SO_4/NaKSO_4$ condensed on this Ca-rich particle. The amorphous phase in other SSAs is between 40-74% (Cyr et al., 2007). In this case, from XRD patterns of fresh and deposited SSA samples it can be inferred that some amorphous phases are present due to the slight hump between 2θ of 10 and 30˚ but the material is not prevalently amorphous. A semi-quantitative method, Reference Intensity Ratio (RIR), based on the diffraction power of a given phase in comparison with alumina, was used to indicate the relative mineral mass fractions in the two SSA. The RIR method indicated that the mass distribution of the major crystalline phases in both SSA were as following: calcium phosphate and quartz > iron oxide and calcium sulphate.

3.2.2. Acid washing of SSA

The percentage of P extracted from the SSA as a function of pH is shown in Figure 4. Storage did not affect the extent of P extraction even at the strongest concentration, 1.0 M, where more than 50 g/kg were extracted. This 40% of total P mobilization is in accordance with the average percentage reported in other works, for the same pH (Ottosen et al., 2013). A pH decrease, other L/S ratios or extracting agents could have increase the total amount of mobilized P (Ottosen et al., 2013).

Regarding storage, the release of a specific element as a function of pH is very similar for fresh and deposited SSA, except for a slight variation of Cd at pH between 2 and 3. The major mineralogy of the material and the phases controlling the solubility of major trace elements (as suggested by the results of mineralogy test) were also not affected, neither the amount of elements extracted. Instead, extraction is mainly correlated with pH changes, particularly at low pH values. At low pH values the mobilized percentages were: Zn 65%, Cu approx. 55%, and less than 33% Ni and Al (Figure 4). Iron was bound strongly in both SSA, and even at the lowest pH, less than 2% was solubilized. This is in accordance to what was expected as Fe_2O_3, which is insoluble in acid (Donatello et al., 2010b), was identified in larger quantities in both SSA. The XRD investigation also showed the presence of $Ca_9(MgFe)(PO_4)_6PO_3OH$ in the SSA. But, since at low pH, only a small amount of Fe was extracted in contrast to more than 35% of P in both samples (Figure 4) these two elements were generally not associated in the SSA, even though Fe was originally used for precipitation of P during the wastewater treatment. As heavy metals mobilization started approximately at the same pH than P mobilization, the obtained acidic liquid solution was a mixture between P and heavy metals, and a further separation step is needed.

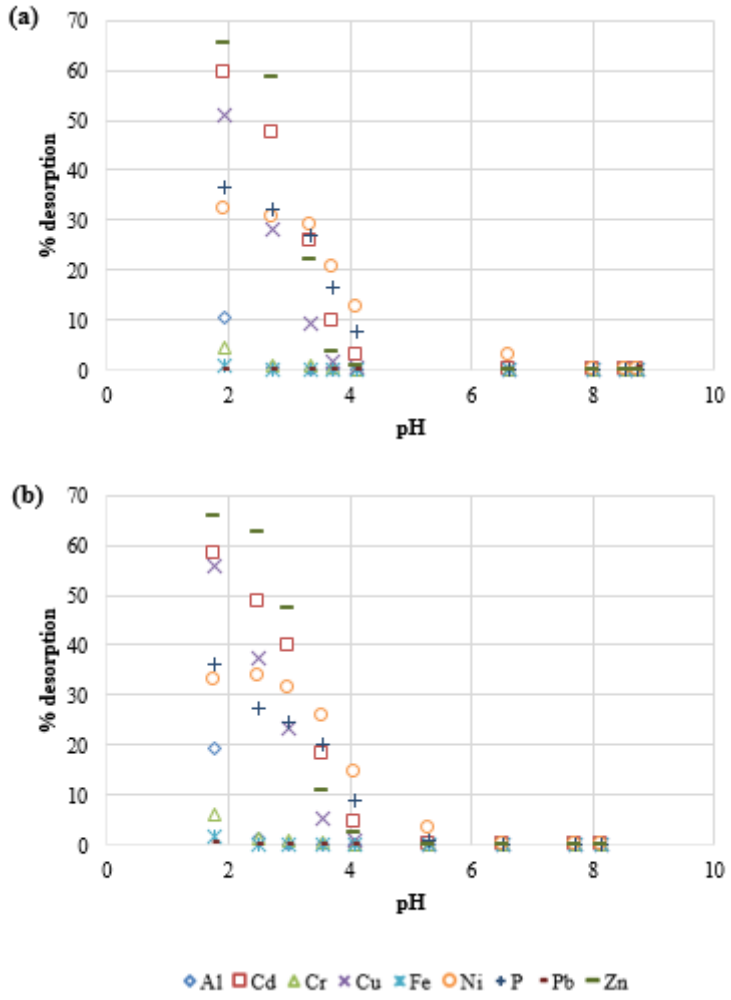

Figure 4. Phosphorus and metal extraction as a function of pH in batch extraction experiments on (a) fresh and (b) deposited SSA Lynettefællesskabet 2012 (1st sampling) using HNO_3.

3.2.2. Electrodialytic P-separation

Table 3 shows the initial conditions and the changes in pH, conductivity and mass loss after the ED experiments. Before the experiment the SSA was suspended in sulphuric acid (0.08 and 0.19M) aiming to convert the precipitated and adsorbed P into mobile ionic forms able to electromigrate during the ED treatments. The initial pH in the central cell compartment varied between 1.0 and 2.6 for the SSA (Table 2). During the ED experiments, pH in the SSA compartment slightly decreased in the 3c-cell and continued to decrease in the 2c-cell due to the generation of H^+ in the anode compartment. Water splitting at the anion exchange membrane may have also contributed for the acidification. The dissolution of ash particles during the ED treatment results in a mass loss that can be quite significant (Guedes et al., 2014b; Ottosen et al., 2006). In the 2c-cell experiments there was

a conductivity increase at the end of the experiments. This is due to the electrolysis at the anode and solubilisation of SSA ions that are not transported out of the suspension as fast as produced. In the 3c-cell the solubilized ions from the SSA suspension are migrating either to the anode or cathode compartments. Consequently, the central compartment is being depleted from ions, which decreases the conductivity of the suspension.

Table 3. Parameters measured at the beginning and at the end of the electrodialytic experiments.

Experiment	Voltage drop (V)		SSA suspension [1] pH		SSA suspension [1] Cond. (mS/cm)		Mass loss (%)
	Start	End	Start	End	Start	End	
F-3-0.19	5.1	4.2	2.25	1.61	22.2	11.7	41
D-3-0.19	6.8	4.4	2.04	1.84	32.4	13.2	40
F-2-0.08	6.7	4.3	2.63	1.68	9.6	22.5	43
D-2-0.08	5.7	4.7	2.47	1.55	14.1	32.8	41
F-2-0.19	5.0	4.5	2.11	1.28	15.9	32.6	42
D-2-0.19	4.8	4.7	2.80	1.24	26.7	33.3	36

[1] Central compartment in the 3 compartment cell and anode compartment in the 2 compartment cell

In the 3c-cell the main objective is to dissolve and mobilize the P from the SSA suspension (central compartment) to the anode compartment and the heavy metals to the cathode compartment. In the 2c-cell the aim is to dissolve P and heavy metals from the SSA suspension keeping P in the suspension whereas the heavy metals are removed into the cathode compartment. Afterwards the suspension is filtered, being the P rich filtrate is clean from ash particles and solubilized heavy metals. In this study, a more concentrated H_2SO_4 solution was used in the 3c-cell compared to the previous work where 0.08M solution was used (Guedes et al., 2014b). The increase in the acid concentration improved P solubilization by 17% (experiments F-3-0.19 and D-3-0.19, Figure 5). In total between 24.9 and 29.4% of P were removed to the anolyte of the 3c-cell, being mainly present as H_3PO_4 (Table 4), whereas in the previous work 17.9 and 18.8% were removed to the anolyte after 7 days (Guedes et al., 2014b). For the heavy metals, generally, higher percentages were solubilized from the SSA when 0.19 M was used. Between more 3% (Fe in the fresh SSA) and 36% (Cd in the deposited SSA) were solubilized from the SSA comparing to the results obtained with 0.08 M (Guedes et al., 2014b). No differences were found for Al in the deposited SSA (D-3-0.19) and Cr and Cu in the fresh SSA (F-3-0.19).

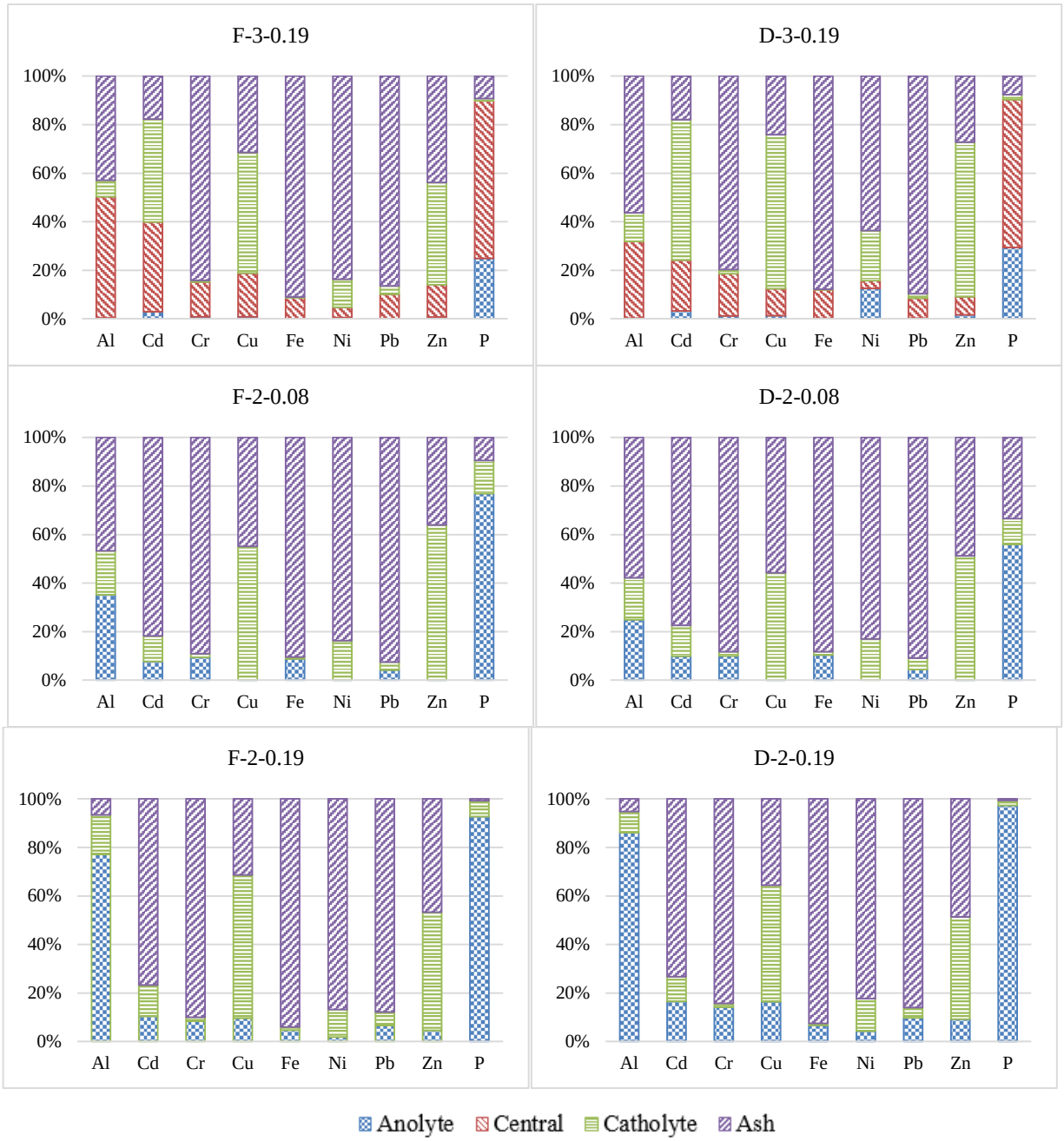

Figure 5. Percentage of heavy metals and phosphorus in the different matrices after the ED treatment in the 3C and 2c-cell design.

When the 2c-cell with 0.08M of H_2SO_4 was used 91% of P for F-2-0.08 and 67% for D-2-0.08 were solubilized. From these, 14 and 11% of P (F-2-0.08 and D-2-0.08, respectively) electromigrated to the cathode compartment, probably due to the complexation with Al, Fe and Ca forming positively charged species (Table 4). At the end, the anolyte solution still contained 77% of P in F-2-0.08 and

56% in D-2-0.08 (Figure 5) being mainly present as H_3PO_4 and $H_2PO_4^-$ (Table 4). One hypotheses is that deposited SSA samples used in experiment D-2-0.08 may contain more acid-insoluble P–complexes (samples heterogeneity) influencing the results. Still, in these two experiments, the type of SSA influenced the total P solubilization by the different setups and, consequently, the amount collected in the anolyte solution. In this case, the best option is to ash collected immediately after incineration.

The increase in the acid concentration in the 2c-cell set-up resulted in higher P solubilization from the SSA, approx. 99% in both cases. From these, 93 and 97% in the F-2-0.19 and D-2-0.19, respectively, remained in the anolyte as H_3PO_4 and $H_2PO_4^-$ (Table 4). Only 7% in F-2-0.19 and 2% in D-2-0.19 electromigrated toward the cathode compartment.

In terms of heavy metals, generally, higher removals were achieved when 0.19M of H_2SO_4 was used compared to the use of 0.08M, independently of the cell design (3c-cell or 2c-compartment). The exception was Cd which removal was higher in the 3c-cell, 82% in both experiments (F-3-0.19 and D-3-0.19) contrasting to the 23 and 27% in the F-2-0.19 and D-2-0.19, respectively.

The use of a 2c-cell setup increased overall efficiency of P recovery after 7 days of experiment, under the conditions here tested. Dissolution of P seems to be faster and more complete in the 2c-cell experiments than in the 3c-cell. Still, in the 2c-cell set-up, the P was not completely separated from the heavy metals (for example, 32% of Al for F-2-0.19 and 45% for D-2-0.19). From the total amount of elements analyzed, the anolyte solution of D-2-0.19 was constituted by 90% of P and 10% of heavy metals, whereas F-2-0.19 anolyte contained 93% of P and the remaining 8% were heavy metals.

Table 4. MINTEQ calculation of major species of phosphate ions (%) for the anolyte concentrations at the end of the treatments.

	Experiments	**F-3-0.19**		**D-3-0.19**		**F-2-0.08**		**D-2-0.08**		**F-2-0.19**		**D-2-0.19**	
	Fe oxidation state	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
P	$H_2PO_4^-$	6.19	6.19	6.69	6.69	27.6	27.6	22.8	22.6	14.6	14.2	13.7	13.3
	H_3PO_4	92.8	92.8	92.2	92.1	57.4	57.1	67.2	66.6	73.7	71.6	76.5	74.2
	$AlHPO_4^+$	-	-	-	-	4.50	4.44	2.29	2.23	1.73	1.68	1.39	1.34
	$Al_2PO_4^{+3}$	-	-	-	-	0.27	0.27	0.07	0.06	0.08	0.08	0.06	0.05
	$CaH_2PO_4^+$	0.93	0.93	1.02	1.02	5.96	5.92	3.17	5.92	3.71	3.62	2.84	2.76
	$FeH_2PO_4^{2+}$	-	0.08	4.26	0.15	4.31	3.09	4.48	3.75	6.17	7.30	5.55	7.05
	$FeHPO_4^+$	-	-	-	0.01	-	-	-	1.64	-	1.49	-	1.33

* Not applicable

4. Conclusions

The SSA from Avedøre and Lynetten incinerator plants showed no large differences between their chemical characteristics, except for those related with SSA heterogeneity. Additionally, samples collected at different stages (fresh and deposited) at the same incineration plant showed no trending differences in metal content and physico-chemical parameters. The exception was the moisture content, which was directly related with the disposal conditions.

All the SSA exceeded Danish EPA Cd and Ni thresholds regarding agriculture application. Their high P concentration (up to 16 wt. %) justifies the need of P recovery. More than 50 g of P/kg was extracted from fresh and deposited Lynetten SSA (2012) by acid washing, together with a high amount of heavy metals.

The P separation from the SSA was tested using an ED cell showing that the 2c-cell achieves higher P solubilisations from the SSA. The best results were achieved when 0.19M of H_2SO_4 were use, up to 99% of P solubilization. In total, approx. 125 g of P/kg of SSA remained in the anolytes. Still, a high amount of heavy metals was presented in the anolyte (e.g. 44.7% of Al).

The use of SSA collected after the incineration or from the deposit influenced the total P solubilization in the 2c-cell when 0.08M of sulfuric acid was used. The deposition of the SSA promoted the decrease in the amount of P solubilized, less 24%. Consequently, less 21% of P were collected in the deposited SSA anolyte.

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References

2003. DS 259, Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry in flame, Dansk Standardiseringsråd.

Adam, C., Peplinski, B., Michaelis, M., Kley, G., Simon, F.G., 2009. Thermochemical treatment of sewage sludge ashes for phosphorus recovery. Waste Management 29, 1122-1128.
Al Sayed, M.H., Madany, I.M., Buali, A.R.M., 1995. Use of sewage sludge ash in asphaltic paving mixes in hot regions. Construction and Building Materials 9, 19-23.
Anderson, M., Elliott, M., Hickson, C., 2002. Factory-scale proving trials using combined mixtures of three by-product wastes (including incinerated sewage sludge ash) in clay building bricks. Journal of Chemical Technology & Biotechnology 77, 345-351.
Bayuseno, A.P., Schmahl, W.W., 2011. Characterization of MSWI fly ash through mineralogy and water extraction. Resources, Conservation and Recycling 55, 524-534.
Biswas, B.K., Inoue, K., Harada, H., Ohto, K., Kawakita, H., 2009. Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. Journal of Environmental Sciences 21, 1753-1760.
Cyr, M., Coutand, M., Clastres, P., 2007. Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials. Cement and Concrete Research 37, 1278-1289.
Donatello, S., Tong, D., Cheeseman, C.R., 2010a. Production of technical grade phosphoric acid from incinerator sewage sludge ash (ISSA). Waste Management 30, 1634-1642.
Donatello, S., Tyrer, M., Cheeseman, C.R., 2010b. EU landfill waste acceptance criteria and EU Hazardous Waste Directive compliance testing of incinerated sewage sludge ash. Waste Management 30, 63-71.
Ebbers, B., Ottosen, L.M., Jensen, P.E., Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash. Chemosphere.
Ebbers, B., Ottosen, L.M., Jensen, P.E., 2015. Comparison of two different electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge ash. Chemosphere 125, 122-129.
Ferreira, C., Ribeiro, A., Ottosen, L., 2003. Possible applications for municipal solid waste fly ash. Journal of Hazardous Materials 96, 201-216.
Franz, M., 2008. Phosphate fertilizer from sewage sludge ash (SSA). Waste Management 28, 1809-1818.
Guedes, P., Couto, N., Ottosen, L., Ribeiro, A., 2014a. Phosphorus recovery from sewage sludge ash through an electrodialytic process. Waste Management 34, 886-892.
Guedes, P., Couto, N., Ottosen, L.M., Ribeiro, A.B., 2014b. Phosphorus recovery from sewage sludge ash through an electrodialytic process. Waste Management 34, 886-892.
Jensen, J.B., Villumsen, A., 1995. Method and apparatus for the decontamination of products containing heavy metal, PCT/DK95/00209.
Levlin, E., Löwén, M., Stark, K., 2003. Phosphorus recovery from sludge incineration ash and supercritical water oxidation residues with use of acids and bases. Report No. 11. Integration and Optimization of Urban Sanitation Systems, Wisla.
Lin, D.-F., Luo, H.-L., Sheen, Y.-N., 2005. Glazed Tiles Manufactured from Incinerated Sewage Sludge Ash and Clay. Journal of the Air & Waste Management Association 55, 163-172.
Mattenberger, H., Fraissler, G., Brunner, T., Herk, P., Hermann, L., Obernberger, I., 2008. Sewage sludge ash to phosphorus fertiliser: Variables influencing heavy metal removal during thermochemical treatment. Waste Management 28, 2709-2722.
Mattenberger, H., Fraissler, G., Jöller, M., Brunner, T., Obernberger, I., Herk, P., Hermann, L., 2010. Sewage sludge ash to phosphorus fertiliser (II): Influences of ash and granulate type on heavy metal removal. Waste Management 30, 1622-1633.
Mihelcic, J.R., Fry, L.M., Shaw, R., 2011. Global potential of phosphorus recovery from human urine and feces. Chemosphere 84, 832-839.
Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., 2014a. Electrodialytic separation of phosphorous and heavy metals from two types of sewage sludge ash. Separation Science and Technology.

433 Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., 2014b. Electrodialytic Separation of Phosphorus and
434 Heavy Metals from Two Types of Sewage Sludge Ash. Separation Science and Technology 49, 1910-
435 1920.
436 Ottosen, L.M., Jensen, P.E., Kirkelund, G.M., Ebbers, B., 2014c. Electrodialytic recovery and
437 purification of phosphorous from sewage sludge ash, sewage sludge and wastewater,
438 PCT/EP2014/068956.
439 Ottosen, L.M., Kirkelund, G.M., Jensen, P.E., 2013. Extracting phosphorous from incinerated sewage
440 sludge ash rich in iron or aluminum. Chemosphere 91, 963-969.
441 Ottosen, L.M., Lima, A.T., Pedersen, A.J., Ribeiro, A.B., 2006. Electrodialytic extraction of Cu, Pb
442 and Cl from municipal solid waste incineration fly ash suspended in water. Journal of Chemical
443 Technology & Biotechnology 81, 553-559.
444 Pan, S.-C., Lin, C.-C., Tseng, D.-H., 2003. Reusing sewage sludge ash as adsorbent for copper
445 removal from wastewater. Resources, Conservation and Recycling 39, 79-90.
446 Parés Viader, R., Jensen, P.E., Ottosen, L.M., Ahrenfeldt, J., Hauggaard-Nielsen, H., Electrodialytic
447 extraction of phosphorus from ash of low-temperature gasification of sewage sludge. Electrochimica
448 Acta.
449 Petzet, S., Peplinski, B., Bodkhe, S.Y., Cornel, P., 2011. Recovery of phosphorus and aluminium
450 from sewage sludge ash by a new wet chemical elution process (SESAL-Phos-recovery process).
451 Water Science & Technology 64, 693-699.
452 Petzet, S., Peplinski, B., Cornel, P., 2012. On wet chemical phosphorus recovery from sewage sludge
453 ash by acidic or alkaline leaching and an optimized combination of both. Water Research 46, 3769-
454 3780.
455 Smith, K.M., Fowler, G.D., Pullket, S., Graham, N.J.D., 2009. Sewage sludge-based adsorbents: A
456 review of their production, properties and use in water treatment applications. Water Research 43,
457 2569-2594.
458 Stark, K., Plaza, E., Hultman, B., 2006. Phosphorus release from ash, dried sludge and sludge residue
459 from supercritical water oxidation by acid or base. Chemosphere 62, 827-832.
460 Sturm, G., Weigand, H., Marb, C., Weiß, W., Huwe, B., 2010. Electrokinetic phosphorus recovery
461 from packed beds of sewage sludge ash: yield and energy demand. Journal of Applied
462 Electrochemistry 40, 1069-1078.
463 Vogel, C., Adam, C., Peplinski, B., Wellendorf, S., 2010. Chemical reactions during the preparation
464 of P and NPK fertilizers from thermochemically treated sewage sludge ashes. Soil Science & Plant
465 Nutrition 56, 627-635.
466 Weigand, H., Bertau, M., Hübner, W., Bohndick, F., Bruckert, A., 2012. RecoPhos: Full-scale
467 fertilizer production from sewage sludge ash. Waste Management.
468 Werther, J., Ogada, T., 1999. Sewage sludge combustion. Progress in Energy and Combustion
469 Science 25, 55-116.
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PAPER VII

POTENTIAL OF THE ELECTRODIALYTIC PROCESS FOR EMERGING ORGANIC CONTAMINANTS REMEDIATION AND PHOSPHORUS SEPARATION FROM SEWAGE SLUDGE

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Potential of the electrodialytic process for emerging organic contaminants remediation and phosphorus separation from sewage sludge

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ABSTRACT

The present work discusses the efficiency of the electrodialytic process (ED) applied to sewage sludge aiming phosphorus recovery and organic contaminants removal. Six emerging organic contaminants were studied: caffeine (CAF), ibuprofen (Ibu), 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), and oxybenzone (MBPh). Three different ED experimental cell designs were tested, in a 2-compartment cell set-up, using sewage sludge spiked with 8 mg/L of each compound. In total, five ED experiments were carried out during 5 days. Two control experiments without current were also carried out. At the end of the experiments, changes in the sewage sludge pH and in the microbial communities were observed and these changes affected contaminants degradation. Still, independently of the cell design used, the application of a low level direct current, improved the degradation of Ibu between 46 and 97%, as well as Caf between 20 and 47% (except in Exp-4), comparing against the control experiments. A contrary effect was observed for MBPh which degradation was less effective when the sewage sludge was subjected to ED, being the only exception the results obtained for Exp-5. This cell design, sewage sludge in the cathode compartment separated from the anode by an anion exchange membrane, also promoted higher contaminants degradation and in the final sludge all contaminants, except MBPh, were below limit of quantification and limit of detection. In terms of P, the highest recovery was achieved when the pH increased to 12.5 in Exp-5, 78 ± 2% of total P was recovered in the electrolyte. Independently of the experiments, the recovered P was still mixed with the studied organic contaminants.

1. Introduction

Phosphorus (P) is essential to all life being and a key ingredient in fertilizers to sustain high crop yields. It has no substitute in food production and in a world of 9 billion people by 2050, securing sufficient P will be critical for future food security [1]. The world's remaining high-grade phosphate rock reserves are concentrated in only a few countries, with Morocco and Western Sahara controlling approximatly 75% of the world's share [2]. This makes phosphate-importing countries like European Union (EU) vulnerable to geopolitical dynamics in producing countries [3].

The use of sludge is considered a viable option to maintain/enhance the recycling of elements with socio-economic value like P, other nutrients and organic matter, being advocated as a means of avoiding the environmental and economic costs of disposal [4]. It has been estimated that in EU-27 by 2020, 43% of the treated sludge will be used in agriculture [5]. However, direct use of treated sewage sludge in agriculture may be difficult due to public perception, odours or difficulties of transport and storage and, in other cases it is not feasible due to the presence of contaminants like organics, heavy metals and pathogens.

Degradation and attenuation during wastewater and sludge treatment remove significant amounts of organic contaminants. But many of these compounds are transferred to sewage sludge and may be present in residual concentrations in the dry solids, depending on their initial amounts, their lipophilicity and the extent of destruction during treatment [6]. The organic contaminants that can be found in low concentrations in the environment often suffer biomagnification and bioaccumulation into biological organisms and cause irreversible damages in biological systems through direct or indirect toxic effects such as endocrine disruption and tumour promotion [7].

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If P recovery from sewage sludge is the final target the process generally aims at: (i) separating contaminants from the valuable P and, if possible, (ii) converting P either into a plant-available form for reuse as fertilizer or into a raw material for the P-industry. If P recovery is successful, it offers the immediate advantage of avoiding the environmental impacts associated with primary production from phosphate rock, complemented with the reuse of an essential nutrient that is being wasted. For these reasons, the present technologies that promote P reuse within the wastewater treatment scheme are particularly attractive, if they achieve a product which is free from contaminants and of high quality as fertiliser.

The electrokinetic process is a method that relies on the application of a low level direct current (DC) for the removal of contaminants from soils and other porous matrices [8]. Electrokinetic treatment relies on several interacting mechanisms but the dominant and most important electron transfer reactions that occur at electrodes during the process is the electrolysis of water, which will cause a pH increase and decrease in the cathode and anode compartments, respectively.

Few studies tested the applicability of the electrokinetic process (EK), using passive membranes, and the electrodialytic process (ED), using ion exchange membranes, for heavy metal [9–13] and surfactant [14] removal from sewage sludge. More recently, the applicability of the EK for the remediation of emerging organic contaminants from soil was carried out in a stationary laboratory cell [15]. The results showed that EK is a viable method for the remediation of organic contaminants, both through mobilization by electroosmotic flow and electrodegradation. Still, to the best of our knowledge, no works have been published regarding P recovery and simultaneous organic contaminants remediation from sewage sludge using ED.

In order to improve the process, adjustments can be made to the earlier established three compartment ED cell [16] depending on the final objective. For example, a stirrer can be introduced in the central cell compartment [17] or the number of cell compartments can be reduced into two [18], introducing the matrix directly into the anode compartment.

In this work, the ED process was applied to the sewage sludge aiming a simultaneous P-separation and organic contaminants remediation. In the case of the contaminants remediation it is expected that bio and/or electrodegradation mechanisms may occur. Six contaminants, classified as emerging, that have been detected in the influent, effluents and sewage sludge samples all over the world [19–21] were selected to the study: two estrogenic steroid hormones, one industrial reagent, one pharmaceutical active compound, one neural stimulant and one sunscreen compound. The target compounds were 17β-oestradiol (E2), 17α-ethinyloestradiol (EE2), bisphenol A (BPA), ibuprofen (Ibu), caffeine (Caf) and oxybenzone (MBPh). Their chemical properties can be found in Table SM1. An evaluation of the biodegradation potential and overall changes in the microbiological community were also assessed in the ED experiments.

Supplementary material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.03.167.

2. Experimental

2.1. Chemicals and standards

Caffeine (≥90%), BPA (≥99%), E2 (≥97%), EE2 (≥98%) were purchased from Aldrich (Steinheim, Germany) and Ibu from Fluka (U.S.A.). All used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). Acetonitrile (ACN), methanol (MeOH) and acetone were gradient grade. The water used for analyte extractions and their analytical determinations was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). Formic acid (LC–MS grade), acetic acid (LC–MS grade) and sodium hydroxide (NaOH) were purchased from Sigma–Aldrich. Sodium nitrate ($NaNO_3$) was reagent grade from Panreac. Individual stock solutions for calibration purposes were prepared at 400 mg/L in MeOH and stored at −18 °C. Working solutions were prepared by the adequate mixture and dilution of the stock solutions.

2.2. Sewage sludge sampling procedure

The sewage sludge samples were collected at a wastewater treatment plant from *Simarsul* located in Quinta do Conde, Sesimbra, Portugal (38°34′13″ N, 9°2′7″ W). The plant has the capacity to treat in the project horizon 19,300 m^3/day of urban wastewater, corresponding to about 94,000 equivalent inhabitants. The level of treatment installed is tertiary. The secondary tank is an aerobic reactor, of suspended biomass, where appropriate conditions are secured to promote the development of a population of microorganisms which ensure biological purification of wastewater conditions. The effluent of the reactor is then routed to the secondary settling tank for phase separation, where the samples were collected. The sampling of the sewage sludge was carried out in January 2014, following the recommendations of the norm NF EN ISO 5667-15 (October 2009) on the conservation and treatment of sludge and sediment samples. Sample characterization was carried out at the wastewater treatment laboratory. The sample presented a pH of 7.01, a conductivity of 710 μS/cm, and a total P concentration of 123 mg P/L. Total solids in suspension and total volatile solids were 4367 and 3783 mg/L, respectively, being the total organic carbon 2011 mg C/L. Five day biochemical and chemical oxygen demand were 1300 and 4700 mg O_2/L, respectively. The sewage sludge presented a total nitrogen concentration of 395 mg N/L, nitrate was <2 mg NO_3/L and ammonia concentration was 3.82 mg NH_4/L. An initial screening of the studied contaminants was carried out in the sewage sludge used in the experiments and none of the compounds was detected in the samples. The samples were packed in wide-mouth bottles of PTFE and frozen until use.

2.3. Extraction procedures for organic contaminants determination

2.3.1. Aqueous samples

The extraction of the analytes present in the electrolytes and effluent (aqueous phase of the sewage sludge) solutions was performed by solid phase extraction (SPE), using Oasis HLB (200 mg, 6 mL) from Waters (Saint-Quentin En Yvelines Cedex, France). The SPE cartridges were conditioned by washing with 3 × 6 mL of methanol, followed by re-equilibrium with 3 × 6 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2, using nitric acid, before extraction. The aqueous samples, 200 mL, were passed through the cartridge at a flow-rate of approx. 10 mL/min by applying a moderate vacuum. After that, the cartridges were dried for approx. 2 min by vacuum. The retained analytes were eluted sequentially with 2 × 3 mL of methanol. All the extracts were collected as one and concentrated under a gentle stream of nitrogen till 1 mL. Samples were transferred to a vial and kept at −18 °C until analysis.

2.3.2. Solid samples

Sludge (solid phase of the sewage sludge) extraction was performed using QuEChERS extraction (adapted from [22]). Extract tubes were obtained from Waters (Dublin, Ireland). The acetate buffer contained 1.5 g NaOAc and 6 g $MgSO_4$. The dispersive phase contained 150 mg PSA (primary and secondary amine) and 900 mg $MgSO_4$. A 2 g aliquot of homogenized sludge was weighed in a 50 mL polypropylene centrifuge tube containing NaOAc and

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$MgSO_4$. Then, 20 mL ACN + acetic acid 1% (v/v) were immediately added and manually shaken for 15 s and then swirled on a vortex mixer for 45 s to homogenize the sample. The extract was centrifuged at 10,000 rpm for 5 min. A 9.5 mL aliquot of the supernatant (ACN phase) was transferred to a 15 mL centrifuge tube containing the PSA and $MgSO_4$ and was manually shaken for 10 s and swirled on a vortex mixer for 60 s. After this step, the extract was centrifuged again (10,000 rpm for 5 min) and 8 mL supernatant were transferred to a 12 mL glass tube. The extract was evaporated under a gentle stream of nitrogen till 0.5 mL. All samples were stored at −18 °C until analysis.

2.4. Analysis by high-performance liquid chromatography with ultraviolet detection

HPLC was performed on a Finnigan MAT HPLC system (Thermo Scientific, USA) equipped with a SP P4000 Pump, a AS 3000 Autosampler, the diode array detector (DAD) was a TSP SpectraSYSTEM UV6000LP with the wavelength set between 200 and 800 nm and a TSP SN 4000 Interface.

The contaminants separation was carried out using Chromolith HighResolution RP-18e column with 100 mm × 4.6 mm from VWR (Darmstadt, Germany) and Onyx SecurityGuard C18 cartridges (5 × 4.6 mm) from Phenomenex (Torrance, USA). All HPLC runs were performed at a constant flow rate of 1 mL/min, in gradient mode, with the oven set to 38 °C. The eluents used were a mixture of ACN/MiliQ water/Formic acid (solution A: 5/94.5/0.5%; solution B: 94.5/5/0.5%). Solution A pH was 3.2 and Solution B was 3.6. Formic acid solution (50% in water) was from Fluka. The gradient run was set to: 5 min; 97% A from 0 to 15 min, then to 95% B until 50 min, where it was held until 53 min, then to 97% A until 55 min. The system re-equilibration was performed for 5 min with 97% A. All operations and data analysis were processed by the Xcalibur software v.1.3. (Thermo Scientific, USA). Method limit of detection (LD) and quantification (LQ) is available in the supplementary material (Table SM2).

Supplementary material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.03.167.

2.5. Phosphorus extraction and analysis

The concentration of P in the solid sludge was determined after a pre-treatment of the sludge in accordance to EPA3051: 0.5 g of dry sludge and 10 mL of HNO_3 (65%) were placed in a vessel and extracted in a Microwave from Milestone Ethos (Bergamo, Italy). The microwave program was set to reach 175 °C in 15 min and then keep the temperature for another 15 min. The samples were then collected and filtered through a 0.45 μm filter and stored until analysis. Liquid samples (effluent and electrolyte) were also filtered through a 0.45 μm filter and stored until analysis. The P content was measured at 178.229 nm in an Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP–AES), Varian 720-ES.

2.6. Biological analysis

Samples before and after ED experiments were observed in an Olympus BX41 microscope (Olympus, Tokyo, Japan). The samples were collected and placed in capped plastic bottles, half of the vial volume. Sewage sludge from the ED cell was collected at half height and if there was the formation of foam at the top of the cell it was collected separately. All samples were then refrigerated and analysed within 5 h after sampling.

2.7. Electrodialytic laboratory cell

Three different ED cell designs were tested in accordance to Fig. 1(a)–(c). The experiments were carried out in a

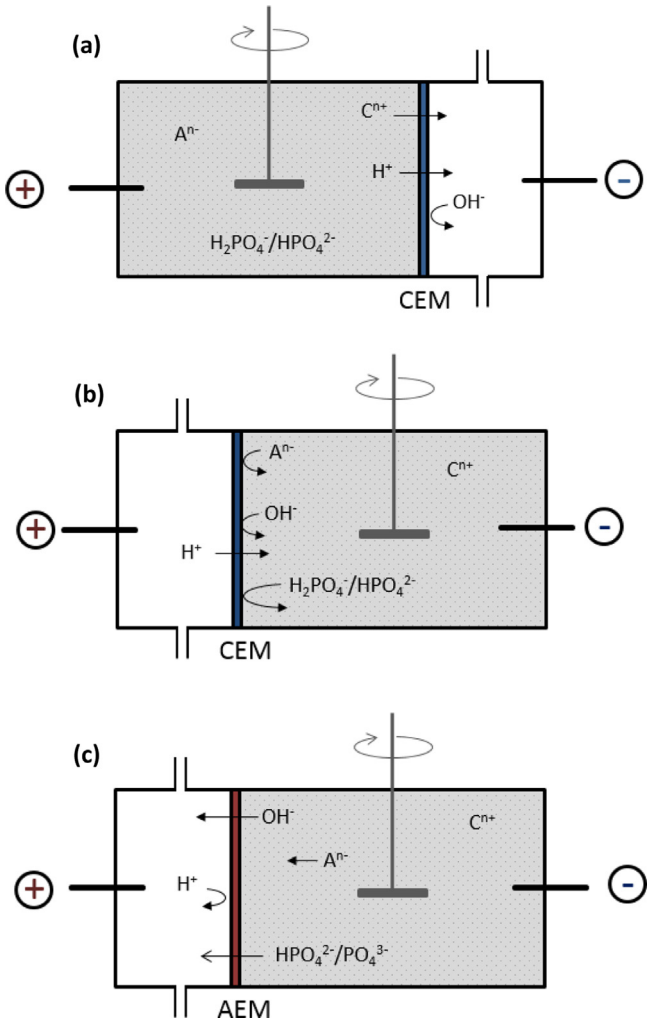

Fig. 1. Schematic design of the three laboratory cell set-ups used were the sludge was placed at the (a) anode with cation exchange membrane (Exp-1 and Exp-2), (b) cathode with cation exchange membrane (Exp-3 and Exp-4) and (c) cathode with anion exchange membrane (Exp-5).

2-compartment ED laboratorial cell [18]. The 2-compartments had an internal diameter of 8 cm, an electrode each, and were separated by a commercial ion exchange membrane, from Ionics (a cation exchange membrane, CR67HUY N12116B, or an anion exchange membrane, AR204 SZRA B02249). The compartment where the sludge was place had an L = 10 cm and was equipped with a stirrer, whereas the electrolyte compartment had an L = 5 cm. The electrodes were platinized titanium bars, with a 3 mm diameter and a length of 5 cm (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC and the voltage drop was monitored (Kiotto KT 1000H multimeter). The fresh electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 2, being circulated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions.

2.8. Electrodialytic experimental conditions

The sludge cell compartment of the ED cell was filled with 350 g of sewage sludge (90–95% water). For this, a funnel was placed in the agitator hole and the sludge was poured through it and, as the sludge was too thick, 50 mL of deionized water were used to help the passage through the funnel. Prior to the beginning of the

experiments, the sludge was spiked with a mixture of the contaminants under study. In order to assess the contaminants' mobilization and remediation/degradation under the influence of ED (one of the study goals), the sewage sludge was spiked with approximately 8 mg/L of each analyte in 1:1 MeOH:Acetone. This was done to assure that all the contaminants would be quantified or detected in all cell compartments at the end of the experiments (sludge, effluent and electrolyte), even in cases of high degradation efficiencies and to test the limits of the technique by using a highly contaminated matrix.

Experiments were carried out according to the experimental conditions presented in Table 1. Two control experiments without the application of electric current were carried out, in Control-1 the sewage sludge was separated from the electrolyte by a cation exchange membrane and in Control-2 the separation was done by an anion exchange membrane. Two experiments with the application of 20 and 50 mA were then carried out using the cell schemes of Fig. 1(a). Another two experiments were carried also with the application of 20 and 50 mA using the scheme of Fig. 1(b). In relation to the cell scheme of Fig. 1(c), taking into consideration the results obtained for 20 mA on the previous set-ups, only one experiment was carried out applying 50 mA. In total seven experiments were done in duplicate, in a fume hood protected from the sunlight.

During the experiments voltage drop, current density and pH were measured. To measure the pH, samples from the sewage sludge and electrolyte were collected to a small beaker, pH measured and then the samples were returned to the cell. Electrolyte pH was manually adjusted to pH between 1 and 2 with 1:1HNO_3 when necessary.

At the end of the experiments the electrolyte samples (catholyte or anolyte) were collected and their pH and volume registered. The sewage sludge in the cell was collected and pH and volume registered. It was filtrated under vacuum to separate the solid (sludge) from the liquid phase (effluent). The filtrated sludge was then extracted (two replicates) for organic contaminants determination as described in Section 2.3.2. The remaining sludge sample was then dried in an oven at 50 °C till constant weight and the water content determined. Finally, for P determination, the dried sludge sample was extracted as described in Section 2.5. The liquid samples, effluent and electrolyte, were then filtered through a 0.45 μm filter and extracted as described in Section 2.3.1 for organic contaminants and 2.5. for P determination.

Membranes and electrodes were soaked in HNO_3 (1 and 5 M, respectively) for 24 h and the liquid used for further P analysis. Afterwards, membranes were again soaked in acetone and placed in an ultrasonic bath for 10 min to promote a better cleaning.

2.9. Electrodegradation experiments

Contaminants' electrodegradation was also assessed in the setup scheme of Fig. 2. Degradation experiments were conducted for 6 h at a constant current of 25 mA. Two containers, one for the cathode and another for the anode, where separated by a cation exchange membrane placed in the middle of the bridge. Two experiments were carried out in duplicate. In one experiment the cathode end contained 200 mL of electrolyte solution spiked with the studied contaminants, and only electrolyte solution in the anode. In the second experiment, the opposite was carried out, with only the anode end being spiked with the studied contaminants. The spiked electrolytes contained approx. 8 mg/L of each contaminant. The electrolyte was a 10^{-2} M $NaNO_3$ solution with pH 2. The power supply, electrodes and cation exchange membrane used were the same as the ones used for the ED experiments. The containers were protected from sunlight. Electrolytes pH was not controlled during treatment. The initial sample was collected and then sampling and pH measurements were carried out every 30 min during the experiments. At the end, the final samples were collected and pH and volume registered. Hydrogen peroxide formation was also controlled using Semi-quantitative test strips Quantofix Peroxide 25 (Macherey-Nagel, Germany).

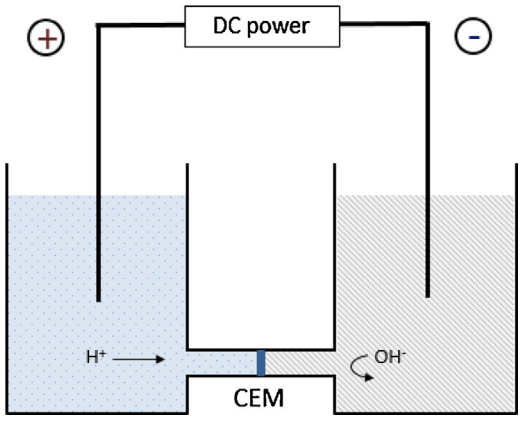

Fig. 2. Scheme of the laboratory cell used for the electrodegradation experiments (CEM-cation exchange membrane).

2.10. Statistical Analysis

Phosphorus and organic contaminants distribution within the cell compartments as well as organic contaminants degradation percentages were comparatively examined. Statistically significant differences among samples for 5% level of significance were evaluated through ANOVA tests using GraphPad Prism software.

3. Results and Discussion

3.1. General results

During the ED treatments, pH variations were recorded along the experiments (Fig. 3(a)). When the sewage sludge was placed in

Table 1
Experimental conditions (electrolyte $NaNO_3$, 10^{-2} M, with pH adjusted to ≤2).

Experiment*	Sludge compartment	Membrane	Current (mA)	Scheme (see figure)
Control-1		CEM	0	
Control-2		AEM	0	
Exp-1	Anode	CEM	20	1a
Exp-2	Anode	CEM	50	1a
Exp-3	Cathode	CEM	20	1b
Exp-4	Cathode	CEM	50	1b
Exp-5	Cathode	AEM	50	1c

Legend: CEM: cation exchange membrane; AEM: anion exchange membrane.
* Two replicates of each experiment were carried out.

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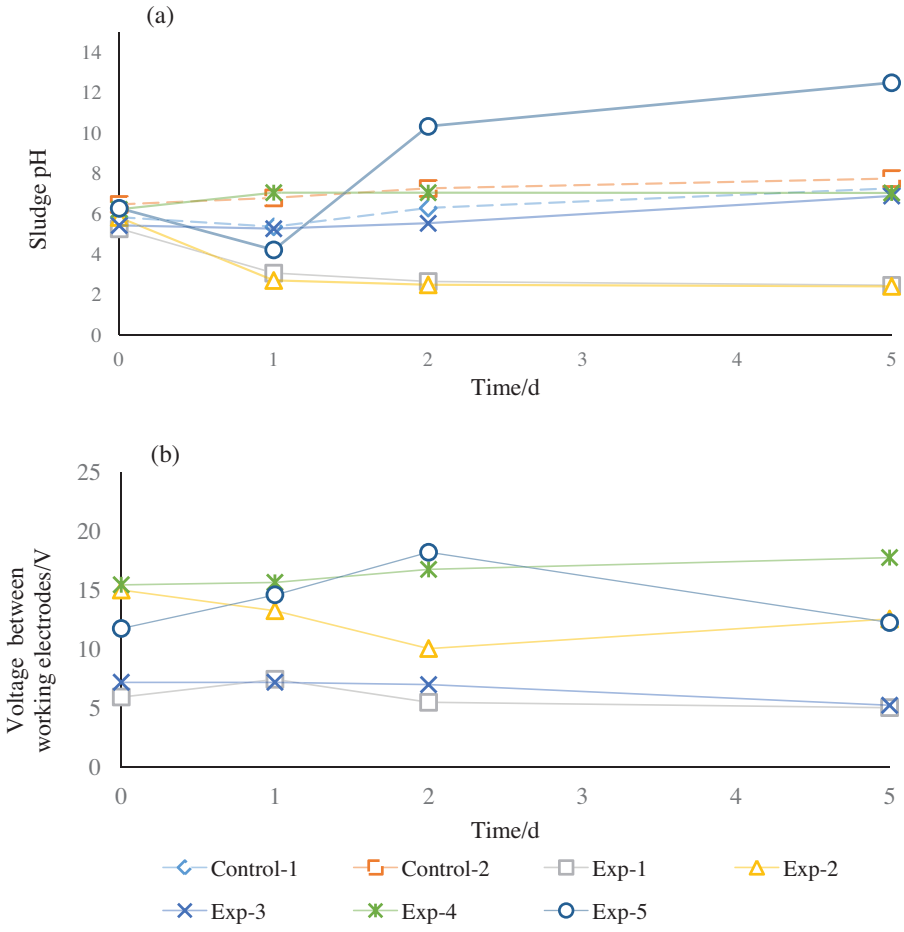

Fig. 3. The development of (a) pH in the sewage sludge compartment during ED and (b) voltage drop between the working electrodes.

the anode compartment, pH decreased till approx. 2.5 ± 0.1 in Exp-1 and 2.4 ± 0.2 in Exp-2. This is mostly due to water electrolysis and formation of H^+ ions in the anode compartment. When the sewage sludge was placed in the cathode compartment and a cation exchange membrane was used, experiments Exp-3 and Exp-4, only slight pH variations were observed, being the final pH approx. 6.9 ± 1.1 and 7.0 ± 1.0, respectively. No major differences were observed between the application of 20 or 50 mA, in the experiments Exp-3 and Exp-4. A slight pH increase could be expected in these cases. A possible explanation is that the pH increase due to the OH^- that are being produced owing to water electrolysis, is being counteracted by H^+ ions that are migrating from the anode to the cathode compartment. The use of an anion exchange membrane prevented this migration, experiment Exp-5, resulting in a high pH increase being observed in the final sewage sludge pH, approx. 12.5 ± 2.9.

In the experiments conducted at 20 mA, independently of the cell design, slight variations were observed in the voltage measured between working electrodes, which was kept between 6.0 and 5.1 V (Fig. 3(b)). This means that the conductivity of the medium was kept somewhat constant along the experiments. In experiment Exp-2 (sewage sludge in the anode compartment, cation exchange membrane, 50 mA) the initial voltage was higher when compared to Exp-1 (same cell design, 20 mA), but after the first day it decreased to approximately 8. When the sewage sludge was placed in the cathode compartment and 50 mA were applied, Exp-4 and Exp-5, the voltage increased, being more pronounced when a cation exchange membrane was used (Exp-4). Experiment Exp-4 also presented a higher voltage in the beginning of the experiment meaning that this cell design resulted in a lower conductivity of the medium.

Since biological processes are extensively used in urban wastewater treatment plants, samples were analysed under the light microscope to observe how ED would affect the microbial community. These changes may affect the potential bioremediation of the contaminants which is an import factor that needs to be considered when further experiments are being designed. Samples prior to ED experiments were defrosted overnight and immediately observed under the light microscope, presenting large compacted flocs with only death bacteria and other animal remains being detected. It was possible to observe protozoa (*Thecamoebae*, swimmers, sessile and bottom cleaners), and rotifer but without activity. After 5 days in the ED cell without direct current, control experiments, the appearance of foam on top of the sewage sludge was detected. After microscope observation a filamentous bacteria, *Thiothrix spp.* was identified and other filamentous bacteria presenting activity were observed. The presence of the hyphae of *fungi* was noticed, probably due to the pH and temperature conditions (no thermal control was done). Death *Arcella hemisphaerica*, algae and vegetal detritus were also observed. In Exp-2, the flocs were more condensed resulting in a very dense sample with high organic content in suspension (very similar to when flocculants are added to the sludge). In both experiments Exp-1 and Exp-2, final pH was below 3 making good conditions for the growth of filamentous bacteria, but only detritus were seen. Algae were also present in the samples. In experiment

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Exp-4, sewage sludge was characterized by condensed organic matter with large flocs. These flocs characteristics are a positive outcome as it may decrease the amount of polyelectrolyte that is needed, as well as the energy used to dehydrate the sludge and, consequently, the cost may decrease in wastewater treatment plants. In terms of biology, less *A. hemispahericas* were detected comparing to control experiments. The filamentous bacteria that were observed in control samples, appear destroyed in the Exp-4 sample. A helical structure was also observed but without cellular wall. The samples presented spiral shaped bacteria, possibly *spirillum* as well as bacteria colonies. In the final samples of experiment Exp-5, *Thecamoebae*, microalgae, filamentous bacteria and vegetal detritus were observed. These results indicate that the electric current and the pH changes will affect the microbial community present in the sewage sludge, supporting the need for further studies to be conducted in order to assess more comprehensively these changes.

3.2. Phosphorus separation

The distribution of P in the different parts of the cell at the end of the ED experiments is shown in Fig. 4, sludge (solid collected after filtration of the sewage sludge), effluent (aqueous phase of the sewage sludge) and electrolyte. In the experiment Control-1, after 5 days, 67 ± 4% of the P was present in the sludge, 28 ± 1% in the effluent and 5 ± 3% was detected in the electrolyte solution (probably due to diffusion). When the control was performed with an anion exchange membrane the effluent presented less 12% of P comparing to Control-1 effluent. The electrolyte of Control-2 presented 16 ± 0.3% of P, being statistically significantly different from Control-1 ($p < 0.05$). Phosphorus has four speciation steps: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-} and the corresponding acid constants (pKa, 298 K) are 2.12, 7.2, and 12. As the pH in the sewage sludge compartment was 7.3 ± 0.3, the P can be present in the forms $H_2PO_4^-$ and HPO_4^{2-}. The ED was then applied, aiming to recover P. In the experiments Exp-1 and Exp-2 (cell design of Fig. 1(a), no statistically significant differences were found between the amount of P that was detected in the sludge, effluent and electrolyte, comparing to Control-1. In both experiments the acidification of the medium did not promote the mobilization of the P from the sludge to the effluent. The P was, in both cases, equally divided between the sludge and effluent, 64 ± 15 % and 35 ± 13%, respectively, for Exp-1 and 56 ± 9% and 39 ± 8% for Exp-2. In Exp-3 (cell design of Fig. 1(b)) still no significant differences were found between the percentages of P in the sludge, effluent and electrolyte. But when 50 mA (Exp-4) were applied in the same cell design, statistically significantly differences were found between the amount of P in the sludge and effluent, comparing to control Control-1 and Control-2. In this case, some amount of P was mobilized from the sludge to the effluent (neutral pH), and at the end of the experiment, 55% ± 5% of P was present in the effluent and 41 ± 1% in the sludge. In all the experiments performed with the cells from Fig. 1(b), a high amount of P was detected in the effluent and, although it was mainly present as anion it did not migrate to the anode end. This was due to the use on the cation exchange membrane to separate de sewage sludge compartment from the anode end that prevented this mobilization.

In experiment Exp-5 (cell design of Fig. 1(c), 78 ± 2% of P were recovered in the electrolyte with only 19 ± 3% remaining in the sludge. This means that the alkaline pH achieved in this experiment helped to mobilize P from the sludge to the effluent. As an anion exchange membrane was used, once in the effluent, P was transported to the anode compartment through electromigration, as it should be mainly present as HPO_4^{2-}/PO_4^{3-}, being this recovery statistically significantly different from Control-2 ($p < 0.05$).

The results show that in the ED tested conditions, P can either be: (i) equally divided between the sludge and the effluent, cell design of Fig. 1(a) at 20 or 50 mA, and of Fig. 1(b) at 20 mA; (ii) recovered in the effluent, cell design of Fig. 1(b) at 50 mA; or (iii) in the electrolyte, cell design of Fig. 1(c).

If the sludge is free of contaminants and rich in P, it can be further treated and if it complies with the legislation it may be applied in agriculture. In experiments Exp-3 and Exp-4, the sludge presents a neutral pH but in the case of experiments Exp-1 and Exp-2, the sludge presents an acidic pH, needing further treatment. In these cases, the effluent also contains P and it can be recovered by promoting, e.g., P precipitation. The same option can be applied for the P recovered in the electrolyte (Exp-5).

3.3. Organic contaminants distribution

The percentage of contaminants detected at the end of the ED experiments in the sludge, effluent and electrolyte are presented in Table 2 (standard deviations are in Table SM3).

Supplementary material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.03.167.

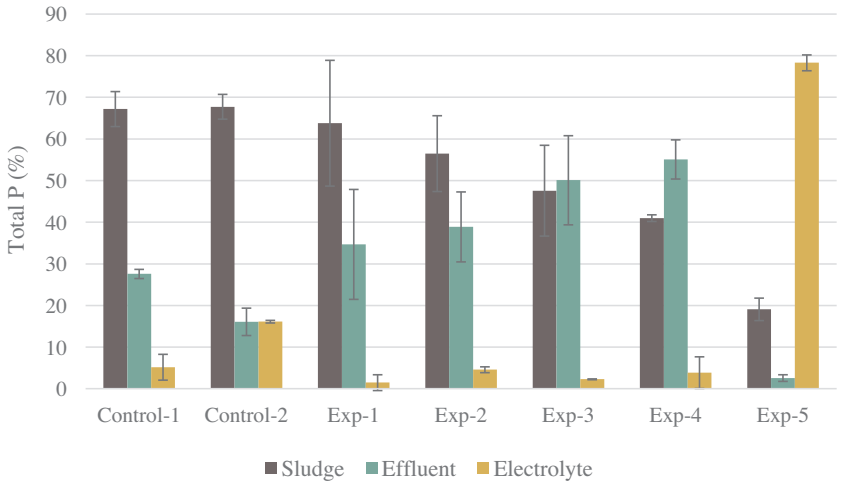

Fig. 4. Distribution of phosphorus at the end of the electrodialytic experiments.

Table 2
Percentage of contaminant detected in the sewage, effluent and electrolyte at the end of the experiments in relation to the initial amount (n = 2).

		Compound					
		Caf	BPA	E2	EE2	IBU	MPBh
Control-1	Sludge	18	32	21	46	93	36
	Effluent	17	7.4	0.7	5.1	6	<LQ
	Elect.	22	2	<LD	14	7.3	<LD
Control-2	Sludge	19	37	32	51	87	38
	Effluent	7	3.2	1.1	3.6	0	5.5
	Elect.	23	0.3	0.5	0.2	26	1.5
Exp-1	Sludge	<LD	33	18	59	43	41
	Effluent	2.3	11	1.3	3.1	2.6	1.8
	Elect.	7.7	<LD	<LD	<LD	<LQ	<LD
Exp-2	Sludge	9.1	35	23	58	37	43
	Effluent	2	7.5	1.1	1.1	2.5	<LQ
	Elect.	3.4	5.7	1.6	2.6	<LQ	<LQ
Exp-3	Sludge	4.2	46	8.7	44	20	57
	Effluent	10	4.9	1	1.9	0.77	0.2
	Elect.	6.6	1.2	<LQ	0.19	3	<LQ
Exp-4	Sludge	29	86	14	80	36	87
	Effluent	15	11	0.3	2	15	<LQ
	Elect.	12	14	2	19	3.2	<LQ
Exp-5	Sludge	<LQ	<LQ	<LD	<LQ	<LD	16.7
	Effluent	<LQ	1.5	0.87	3	0.33	<LQ
	Elect.	29	12	6	14	2.9	<LQ

The majority of the organic contaminants present a log Kow higher than 3.3 and, consequently, at the end of the control experiments, they were mainly detected in the solid phase, sludge, together with P. Some amounts of the contaminants were also detected in the effluent and were able to pass through the ion exchange membranes to the electrolyte compartment, e.g. 22 and 23 % of Caf for Control-1 and Control-2, respectively. Some differences in the contaminants distribution was observed in the control experiments according to the use of an anion or cation exchange membrane. Ibuprofen has a high log Kow (3.97), at the end of control experiments the pH in the sludge was between 7.3–7.7, being mainly in its ionized form, making it more soluble and able to pass through diffusion to the electrolyte. When the control was carried out using an anion exchange membrane, more 19% of Ibu was detected in the electrolyte. A contrary result was observed for EE2 where more 14% was detected in the electrolyte when the cation exchange membrane was used.

In experiments Exp-1 and Exp-2 (cell design of Fig. 1(a), a higher percentage of contaminants was still detected in the sludge. When 20 mA were applied (Exp-1) the contaminants in the electrolyte, except Caf were below limit of quantification and limit of detection, meaning that even if they reached the cathode end, they were effectively degraded. Using the design of Fig. 1(b) and applying 20 mA (Exp-3) resulted in less contaminants being detected in the sludge. In general, higher amounts of contaminants were detected in the sludge and effluent, when the current was increased to 50 mA (Exp-4).

The design used in experiment Exp-5 (Fig. 1(c), with an anion exchange membrane, resulted in the lowest amount of contaminants present in the sludge, as all contaminants were below method limits, except MBPh. As the pH in the sewage sludge compartment was 12.5 ± 2.9, all compounds except Caf were in their ionized form, which made them more soluble and able to migrate to the anode compartment through the anion exchange membrane.

3.4. Organic contaminants degradation

The parallel degradation experiments conducted in the controlled conditions (described in Section 2.9) aimed to assess if the studied organic contaminants could suffer electrodegradation. After 6 h, at the end of the experiments, due to water electrolysis, pH was 13.0 ± 0.1 and 2.5 ± 0.1 in the cathode and anode end, respectively. Solution pH in the cathode end is higher than contaminants pKa, meaning that they will mainly be in their ionized forms. All compounds are assumed to suffer electrodegradation, with estimated percentages between 7.5 and 25% in the anode end, and between 5.5 and 27% at the cathode end, with no statistically significant differences at $p < 0.05$ (Table 3). Hydrogen peroxide was below detection limit in all experiments (0.5 mg/L H_2O_2). Along the ED experiments, the differences found in the degradation percentages are mainly attributed to their chemical structures (Table SM1), reactivity and mechanisms previously studied by different authors [23,24]. The formation of new peaks, corresponding to new or related compounds, was assessed by HPLC-DAD in the samples collected during the experiments. In the anode samples, 6 new peaks were identified and none in the cathode samples. However, the establishment of the degradation mechanisms and products identification was not the objective of the present work and further studies are foreseen for their accomplishment.

In the control experiments, with no applied current (Control-1 and Control-2), the compound that presented higher degradation was E2, followed by MBPh and BPA, Caf and EE2, whereas Ibu was not degraded (Table 3). This degradation is mainly attributed to bioremediation mechanisms, as after the 5 days experiment, bacteria activity was observed in the collected samples (see Section 3.1). Volatilization is not expected to be an important fate process based upon the estimated Henry's Law constant of the here studied compounds (Table SM1). Although differences were observed in contaminants distribution within the cell, no statistical significant differences ($p < 0.05$) were observed for the contaminants degradation between the two control experiments (Control-1 and Control-2).

By using the cell design of Fig. 1(a), it was possible to increase the degradation of Ibu both in Exp-1 and Exp-2 comparing to both controls and Caf in Exp-1 comparing to Control-1 (statistically different, $p < 0.05$). The degradation of the other compounds did not show statistically significant differences ($p < 0.05$) compared to the control experiments, but a tendency to an increased degradation was observed for the estrogens and a decrease in the case of BPA and MBPh.

When the ED cell design of Fig. 1(b) was used, still higher degradations of Ibu were achieved, more 76% in Exp-3 and 46% in Exp-4 comparing to the control experiments, but BPA and EE2 in Exp-4 did not present improved degradations. In these experiments, the electric field promoted the death or changes of the microorganisms present in the sewage sludge, which may have contributed to a decrease in the remediation potential of the medium. The use of 50 mA in Exp-4 decreased the degradation of all contaminants compared to the 20 mA (Exp-3). The results obtained with the cell designs of Fig. 1(a)–(b) are similar for Exp-1/Exp-2 and Exp-3. But the use of 50 mA in Exp-4, resulted in lower degradations than Exp-1 for Caf BPA and MBPh, and than Exp-2 for BPA and MBPh (statistically different, $p < 0.05$).

The higher degradation improvement was found when 50 mA were applied to the sewage sludge placed in the cathode compartment separated from the anode compartment with the anion exchange membrane, cell design of Fig. 1(c). In this case, all degradations were between 71% (Caf) and 97% (Ibu). Comparing to the control experiments, a general tendency for higher degradations was observed for all compounds being statistically different

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Table 3
Degradation percentage* (n = 2).

			Contaminant					
			Caf	BPA	E2	EE2	Ibu	MBPh
Electrodegradation tests	Anode end	$\bar{X}$	7.5	8.5	19	13	25	11
		SD	2.1	3.5	7.1	4.2	4.9	7.8
	Cathode end	$\bar{X}$	5.5	15	16	15	27	19
		sd	2.1	5.7	1.4	0.7	1.4	4.2
Electrodialytic cell experiments	Control-1	$\bar{X}$	43[a]	59[b]	78	35	WD[c]	64[d]
		SD	13	7.7	5.2	27	4.3	5.9
	Control-2	$\bar{X}$	51	60[e]	66[f]	45	WD[g]	55[h]
		sd	5.0	1.8	0.5	2.8	1.5	0.6
	Exp-1	$\bar{X}$	90[a,i]	56[j]	81	38	54[c,g,k]	57[l]
		SD	8.5	0.2	1.0	4.2	13	6.8
	Exp-2	$\bar{X}$	85	52[m]	74[n]	38	61[c,g,o]	57[p]
		sd	9.2	0.9	2.9	11	3.2	0.2
	Exp-3	$\bar{X}$	79	48[q]	90[f,n]	54[r]	76[c,g]	43[s]
		SD	19	2.5	4.0	8.7	13	0.2
	Exp-4	$\bar{X}$	43[i]	WD[b,e,j,m,q,t]	84[f]	WD[r,u]	46[c,g,v]	13[d,h,l,p,w]
		sd	7.9	2.3	6.9	3.9	9.7	15
	Exp-5	$\bar{X}$	71	87[b,e,j,m,q,t]	93[f,n]	83[u]	97[c,g,k,o,v]	83[s,w]
		sd	4.6	15	3.6	12	4.2	12

*% of contaminant degraded = [1 − ∑(mass of contaminant detected in all cell compartments)/(mass of contaminant added to the sewage sludge)] × 100.
WD – Without observed degradation.
Statistics: degradation statistically significantly different at $p < 0.05$ comparing to:
[a] Caf Control-1.
[b] BPA Control-1.
[c] Ibu Control-1.
[d] MBPh Control-1.
[e] BPA Control-2.
[f] E2Control-2.
[g] Ibu Control-2.
[h] MBPh Control-2.
[i] Caf Exp-1.
[j] BPA Exp-1.
[k] Ibu Exp-1.
[l] MBPh Exp-1.
[m] BPA Exp-2.
[n] E2 Exp-2.
[o] Ibu Exp-2.
[p] MBPh Exp-2.
[q] BPA Exp-3.
[r] EE2 Exp-3.
[s] MBPh Exp-3.
[t] BPA Exp-4.
[u] EE2 Exp-4.
[v] Ibu Exp-4.
[w] E2 Exp-4.

for BPA, Ibu comparing to Control-1 and BPA, E2 and Ibu comparing to Control-2 ($p < 0.05$). In the case of MBPh this was the only experiment in which its degradation seems to have improved compared to control tests. By comparing Exp-5 with the other ED experiments, higher degradations were achieved for: BPA than in all the others, EE2 comparing to Exp-4, Ibu in all experiments except Exp-3 and MBPh in Exp-4 and Exp-3, being all statistically different ($p < 0.05$).

In general, ED showed potential to enhance the degradation of the contaminants being the process mainly dependent on the intensity of the applied DC field and the cell design. Some studies have shown that the application of a low level DC field may enhance microorganisms' activity in wastewater [25]. In the conducted experiments, a decrease in the microbial community was observed (Section 3.2), which may have led to a low bioremediation potential within the ED cell. Therefore, if the conditions are optimized to combine the effect of both bio and electrodegradation, higher remediation efficiencies may be achieved. Also, in this study, the initial contaminants concentration was approximately 8 mg/L and at lower concentrations, more similar to the ones entering the wastewater treatment plant, higher electrodegradation percentages may be achieved, e.g. 52% for BPA at 10 mA [15].

4. Conclusions

The application of a low level DC field improved the degradation of Ibu between 46 and 97%, as well as Caf between 20 and 47% (except in Exp-4), comparing to the control experiments, independently of the cell design used. A weaker remediation effect was observed for MBPh, which degradation was less effective when the sewage sludge was subjected to ED, being the only exception the results obtained for Exp-5. In these cases, electrodegradation, promoting changes in the microbial community, may have increased the remediation potential of the medium. As changes in the microbial community were observed in all experiments after the 5 days, this factor needs to be addressed in the design of future experiments.

If the final objective is to remove P from the sludge, the data suggests the use of an ED cell where the sewage sludge is placed at the cathode and the compartment separation is done by an anion

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exchange membrane (experiment Exp-5) as the most viable option. In this case the pH was the main factor affecting the P solubilization from the sludge to the liquid phase. Once in the liquid phase, P electromigrated to the anode end from where it can be recovered by, e.g., precipitation. In total, $78 \pm 2\%$ of P were recovered in the anolyte. However, it also contained five of the six studied contaminants, and further studies are needed in order to improve contaminants' degradation. This cell design also shows the higher potential for contaminants degradation, as in the final sludge all contaminants, except MBPh, were below limit of quantification and limit of detection.

If the aim is to mobilize the P from the sludge to the effluent, the data suggest the placement of the sewage sludge in the cathode compartment separated by a cation exchange membrane as the best option. In this case, the application of 50 mA (Exp-4) resulted in $55 \pm 5\%$ of the P being present in the effluent, and if the current intensity is increased higher recoveries may be achieved. The other experiments resulted in equally divided percentages of P between the sludge and the effluent that were not statistically different ($p < 0.05$) from the control experiments.

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References

[1] D. Cordell, A. Rosemarin, J.J. Schröder, A.L. Smit, Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options, Chemosphere 84 (2011) 747–758.
[2] U.S. Geological Survey, Mineral commodity summaries 2014, U.S. Geological Survey, Reston, Virginia, 2014, pp. 118–119.
[3] D. Cordell, M. Jackson, S. White, Phosphorus flows through the Australian food system: Identifying intervention points as a road map to phosphorus security, Environ. Sci. Policy 29 (2013) 87–102.
[4] European Commission, Disposal and recycling routes for sewage sludge; Part 2–Regulatory report, European Communities, Office for Official Publications of the European Communities, Luxembourg, 2001.
[5] European. Commission, Environmental, economic and social impacts of the use of sewage sludge on land. Final Report. Part III: Project Interim Reports., 2010.
[6] B. Clarke, S. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environ Int. 37 (2011) 226–247.
[7] M. Barret, L. Delgadillo-Mirquez, E. Trably, N. Delgenes, F. Braun, G. Cea-Barcia, J. Steyer, D. Patureau, Anaerobic Removal of Trace Organic Contaminants in Sewage Sludge: 15 Years of Experience, Pedosphere 22 (2012) 508–517.
[8] J. Virkutyte, M. Sillanpää, P. Latostenmaa, Electrokinetic soil remediation — critical overview, Sci. Total Environ. 289 (2002) 97–121.
[9] M.R. Jakobsen, J. Fritt-Rasmussen, S. Nielsen, L.M. Ottosen, Electrodialytic removal of cadmium from wastewater sludge, J. Hazard. Mater. 106 (2004) 127–132.
[10] L.M. Ottosen, A.J. Pedersen, H.K. Hansen, A.B. Ribeiro, Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method, Electrochim. Acta 52 (2007) 3420–3426.
[11] J. Gao, Q.-S. Luo, J. Zhu, C.-B. Zhang, B.-Z. Li, Effects of electrokinetic treatment of contaminated sludge on migration and transformation of Cd, Ni and Zn in various bonding states, Chemosphere 93 (2013) 2869–2876.
[12] G. Peng, G. Tian, J. Liu, Q. Bao, L. Zang, Removal of heavy metals from sewage sludge with a combination of bioleaching and electrokinetic remediation technology, Desalination 271 (2011) 100–104.
[13] J.-Y. Wang, D.-S. Zhang, O. Stabnikova, J.-H. Tay, Evaluation of electrokinetic removal of heavy metals from sewage sludge, J. Hazard. Mater. 124 (2005) 139–146.
[14] V. Ferri, S. Ferro, C.A. Martínez-Huitle, A. De Battisti, Electrokinetic extraction of surfactants and heavy metals from sewage sludge, Electrochim. Acta 54 (2009) 2108–2118.
[15] P. Guedes, E.P. Mateus, N. Couto, Y. Rodríguez, A.B. Ribeiro, Electrokinetic remediation of six emerging organic contaminants from soil, Chemosphere 117 (2014) 124–131.
[16] J.B. Jensen, A. Villumsen, Method and apparatus for the decontamination of products containing heavy metal, Patent Version Number PCT/DK95/00209, 1995.
[17] L.M. Ottosen, H.K. Hansen, C.B. Hansen, Water splitting at ion-exchange membranes and potential differences in soil during electrodialytic soil remediation, J. Appl. Electrochem. 30 (2000) 1199–1207.
[18] L.M. Ottosen, P.E., Jensen, G.M., Kirkelund, B. Ebbers, Electrodialytic recovery and purification of phosphorous from sewage sludge ash, sewage sludge and wastewater, Patent Version Number PCT/EP2014/068956, 2014.
[19] R. Salgado, R. Marques, J.P. Noronha, J.T. Mexia, G. Carvalho, A. Oehmen, M.A. Reis, Assessing the diurnal variability of pharmaceutical and personal care products in a full-scale activated sludge plant, Environ. Pollut. 159 (2011) 2359–2367.
[20] P. Gao, Y. Ding, H. Li, I. Xagoraraki, Occurrence of pharmaceuticals in a municipal wastewater treatment plant: mass balance and removal processes, Chemosphere 88 (2012) 1–24.
[21] N. Ratola, A. Cincinelli, A. Alves, A. Katsoyiannis, Occurrence of organic microcontaminants in the wastewater treatment process. A mini review, J. Hazard. Mater. 239–240 (2012) 1–18.
[22] W. Peysson, E. Vulliet, Determination of 136 pharmaceuticals and hormones in sewage sludge using quick, easy, cheap, effective, rugged and safe extraction followed by analysis with liquid chromatography–time-of-flight-mass spectrometry, J. Chromatogr. A 1290 (2013) 46–61.
[23] S. Yuan, N. Gou, A.N. Alshawabkeh, A.Z. Gu, Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode, Chemosphere 93 (2013) 2796–2804.
[24] N. Xu, Y. Zhang, H. Tao, S. Zhou, Y. Zeng, Bio-electro-Fenton system for enhanced estrogens degradation, Bioresource Technol. 138 (2013) 136–140.
[25] M. Zeyoudi, S.W. Hasan, Evaluation of microbial communities, growth rates and susbtrate consumption under electrical field, in: J.M.R. Maroto, R. García-Delgado, F. García-Herruzo, C. Gómez-Lahoz, C. Vereda-Alonso, M. Villén-Guzmán (Eds.), 13th Symposium on Electrokinetic Remediation, EREM14, Málaga, Spain, 2014, pp. 194.

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PAPER VIII

ELECTRODIALYTIC TREATMENT OF SEWAGE SLUDGE: CURRENT INTENSITY INFLUENCE OF ON PHOSPHORUS RECOVERY AND ORGANIC CONTAMINANTS REMOVAL

Electrodialytic treatment of sewage sludge: current intensity influence on phosphorus recovery and organic contaminants removal

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Abstract

Simultaneous phosphorus (P) recovery and removal of emerging organic contaminants (caffeine, bisphenol A, 17α-ethynylestradiol and oxybenzone) from sewage sludge (SS) was assessed using the electrodialytic (ED) process. The SS samples were collected at the secondary settling tank between May and July, 2015. Different current intensities were tested continuously or sequentially, in a 2 compartment cell, placing the SS in the cathode end, separated from the anode end through an anion exchange membrane. After 24 h, between 45 and 55 % of P electromigrated to the anode end in all experiments. The best results were obtained when 100 mA (0.21 mA/cm^2) were applied for 72 h: 71 % of P in anolyte and between 79 and 96 % of organic compounds degradation. Still, the obtained anolyte enriched in P was not free of organic contaminants.

Keywords: *electrodialysis, sewage sludge, phosphorus separation, emerging organic contaminants degradation.*

1. Introduction

Current population growth requires an increased supply of staple foods, which implies the use of fertilizers to maintain a sufficient nutrient level in agricultural soils. Phosphorus (P) is an essential nutrient for plant growth and its primary source, phosphate rock, is becoming progressively limited (Cordell et al. 2011), being already included in the EU list as one of the 20 Critical Raw Materials (2014). Independently of the time when "P peak" will occur (50-250 years), there is a general consensus that the quality of remaining reserves is in decline (in terms of P_2O_5 content and the presence of heavy metals and other contaminants), that phosphate layers are becoming more physically difficult to access, more waste is being generated and costs are increasing (Schröder et al. 2010).

Sewage sludge (SS) from wastewater treatment plants (WWTP) is a possible secondary P source. Several methods were developed in order to remove P from wastewater, e.g. chemical or biological P precipitation. However, these approaches do not recycle it as a truly sustainable product since P is removed from the liquid phase together with other waste products, such as organic chemicals (Matamoros et al. 2016, Petrie et al. 2015, Murray et al. 2010, Salgado et al. 2011 , Gao et al. 2012 , Ratola et al. 2012), metals (Basta et al. 2005) or pathogens (Gerba and Smith 2005, Elliott and O'Connor 2007, Sidhu and Toze 2009).

The electrokinetic (EK) process is based on the application of a low level current density (direct or alternate; DC or AC), of a few mA/cm and a low potential gradient of V/cm, between suitably located electrodes (Acar and Alshawabkeh 1993). EK based technologies have already demonstrated to have potential to remove different types of contaminants from several contaminated matrices alone and/or coupled with other technologies (Couto et al. 2015a, Couto et al. 2015b, Guedes et al. 2014a, Guedes et al. 2014b, Kirkelund et al. 2015, Mateus et al. 2010, Hansen et al. 2008). In the electrodialytic process (ED) ion-exchange membranes are used as they allow selective separation of anions and cations. Cationic species move towards the cathode through a cation exchange membrane (CEM) that only allows the passage of cations. On the other hand, the anions (e.g., PO_4^{3-}) move towards the anode through an anion exchange membranes (AEM) that only allows the passage of anions. This process provides cations and anions separation in concentrated solutions.

Recently, ED was tested with different cell set-ups aiming simultaneous P recovery and organic contaminants (OCs) removal from frozen SS (Guedes et al. 2015). Overall, the most promising results were achieved when sludge was directly placed in the cathode compartment with an AEM and a current of 50 mA. In this experiment, P was solubilized from the SS due to the high pH achieved in the cathode compartment (pH 13), and then electromigrated to anode compartment. After 5 days, 78% of P was recovered (Guedes et al. 2015). Since the work was carried out with

frozen SS, matrix heterogeneity along the days and consequent differences in its physico-chemical properties were not taken into account.

In this work, the ED process was applied to fresh SS aiming a simultaneous P-separation and OCs removal. Different current intensities were tested, either constant or sequentially. Four contaminants classified as emerging that have been detected all over the world in influents, effluents, SS and fresh water (Matamoros et al. 2016, Petrie et al. 2015, Murray et al. 2010, Salgado et al. 2011 , Gao et al. 2012 , Ratola et al. 2012), were selected for the study. A neural stimulant, caffeine (Caf), an industrial reagent, bisphenol A (BPA), a sunscreen compound, oxybenzone (MBPh) and a synthetic estrogenic steroid hormone, 17α-ethinyloestradiol (EE2). Their chemical properties are presented in Table 1.

Table 1. Chemical structure and properties of the emerging organic contaminants.

Compound	Formula	Log K_{ow} [a]	pKa[b]	Henry's constant (atm-cu m/mole)	Solubility in water (mg/L)	CAS-No
Caffeine (Caf)	$C_8H_{10}N_4O_2$	-0.07	14.0	3.6×10^{-11}	2.16×10^{4} [c]	58-08-2
Bisphenol A (BPA)	$C_{15}H_{16}O_2$	3.32	9.6	1.0×10^{-11}	120 [c]	80-05-7
2-hydroxy-4-methoxybenzophenone (MBPh)	$C_{14}H_{12}O_3$	3.82	7.6	1.5×10^{-8}	69 [c]	131-57-7
17α-ethinyloestradiol (EE2)	$C_{20}H_{24}O_2$	3.67	10.3	7.9×10^{-12}	11.3 [d]	57-63-6

References: http://pubchem.ncbi.nlm.nih.gov/, www.chemicalbook.com, http://SigmaAldrich.com.
Notes: [a] logarithm of the octanol-water partition coefficient; [b] logarithm of acid dissociation constant; [c] at 25 ºC; [d] at 27 ºC.

2. Experimental

2.1. Chemicals and standards

Caffeine (≥90%), BPA (≥99%), EE2 (≥98%) were purchased from Aldrich (Steinheim, Germany) and MBPh (≥98%) from Alfa Aesar (U.S.A.). All used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). Acetonitrile (ACN), methanol (MeOH) and acetone were gradient grade. The water used for analyte extraction and determination was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). Acetic acid (LC–MS grade), sodium hydroxide (NaOH) were purchased from Sigma–Aldrich. Formic acid (LC–MS grade) was from Fluka and sodium nitrate ($NaNO_3$) was reagent grade from Panreac. Individual stock solutions for calibration purposes

were prepared at 400 mg/L in MeOH and stored at −18 °C. Working solutions were prepared by the adequate mixture and dilution of the stock solutions.

2.2. Sewage sludge sampling procedure

The SS samples were collected at a WWTP located in Quinta do Conde, Sesimbra, Portugal (38°34'13" N, 9°2'7" W). The plant has the capacity to treat in the project horizon 19,300 m^3/day of urban wastewater, corresponding to about 94,000 equivalent inhabitants. The level of treatment installed is tertiary. The secondary tank is an aerobic reactor of suspended biomass where appropriate conditions are secured to promote the development of a population of microorganisms which ensure biological purification of wastewater. The effluent of the reactor is then routed to the secondary settling tank for phase separation, where the SS samples were collected, following the recommendations of the norm NF EN ISO 5667-15 (October 2009) on the conservation and treatment of sludge and sediment samples. The samples were then transported to the laboratory (maximum 20 min) and experiments started immediately. Total suspended solids (TSS) determination in the initial samples was carried out at the WWTP laboratory.

2.3. Extraction procedures

2.3.1. Aqueous samples

The extraction of the analytes present in the anolyte and in the aqueous phase of the SS was performed by solid phase extraction (SPE), using Oasis HLB (200 mg, 6 mL) from Waters (Saint-Quentin En Yvelines Cedex, France). The SPE cartridges were conditioned by washing with 3 × 6 mL of methanol, followed by re-equilibrium with 3 × 6 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2 before extraction, using nitric acid. The aqueous samples (200 mL) were passed through the cartridge at a flow-rate of approx. 10 mL/min by applying a moderate vacuum. After, cartridges were dried for approx. 2 min by vacuum. Retained analytes were eluted sequentially with 2 × 3 mL of methanol. All the extracts were collected as one and concentrated under a gentle stream of nitrogen till 0.5 mL. Samples were transferred to a vial and kept at −18 °C until analysis.

2.3.2. Solid samples

Sludge (solid phase of the SS) extraction was performed using QuEChERS extraction (adapted from [22]). Extract tubes were obtained from Waters (Dublin, Ireland). The acetate buffer contained 1.5 g NaOAc and 6 g $MgSO_4$. The dispersive phase contained 150 mg PSA (primary

and secondary amine) and 900 mg $MgSO_4$. A 2 g aliquot of homogenized sludge was weighed in a 50 mL polypropylene centrifuge tube containing NaOAc and $MgSO_4$. Then, 20 mL ACN + acetic acid 1% (v/v) were immediately added and manually shaken for 15 s and then swirled on a vortex mixer for 45 s to homogenize the sample. The extract was centrifuged at 10,000 rpm for 5 min. A 9.5 mL aliquot of the supernatant (ACN phase) was transferred to a 15 mL centrifuge tube containing the PSA and $MgSO_4$, and was manually shaken for 10 s and swirled on a vortex mixer for 60 s. After this step, the extract was centrifuged again (10,000 rpm for 5 min) and 8 mL supernatant were transferred to a 12 mL glass tube. The extract was evaporated under a gentle stream of nitrogen till 0.5 mL. All samples were stored at −20 °C until analysis.

2.4. Analysis by high-performance liquid chromatography with ultraviolet detection

HPLC was performed on a Finnigan MAT HPLC system (Thermo Scientific, USA) equipped with a SP P4000 Pump, a AS 3000 Autosampler, the diode array detector (DAD) was a TSP SpectraSYSTEM UV6000LP with the wavelength set between 200 and 800 nm and a TSP SN 4000 Interface.

The contaminants separation was carried out using Chromolith HighResolution RP-18e column with 100 mm × 4.6 mm from VWR (Darmstadt, Germany) and Onyx SecurityGuard C18 cartridges (5 × 4.6 mm) from Phenomenex (Torrance, USA). All HPLC runs were performed at a constant flow rate of 1 mL/min, in gradient mode, with the oven set to 38 °C. The eluents used were a mixture of ACN / MiliQ water / Formic acid 50% in water (solution A: 5 / 94.5 / 0.5 %; solution B: 94.5 / 5 / 0.5 %), with pH 3.2 and 3.6 for solutions A and B, respectively. The gradient run was set to: 5 min; 97 % A from 0 to 15 min, then to 95% B until 50 min, where it was held until 53 min, then to 97 % A until 55 min. The system re-equilibration was performed for 5 min with 97 % A. All operations and data analysis were processed by the Xcalibur software v.1.3. (Thermo Scientific, USA). Method limit of detection (LD) and quantification (LQ) is available in the supplementary material (Table SM1).

2.5. Phosphorus extraction and analysis

The concentration of P in the solid sludge was determined after its pre-treatment in accordance to EPA3051: 0.5 g of dry sludge and 10 mL of HNO_3 (65%) were placed in a vessel and extracted in a Microwave from Milestone Ethos (Bergamo, Italy). The microwave programme was set to reach 175 ºC in 15 min, and then keep the temperature for another 15 min. After, the samples were collected and filtered through a 0.45 µm filter and stored until analysis. Liquid samples (anolyte and effluent) were also filtered through a 0.45 µm filter and stored until analysis. The P

content was measured in an Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP–AES), Varian 720-ES.

2.6. pH desorption tests

To determine the pH dependent P desorption, 4 g of filtered SS was suspended in 20 mL of different concentrations of HNO_3 and NaOH, as well as in deionized H_2O, in order to have solutions with pH between 1 and 14. The suspensions were placed at an agitating table for 24 h at room temperature. At the end, pH was measured, suspensions were filtered by vacuum using 0.45 µm filters and P concentrations were measured by ICP-AES.

2.7. Electrodialytic laboratory cell

The experiments were carried out in a 2 compartment (2C) ED laboratorial cell [18] (Figure 1). The 2C-cell had an internal diameter of 8 cm, an electrode each, and were separated by a commercial anion exchange membrane, from Ionics (AR204 SZRA B02249). The compartment where the sludge was place had a L = 10 cm and was equipped with a stirrer, whereas the anolyte compartment had a L = 5 cm. The electrodes were platinized titanium bars, with a 3 mm diameter and a length of 5 cm (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark). A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC and voltage drop was also monitored (Kiotto KT 1000H multimeter). The electrolyte, 10^{-2} M $NaNO_3$, was recirculated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions.

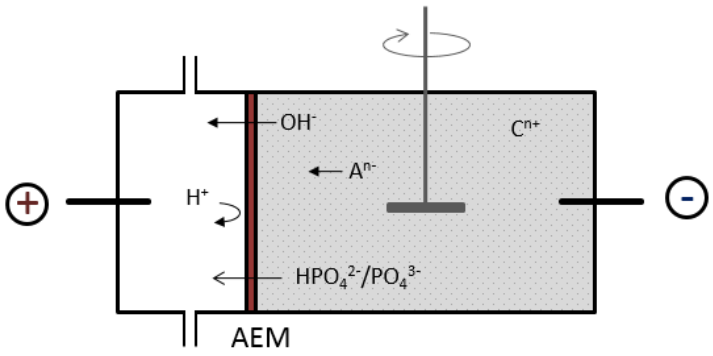

Figure 1. Schematic design of the 2 compartment electrodialytic laboratory cell. AEM – anion exchange membrane; A^{n-} – anions; C^{n+} – cations)

2.8. Electrodialytic experimental conditions

The ED cell sludge compartment (cathode) was filled with 350 g of SS (90-95% water). For this, a funnel was placed in the agitator hole and the sludge was poured through it and, since the sludge was too thick, 50 mL of deionized water were added to help the passage through the funnel. Prior to the beginning of the experiments, the sludge was spiked with a mixture of the contaminants under study. In order to assess the contaminants´ mobilization and removal under the influence of ED, the SS was spiked with approximately 7.5 mg/L of each analyte in 1:1 MeOH:Acetone (7.00 ppm Caf; 7.24 ppm BPA; 7.46 ppm EE2; 7.51 ppm MBPh). These high concentrations aimed to assure that all the contaminants would be quantified or detected in all cell compartments at the end of the experiments (anolyte, sludge and effluent), even if high degradation efficiencies happened, in order to test technique limits.

Laboratory assays were carried out for 3 days according to the experimental conditions presented in Table 2. In total six experiments were done in duplicate, in a fume hood protected from sunlight. A control experiment without the application of electric current (Control), and three other with the application of 50, 75 and 100 mA. One experiment was carried out increasing the current intensity every 24 h, 50-75-100 mA, and another decreasing, 100-75-50 mA. In the experiments the application 50 mA to 0.10 mA/cm^2, 75 mA to 0.16 mA/cm^2 and 100 mA to 0.21 mA/cm^2.

During the experiments, voltage drop, current intensity, pH and conductivity were measured, as well as anolyte sampled for total-P analysis. To measure the pH and conductivity, samples from the SS and the anolyte were collected to a small beaker, measured and then returned to the ED cell.

At the end of the experiments anolyte samples were collected. The SS was also collected, centrifuged and filtrated under vacuum to separate the solid (sludge) from the liquid phase (effluent). The filtrated sludge was then extracted (two replicates) for OCs determination as described in section 2.3.2. The remaining sludge sample was then dried in an oven at 50 ºC till constant weight and the water content determined. Finally, for P determination, the dried sludge sample was extracted as described in section 2.5. The liquid samples, effluent and anolyte, were then filtered through a 0.45 µm filter and extracted as described in section 2.3.1. for OCs, and section 2.5. for P ICP-AES determination.

The membrane and cathode were soaked in HNO_3 (1 and 5 M, respectively) for 24 h and the liquid was used for further P analysis.

Table 2. Experimental conditions (anolyte $NaNO_3$, 10^{-2}M).

Experiment*	Fresh sewage sludge		Current intensity (mA) δ	Time (day)
	Code	Sampling date		
Control	S1	12-05-2015	0	3
Exp-1	S2	19-05-2015	50	
Exp-2	S3	02-06-2015	75	
Exp-3	S4	16-06-2015	100	
Exp-4	S5	30-06-2015	50-75-100	
Exp-5	S6	07-07-2015	100-75-50	

* Two replicates of each experiment were carried out.

δ 50 mA = 0.10 mA/cm^2 ; 75 mA = 0.16 mA/cm^2; 100 mA = 0.21 mA/cm^2.

2.9. Statistical Analysis

Statistically significant differences among samples for 5% level of significance were evaluated through ANOVA tests using GraphPad Prism software. Statistical differences were analysed for P distribution within the different matrices in the same experiment, as well as between the different experiments for the same matrices. In terms of organic compounds, degradation percentages of each compound in the control were, firstly, individually compared to the different experiments with current and, secondly, different compounds in the same experiment. The distribution was analysed in three variables: (i) same compound, same experiment, different matrices; (ii) same compound, different experiments, same matrices, and (iii) different compounds, different experiments, same matrices.

3. Results and Discussion

3.1. General results

The initial fresh SS sample presented an average P content (n=12) of 4.68 ± 0.62% (Table 3). Total suspended solids (TSS) were between a maximum of 33600 mg/L in the sample collected on May 5, 2015, and a minimum of 22700 mg/L in the sample collected on July 9, 2015. During the control experiment, SS pH slightly increased from 6.4 to 7.4 (RSD of 10%). After applying ED, SS pH increased to values between 9.8 (RSD of 35%) and 10.6 (RSD of 34%), in relation to SS initial pH (Table 3). This increase occurred due to the formation of OH^- from water electrolysis. The initial sample conductivity varied between 873 and 1054 µS/cm (RSD of 7%). After the application of the electric field conductivity increased to values between 1502 µS/cm in Exp-1 (RSD of 25%, comparing to the initial value) and 2920 µS/cm in Exp-2 (RSD of 70%,

245 comparing to the initial value). This variation may be due to the solubilization of the different
246 ionic species present in the sample, decreasing system resistance and promoting voltage decrease
247 along the experiments. In the anolyte, pH decreased due to the formation of H^+ and the
248 conductivity increased. In terms of voltage drop, a decrease was always observed between the
249 initial and the final of the experiments, suggesting that during the 3 days, fouling was not
250 occurring.

Table 3. Parameters measured at the beginning and at the end of the electrodialytic experiments.

	before ED							after ED						
	Sewage sludge					Anolyte		Sewage sludge			Anolyte		Voltage drop (V)	
Exp.	**P (g/kg d.w.)**	**TSS (mg/L)**	**pH**	**Conductivity (µS/cm)**	**% H_2O**	**pH**	**Conductivity (µS/cm)**	**pH**	**Conductivity (µS/cm)**	**% H_2O**	**pH**	**Conductivity (µS/cm)**	**Initial**	**Final**
Control	45.5 ± 3.1	33600	6.4	873	93.0	5.5	1211	7.4 ± 0.4	1703 ± 501	96.6 ± 0.4	7.8 ± 0.3	1042 ± 11	-	-
Exp-1	51.1± 8.5	32600	6.5	1054	94.1	6.1	1342	10.6 ± 0.5	1502 ± 81	96.9 ± 0.2	2.1 ± 0.0	3945 ± 318	32 ± 3	19 ± 0
Exp-2	45.5 ± 3.0	28250	6.7	983	93.2	5.2	1194	10.1 ± 1.2	2920 ± 1499	91.3 ± 1.0	1.6 ± 0.1	6515 ± 2044	48 ± 2	32 ± 10
Exp-3	56.9± 1.3	32550	7.0	1054	91.9	5.7	1158	10.0 ± 0.9	2418 ± 1531	93.5 ± 0.5	1.9 ± 0.1	4705 ± 431	38 ± 3	25 ± 4
Exp-4	41.0± 5.5	27400	6.8	989	93.0	6.9	1146	10.0 ± 1.4	2161 ± 1300	90.6 ± 2.8	1.6 ± 0.0	4985 ± 78	27 ± 0	29 ± 1
Exp-5	41.0± 6.4	22700	6.8	974	92.1	7.2	1372	9.8 ± 0.7	1824 ± 198	92.5 ± 1.7	1.4 ± 0.0	6620 ± 269	50 ± 3	17 ± 6

3.2. Organic contaminants degradation and distribution

The amount of contaminants not detected (electrolyte, effluent and sludge) was considered as degraded (values presented in Table 4). Degradations observed in the Control experiment may be attributed to bioremediation (Guedes et al. submitted), fluctuating between 65% for EE2 and 87% for Caf, with no statistically differences (p<0.05) among compounds. Comparing these results with the study carried out with frozen sludge (Guedes et al. 2015), higher degradations were achieved when a fresh SS was used, which increased 36%, 26%, 20% and 17% for Caf, BPA, EE2 and MBPh, respectively. Similar degradations/removals have been obtained in other studies (Melcer and Klečka 2011, Onesios et al. 2009). Although removal efficiencies differ, reported average for BPA in full-scale facilities was 84% (Melcer and Klečka 2011), for CAF was greater than 80% in full scale, pilot scale membrane bioreactor, subsurface flow and a batch system (Onesios et al. 2009). For EE2, removals were 75% and 85% in anaerobic digesters, whereas in batch experiments they were 100% and 20% (Melcer and Klečka 2011). Using a membrane bioreactor, MBPh removal achieved 41% and 50% in pilot-scales and 99% in batch experiments (Melcer and Klečka 2011).

After the application of a direct current, compounds degradation improved (between more 2 and 18% of degradation), with a a few exceptions (Figure 1). The best improvement was observed for EE2 that was always 10% higher in all ED experiments, although no statistically significant differences were observed (p<0.05). MBPh also presented improvements, between 7.5% and 14%. The lowest degradation rate was obtained for CAF in Exp-4, which decreased approx. 24% when compared to Control (no observed statistically differences, p<0.05). BPA presented the lowest results after the application of a direct current. Its degradation only improved in Exp-1 and Exp-5 (5 and 6%, respectively) comparing to the Control.

Table 4. Percentage of contaminant detected in the effluent, sewage and anolyte (electrolyte for the Control experiments) and degraded at the end of the experiments in relation to the initial amount (n=2).

		Compound			
		Caf	**BPA**	**MBPh**	**EE2**
Control	Sludge	<LD [a, b]	13 ± 6 [a]	28 ± 7[B]	34 ± 1[A]
	Effluent	11 ± 12	1.2 ± 1.3	0.28 ± 0.16 [b]	0.93 ± 0.48 [a]
	Electrolyte	2.7 ± 0.3	<LD	<LD [b]	<LD [a]
	Degradation	87 ± 12	86 ± 7	72 ± 7	65 ± 1
Exp-1	Sludge	8.6 ± 0.4	<LD	16 ± 1	13 ± 3 [a]
	Effluent	3.1 ± 4.4[d]	2.2 ± 1.2	1.3 ± 0.2	1.1 ± 0.6
	Anolyte	[δ]	6.0 ± 3.4	1.2 ± 0.5	2.7 ± 0.4
	Degradation	88 ± 4	92 ± 5	82 ± 1	83 ± 2
Exp-2	Sludge	4.5 ± 0.2 [c]	13 ± 11	18 ± 2	26 ± 8 [C]
	Effluent	6.0 ± 2.7	5.1 ± 0.4	0.83 ± 0.34	2.2 ± 0.5 [c]
	Anolyte	[δ]	7.9 ± 2.9	0.21 ± 0.23	2.4 ± 2.1 [c]
	Degradation	89 ± 3 [f]	74 ± 8	81 ± 1	70 ± 5
Exp-3	Sludge	<LD	4.1 ± 5.9	14 ± 2	18 ± 3
	Effluent	3.8 ± 0.2	5.1 ± 2.8	0.90 ± 0.45	2.7 ± 0.8
	Anolyte	<LD	10.0 ± 13.1	0.67 ± 0.85	0.15 ± 0.21
	Degradation	96 ± 0[f]	81 ± 5	85 ± 1	79 ± 2
Exp-4	Sludge	14 ± 9	6.3 ± 8.9	19 ± 14	17 ± 0
	Effluent	22.7 ± 4.2 [D]	3.8 ± 4.4	0.76 ± 0.34 [d]	2.2 ± 1.0 [d]
	Anolyte	<LD [d]	6.7 ± 8.8	0.76 ± 0.73	<LD
	Degradation	63 ± 13 [F]	83 ± 5	79 ± 14	80 ± 1
Exp-5	Sludge	6.9 ± 1.0	6.9 ± 0.2	16 ± 4	25 ± 8
	Effluent	0.57 ± 0.19 [d]	2.0 ± 1.0	0.57 ± 0.19	<LD [e]
	Anolyte	<LD	0.64 ± 0.91	0.24 ± 0.09	<LD[e]
	Degradation	93 ± 10 [f]	91 ± 2	83 ± 5	75 ± 8

% OC degraded = [1- ∑(OC mass detected in all cell compartments)/(OC mass added to sewage sludge)]*100;
< LD: Below detection limit;
[δ] Compound not quantified due to co-elution during the analysis;
Statistics: percentage statistically significantly different at $p<0.05$ comparing to:
[a] EE2 sludge Control;
[b] MBPh sludge Control;
[c] EE2 sludge Exp-2;
[d] Caf effluent Exp-4
[e] EE2 sludge Exp-5;
[f] CAF degradation Exp-4;

In general, the increase in the current intensity (from 50 to 100 mA) did not improve contaminants degradation. The only statistical difference (p<0.05) was found for Caf, which degradation in Exp-4 (50-75-100 mA) was lower than Exp-2, Exp.3 and Exp-5. This may be attributed to the sequential current applied and also to a decrease in biodegradation potential of the medium when compared to the other experiments (Guedes et al. submitted).

In terms of OC profile within the cell, compounds percentage detected in sludge increases 0% Caf < 13% BPA < 28% MBPh ≈ 34% EE2 as the log K_{ow} increases and the solubility decreases (Table 1). In the case of EE2 and MBPh, which have similar log K_{ow} (3.67 and 3.82, respectively), the lower solubility of EE2 (11.3 mg/L vs. 69 mg/L) may have influenced the results. In the sludge, the amount of EE2 is statistically higher than the amount of the others compounds (except MBPh). In the effluent, although statistically differences (p<0.05) were not observed, the opposite trend is observed as the amount of compounds detected decreases as the log K_{ow} increases. The percentage of EE2 detected in the sludge of the Control experiment was statistically different (p<0.05) from the amounts detected in the effluent and electrolyte. Diffusion through the AEM after 3 days was only observed for Caf (3% in the electrolyte). One hypotheses, is that caffeine may have been able to pass through the AEM due to similarities between its functional group and membrane charged groups (e.g. $–NH_3+$, $–NRH_2^+$, $–R_2H^+$, $–NR_3^+$) as well as its high solubility.

When current was applied pH in the cathode compartment increased in all experiments to values above compounds pKa, except for Caf (pKa 14). This means that BPA, EE2 and MBPh suffered deprotonation, being mainly present as anions bing able to electromigrate to the anode compartment. Once in the anode compartment, these compounds may suffer anodic oxidation. In Exp-5, the electrolyte presented the lowest amount of compounds comparing to the other experiments with current. In this experiment, only two compounds were detected in the anolyte at a very low concentration (below 0.64 ppm).

Changes in compounds profile due to the application of a DC were also observed in the experiments. Differences (p<0.05) were found in the amount of EE2 detected in the sludge of Exp-1 comparing to Control-3, showing that the application of 50 mA, decreased the amount of compound adsorbed to the sludge. This may occur due to the increase in the increased degradation and, as the compound was mainly ionized (pKa<pH), to its distribution within the cell.

Tested conditions showed that compounds degradation were not complete. Still, concentrations higher than the ones found in the environment were used in the experiments to allow assess OCs behaviour within the cell. The use of different electrodes may also be an option in trying to increase compounds degradations (Sirés and Brillas 2012, He et al. 2013, Martín de Vidales et al. 2015, Cong et al. 2014, Indermuhle et al. 2013). Also, in the present study, OCs were considered removed as the elimination of parent organic compound. The extent of biodegradation and parent

compound loss indicates biotransformation of an unknown degree, and not necessarily mineralization. Further studies are needed to assess degradation extent, mechanisms and by-product formation.

3.3. Phosphorus separation

For P recovery through electromigration, four speciation states, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^3, need to be considered. The corresponding acidity constants (pKa, 298 K) are 2.12, 7.2, and 12. At pH below 2, phosphate dominantly exists as phosphoric acid and has no charge, being unaffected by the electric field. Under alkaline conditions (pH 7), bi- and trivalent species prevail, which implies a double or a triple amount of energy to move one phosphate ion (Sturm et al. 2010). Phosphorus desorption was initially assessed at pH values between 1 and 14. The highest desorption as obtained at approx. pH 13, when 123 mg P/L were solubilized from sludge. For the other tested pH, 48 mg/L of P at pH 1.06 were desorbed and only 7 and 12 mg/L of P at pH 5.84-6.19. Therefore, in ED experiments is expected that, the high pH reached in the cathode compartment (Table 3) results in high P solubilization from the sludge to the effluent. Once P is present in an ionic form, it will be able to migrate to the anolyte.

Table 5. Parameters measured at the beginning and at the end of the electrodialytic experiments (n = 2).

Compartment	Control	Exp-1	Exp-2	Exp-3	Exp-4	Exp-5
Anolyte*	29.2 ± 1.1$^{a, G}$	53.3 ± 9.7$^{b, g, i}$	62.9 ± 0.7$^{c, g}$	70.3 ± 2.0$^{d, g, I}$	59.9 ± 3.6$^{e, g}$	56.7 ± 2.1$^{f, g}$
Effluent	8.90 ±2.13^{a}	5.91 ± 1.41^{B}	2.06 ± 0.77^{c}	3.68 ± 2.48^{d}	2.52 ± 0.50^{e}	2.47 ± 1.97^{F}
Sludge	61.9 ±3.2$^{a, H}$	40.7 ± 1.1$^{b, h}$	35.0 ± 0.1$^{c, h}$	26.0 ± 0.5$^{d, h}$	37.5 ± 4.1$^{e, h}$	40.8 ± 0.3$^{f, h}$

*in the case of the Control experiments, anolyte is regarded as Electrolyte
Statistics: percentage statistically significantly different at $p<0.05$:
[a]between Control matrices;
[b]comparing to Exp-1 effluent ;
[c]between Exp-2 matrices;
[d]between Exp-3 matrices;
[e]between Exp-4 matrices;
[f]comparing to Exp-5 effluent;
[g]comparing to Control electrolyte;
[h]comparing to Control sludge;
[i]comparing to Exp-3 anolyte.

All SS samples used in the experiments were initially analyzed to assess P distribution. A value of 7.2 ± 3.9% of the total P (n = 12) was present in the effluent whereas 93.0 ± 2.6% was in the sludge. At the end of the ED experiments, P distribution in the different parts of the cell, such as sludge (solid collected after filtration of the SS), effluent (aqueous phase of the SS) and

electrolyte, are presented in Table 5. After 3 days, Control experiment showed that29% of P were able to pass through the AEM, being detected in the electrolyte, with 62% of P remaining in the sludge.

When the electric current was applied, the amount of P detected in the electrolyte at the end of the experiments increased in all treatments compared to control (more 24-41%), whereas the amount in the sludge decreased (statistically significantly different in all treatments, $p<0.05$). Between the experiments conducted with current, no statistical differences ($p<0.05$) were found in the amount of P detected in the sludge, although a tendency can be seen: increasing the current seems to increase the amount of P extracted from the sludge (Exp-1, Exp-2 and Exp3; linear tendency with m = 0.3399, $r^2 = 0.9949$). In all experiments the percentage of P detected in the sludge ranged between 26% (Exp-3) and 41% (Exp-5). The highest recovery in the electrolyte was 70% in Exp-3 (100 mA) and the lowest 53% in Exp-1, being these two values statistically different ($p<0.05$). The use of a sequential current (Exp-4 and Exp-5) did not improve P recovery.

Initial samples were mainly characterized by inorganic-P (90%). After ED the electrolyte contained between 57% (Exp-1) and 99% (Exp-5) of organic-P. One hypotheses is that P may have reacted with other compounds containing carbon present in the system, either in the sludge compartment or in the anode compartment.

Observing the amount of P that reached the anolyte along the 72 h of experiment (Figure 3), it can be seen that the maximum percentage of P recovered was achieved during the first 24 h of all experiments. The highest recovery velocity was verified in Exp-3 (100 mA), 22 mg P *per* kg d.w. *per* min in the first 24 h after which, recoveries velocity decreases. A similar pattern was also reported by Ebbers et al. (Ebbers et al. 2015). This can be explained by the precipitation of P as calcium phosphate e.g. in the form of hydroxyapatite (eq. 1) at higher pH values (8∼10) (Ferguson et al. 1973).

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \longrightarrow Ca_5(PO_4)OH \quad \textbf{(eq. 1)}$$

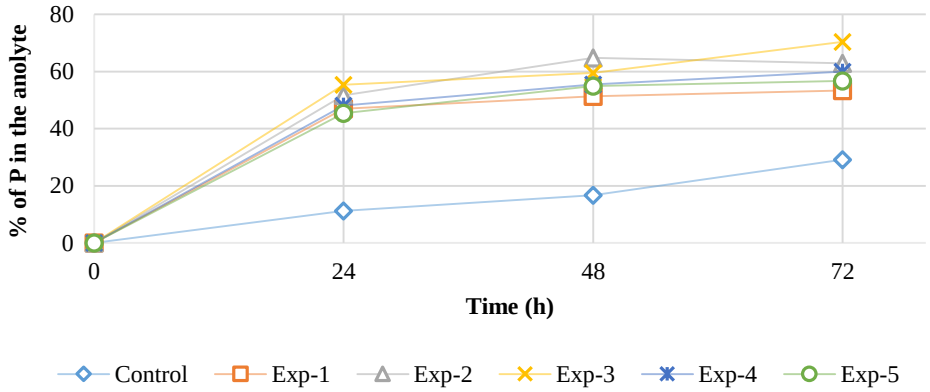

Figure 3. Percentage of P detected in the anolyte along the experiments (t1, t2 and t3).

4. Conclusions

In general, the application of a DC improved the organic compounds degradation in the fresh SS. An increase in the current intensity did not result in higher contaminants removal. At the end of the experiments, a free of OCs P solution was not achieved.

The highest P recovery obtained was 70.3± 2.0%, when 100 mA were applied for 3 days. Tested conditions demonstrated that P recovery could have been carried out only for 24 h decreasing associated energetic costs, since P recovery was 55 ± 3.5%.

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References

Cordell, D., Rosemarin, A., Schröder, J.J. and Smit, A.L. (2011) Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. Chemosphere 84(6), 747-758.

Schröder, J.J., Cordell, D., Smit, A.L. and Rosemarin, A. (2010) Sustainable Use of Phosphorus, EU Tender ENV.B.1/ETU/2009/0025.

Matamoros, V., Rodríguez, Y. and Albaigés, J. (2016) A comparative assessment of intensive and extensive wastewater treatment technologies for removing emerging contaminants in small communities. Water Research 88, 777-785.

Petrie, B., Barden, R. and Kasprzyk-Hordern, B. (2015) A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Research 72, 3-27.

Basta, N.T., Ryan, J.A. and Chaney, R.L. (2005) Trace element chemistry in residual-treated soil: key concepts and metal bioavailability. Journal of Environmental Quality (34), 49-63.

Gerba, C.P. and Smith, J.E. (2005) Sources of Pathogenic Microorganisms and Their Fate during Land Application of Wastes. Journal of Environmental Quality 34(1), 42-48.

Elliott, H.A. and O'Connor, G.A. (2007) Phosphorus management for sustainable biosolids recycling in the United States. Soil Biology and Biochemistry 39(6), 1318-1327.

Sidhu, J.P.S. and Toze, S.G. (2009) Human pathogens and their indicators in biosolids: A literature review. Environment International 35(1), 187-201.

Acar, Y.B. and Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation. Environmental Science & Technology 27(13), 2638-2647.

Couto, N., Guedes, P., Zhou, D.-M. and Ribeiro, A. (2015a) Integrated perspectives of a greenhouse study to upgrade an antimony and arsenic mine soil – Potential of enhanced phytotechnologies. Chemical Engineering Journal 262, 563-570.

Couto, N., Guedes, P., Ferreira, A.R., Teixeira, M.R., Mateus, E.P. and Ribeiro, A.B. (2015b) Electrodialytic process of nanofiltration concentrates – phosphorus recovery and microcystins removal. Electrochimica Acta 181, 200-207.

Guedes, P., Mateus, E.P., Couto, N., Rodríguez, Y. and Ribeiro, A.B. (2014a) Electrokinetic remediation of six emerging organic contaminants from soil. Chemosphere 117(0), 124-131.

Guedes, P., Couto, N., Ottosen, L.M. and Ribeiro, A.B. (2014b) Phosphorus recovery from sewage sludge ash through an electrodialytic process. Waste Management 34(5), 886-892.

Kirkelund, G.M., Magro, C., Guedes, P., Jensen, P.E., Ribeiro, A.B. and Ottosen, L.M. (2015) Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension – test of a new two compartment experimental cell. Electrochimica Acta 181, 73-81.

Mateus, E., Zrostlíková, J., Gomes da Silva, M., Ribeiro, A. and Marriott, P. (2010) Electrokinetic removal of creosote from treated timber waste: a comprehensive gas chromatographic view. Journal of Applied Electrochemistry 40(6), 1183-1193.

Hansen, H.K., Rojo, A., Pino, D., Ottosen, L.M. and Ribeiro, A.B. (2008) Electrodialytic remediation of suspended mine tailings. Journal of Environmental Science and Health, Part A 43(8), 832-836.

Guedes, P., Magro, C., Couto, N., Mosca, A., Mateus, E.P. and Ribeiro, A.B. (2015) Potential of the electrodialytic process for emerging organic contaminants remediation and phosphorus separation from sewage sludge. Electrochimica Acta (0).

460 Murray, K.E., Thomas, S.M. and Bodour, A.A. (2010) Prioritizing research for trace pollutants
461 and emerging contaminants in the freshwater environment. Environmental Pollution 158(12),
462 3462-3471.
463 Salgado, R., Marques, R., Noronha, J.P., Mexia, J.T., Carvalho, G., Oehmen, A. and Reis, M.A.
464 (2011) Assessing the diurnal variability of pharmaceutical and personal care products in a
465 full-scale activated sludge plant. Environmental Pollution 159 2359-2367.
466 Gao, P., Ding, Y., Li, H. and Xagoraraki, I. (2012) Occurrence of pharmaceuticals in a municipal
467 wastewater treatment plant: mass balance and removal processes. Chemosphere 88, 1-24.
468 Ratola, N., Cincinelli, A., Alves, A. and Katsoyiannis, A. (2012) Occurrence of organic
469 microcontaminants in the wastewater treatment process. A mini review. Journal of Hazardous
470 Materials 239–240(0), 1-18.
471 Guedes, P., Rodrigues, A., Almeida, J., Couto, N., Mateus, E.P. and Ribeiro, A.B. (submitted)
472 Electrodialytic treatment of sewage sludge: influence on microbiological community.
473 Melcer, H. and Klečka, G. (2011) Treatment of wastewaters containing bisphenol A: State of the
474 science review. Water Environment Research 83(7), 650-666.
475 Onesios, K., Yu, J. and Bouwer, E. (2009) Biodegradation and removal of pharmaceuticals and
476 personal care products in treatment systems: a review. Biodegradation 20(4), 441-466.
477 Sirés, I. and Brillas, E. (2012) Remediation of water pollution caused by pharmaceutical residues
478 based on electrochemical separation and degradation technologies: A review. Environment
479 International 40, 212-229.
480 He, J., Yu, H., Fugetsu, B., Tanaka, S. and Sun, L. (2013) Electrochemical removal of bisphenol
481 A using a CNT-covered polyester yarn electrode. Separation and Purification Technology 110,
482 81-85.
483 Martín de Vidales, M.J., Millán, M., Sáez, C., Pérez, J.F., Rodrigo, M.A. and Cañizares, P. (2015)
484 Conductive diamond electrochemical oxidation of caffeine-intensified biologically treated
485 urban wastewater. Chemosphere 136, 281-288.
486 Cong, V.H., Iwaya, S. and Sakakibara, Y. (2014) Removal of estrogens by electrochemical
487 oxidation process. Journal of Environmental Sciences 26(6), 1355-1360.
488 Indermuhle, C., Martín de Vidales, M.J., Sáez, C., Robles, J., Cañizares, P., García-Reyes, J.F.,
489 Molina-Díaz, A., Comninellis, C. and Rodrigo, M.A. (2013) Degradation of caffeine by
490 conductive diamond electrochemical oxidation. Chemosphere 93(9), 1720-1725.
491 Sturm, G., Weigand, H., Marb, C., Weiß, W. and Huwe, B. (2010) Electrokinetic phosphorus
492 recovery from packed beds of sewage sludge ash: yield and energy demand. Journal of Applied
493 Electrochemistry 40(6), 1069-1078.
494 Ebbers, B., Ottosen, L.M. and Jensen, P.E. (2015) Comparison of two different electrodialytic
495 cells for separation of phosphorus and heavy metals from sewage sludge ash. Chemosphere
496 125(0), 122-129.

497 Ferguson, J.F., Jenkins, D. and Eastman, J. (1973) Calcium Phosphate Precipitation at Slightly
498 Alkaline pH Values. Journal of the Water Pollution Control Federation 45(4), 620-631.

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500