Joana Sofia Guerreiro Pinto

Licenciada em Engenharia do Ambiente

Removal of organic contaminants from wastewater using the electrodialytic process

Dissertação para obtenção do Grau de Mestre em
Engenharia do Ambiente, Perfil de Engenharia Sanitária

Orientador: Doutora Maria da Nazaré Parada Figueiredo
de Sousa Couto Alves, CENSE, FCT-UNL

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Setembro de 2015

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Resumo

Os produtos farmacêuticos e de cuidado pessoal (PFCPs) são utilizados no dia-a-dia, um pouco por todo o mundo. Após a sua utilização chegam às estações de tratamento de águas residuais (ETAR) e, sendo tão diferentes entre si do ponto de vista físico-químico, torna-se difícil a sua remoção completa através dos processos convencionais. Não existe ainda legislação relativamente a limites de descarga de PFCPs no efluente. No entanto, mesmo em quantidades vestigiais, estes contaminantes representam riscos ambientais nomeadamente devido ao seu potencial de desregulação endócrina. Existe portanto a necessidade de procurar alternativas para a remoção destes compostos nas ETARs. Este trabalho tem como principal objetivo estudar a utilização do processo eletrodialítico (ED) para a remoção de PFCPs do efluente a ser descarregado. Foi usada uma célula ED de dois compartimentos tendo sido testada (i) a posição do efluente na célula (ânodo e cátodo); (ii) o uso de membrana de troca aniónica (AEM) e catiónica (CEM); (iii) o período de tratamento ED (6, 12, 24 horas); (iv) a recirculação do efluente e aumento de corrente; (v) a viabilidade de tratamentos sequenciais. Foi também avaliada a remoção de fósforo (P) do efluente e os custos associados ao tratamento. Consideraram-se cinco PFCPs – cafeína (CAF), bisphenol A (BPA), 17 β-estradiol (E2), etinil estradiol (EE2) e oxibenzona (MBPh). O processo ED demonstrou ser mais eficiente colocando o efluente no compartimento do ânodo. Considera-se que a oxidação é o principal processo de remoção, conseguindo-se remoções entre 88 e 96%, para todos os compostos, em 6 horas. Foram detetados possíveis intermediários/produtos de degradação em alguns casos. Percebeu-se que a recirculação do efluente exige maior tempo de residência do efluente na célula ED. O aumento de corrente (efluente no ânodo) aumentou a eficiência de remoção (remoções superiores a 80%, para todos os PFCPs). Os tratamentos sequenciais (efluente no ânodo) provaram ser eficientes em ambas as etapas, atingindo remoções entre 80 – 95% e 73 – 88% com AEM e CEM, respetivamente. A oxidação no compartimento do ânodo é considerada o principal processo de remoção. Houve um aumento de CBO_5 e CQO atribuído à fortificação do efluente, o que limita a descarga do efluente. A utilização de AEM aumentou a remoção de P do efluente, minimizando o risco de eutrofização. Os custos energéticos são de aproximadamente 0,80€/m^3 de efluente (tratamento de 6 horas), valores considerados baixos comparativamente com tratamentos com o mesmo objetivo.

Palavras-chave: PPCPs; Poluentes emergentes; Processo electrodialítico; Efluente de ETAR.

Abstract

Pharmaceuticals and personal care products (PPCPs) are widely used on a daily basis. After their usage they reach the wastewater treatment plants (WWTPs). These compounds have different physico-chemical characteristics, which makes them difficult to completely remove in the WWTPs, througth conventional treatments. Currently, there is no legislation regarding PPCPs thresholds in effluent discharge. But, even at vestigial concentrations, these compounds enclose environmental risks due to, e.g., endocrine disruption potential. There is a need of alternative techniques for their removal in WWTPs. The main goal of this work was to assess the use of electrodialytic (ED) process to remove PPCPs from the effluent to be discharged. A two-compartment ED cell was used testing (i) the effluent position in the cell (anode and cathode compartment); (ii) the use of anion (AEM) and cation exchange membrane (CEM); (iii) the treatment period (6, 12 and 24 hours); (iv) effluent recirculation and current steps; (v) the feasibility of sequential treatments. Phosphorus (P) removal from effluent and energetic costs associated to the process were also evaluated. Five PPCPs were studied – caffeine (CAF), bisphenol A (BPA), 17 β-estradiol (E2), ethinyl estradiol (EE2) and oxybenzone (MBPh). The ED process showed to be effective in the removal when effluent is in the anode compartment. Oxidation is suggested to be the main removal process, which was between 88 and 96%, for all the compounds, in 6 hours. Nevertheless, the presence of intermediates and/or by-products was also observed in some cases. Effluent recirculation should have a retention time in the ED cell big enough to promote removal whereas the current steps (effluent in anode compartment) slightly increased removal efficiencies (higher than 80% for all PPCPs). The sequential set of ED treatment (effluent in anode compartment) showed to be effective during both periods with a removal percentage between 80 and 95% and 73 to 88% in the case of AEM and CEM, respectively. Again, the main removal process is strongly suggested to be oxidation in the anode compartment. However, there was an increase of BOD_5 and COD, which might be explained by effluent spiking, these parameters limiting the effluent discharge. From these treatments, the use of AEM, enhanced the P removal from effluent to minimize risk of eutrophication. Energetic costs of the best set-up (6 hours) are approximately 0,8€/m^3 of wastewater, a value considered low, attending to the prices of other treatment processes.

Keywords: PPCPs; Emerging pollutants; Electrodialytic process; WWTP effluent.

Table of contents

Acknowledgement VII
Resumo IX
Abstract XI
Table of contents XIII
List of figures XV
List of tables XVII
Abbreviations and symbols XIX
1. Introduction 1
  1.1 Considerations and objectives 1
  1.2 Dissertation structure 2
2. Literature review 3
  2.1 Pharmaceutical and personal care products 3
    2.1.1 Occurrence and fate in environment 4
    2.1.2 PPCPs in study 7
    2.1.3 Physico-chemical properties 10
  2.2 PPCPs removal in wastewater treatment systems 12
    2.2.1 Conventional systems 13
    2.2.2 Technologies based on advanced oxidation processes 14
  2.3 Electrodialytic Process 17
    2.3.1 Transport mechanisms 17
    2.3.2 Applicability of ED process 20
  2.4 PPCPs analysis and determination 20
    2.4.1 Extraction methods 20
    2.4.2 Analytical methods 22
3. Material and methods 25
  3.1 Experimental procedures 25
    3.1.1 Effluent collection site 26
    3.1.2 Effluent sampling 26
  3.2 Reagents and material 27
  3.3 Electrodialytic experiments 27
  3.4 PPCPs analysis 32
    3.4.1 Sample preparation 32
    3.4.2 HPLC conditions 33
    3.4.3 Calibration curve and recovery of the analytical procedure 33
    3.4.4 Statistical analysis 33
4. Results and discussion 35
  4.1 Analytical analysis 35

- 4.1.1 Calibration 35
- 4.1.1 Limit of detection and limit of quantification 38
- 4.1.2 Method recovery 39
- 4.2 ED experiments results 41
  - 4.2.1 pH, conductivity and voltage 42
  - 4.2.2 PPCPs removal 46
  - 4.2.3 Phosphorus removal 54
  - 4.2.4 Other results 55
- 4.3 Energy costs 57
  - 4.3.1 SWOT analysis 59

5. Conclusions 61
6. Future developments 63
7. References 65
8. Appendix 73

List of figures

Figure 2.1 - Major pathways of PPCPs release into the environment. 5

Figure 2.2 - (a): Cartridge used for SPE; (b): Sample loading. 21

Figure 2.3 - Scheme of HPLC system. 23

Figure 3.1 - Experimental procedures made before each experiment. 25

Figure 3.2 - Experimental procedures made after each experiment. 25

Figure 3.3 - Wastewater treatments applied in WWTP of Quinta do Conde. 26

Figure 3.4 - ED laboratory cell. 28

Figure 3.5 – Schematic representation of the five laboratory cell set-ups used in which the effluent was placed at the: (a) cathode end with AEM; (b) cathode with CEM; (c) anode with AEM; (d) anode with CEM and (e) anode with CEM with both electrolyte and effluent recirculation. 29

Figure 3.6 - Sequential analytical procedures for the aqueous samples: (a) pH adjustment; (b) Filtration; (c) SPE; (d) N_2 concentration; (e) HPLC analysis. 32

Figure 4.1 - Example of a chromatogram obtained for a standard solution (8 mg L^{-1}). 35

Figure 4.2 - CAF calibration curve. 37

Figure 4.3 - BPA calibration curve. 37

Figure 4.4 - E2 calibration curve. 37

Figure 4.5 - EE2 calibration curve. 37

Figure 4.6 - MBPh calibration curve. 37

Figure 4.7 - Graphic representation of the percentage recoveries for each contaminant and respective standard deviation (n=2), for 6, 12 and 24 hours. 40

Figure 4.8 - Values of pH for both anolyte and catholyte after each ED experiment. 42

Figure 4.9 - Measured conductivity for each experiment (anolyte and catholyte). 43

Figure 4.10 - Voltage drop between the working electrodes for each experiment (initial and final) 45

Figure 4.11 - Comparison of the obtained chromatograms for effluents of the experiments A.CEM.24, A.AEM.24, C.CEM.24 and C.AEM.24, respectively. 48

Figure 4.12 - Microscopic observation of a microorganism present in effluent. 56

Figure 4.13 - Microscopic observation of the crystals. 56

Figure 4.14 - Images found for triple phosphate. 57

List of tables

Table 2.1 - Physico-chemical properties from the PPCPs in study 11
Table 3.1 - Experimental conditions 30
Table 4.1 – LOD and LOQ values for HPLC analysis. 39
Table 4.2 - Initial characteristics of the effluent used in the ED experiments 41
Table 4.3 - Initial characteristics of electrolyte used in the ED experiments 42
Table 4.4 - Percentage of contaminants removed in each ED experiment 46
Table 4.5 - Characteristic WWTP parameters values, after the final ED experiments 53
Table 4.6 - Results of phosphorus analysis for each sample 55
Table 4.7 - Energy costs associated to each experiment 58
Table 4.8 - SWOT analysis 59
Table 8.1 - Percentage of contaminant detected in the effluent and electrolyte after the ED experiments, in relation to the initial amount 73

Abbreviations and symbols

2C – cell design with two compartments
ACN – acetonitrile
AEM – anion exchange membrane
ANOVA – analysis of variance
AOP – advanced oxidation processes
AST – activated sludge treatment
BOD_5 – biochemical oxygen demand
BPA – bisphenol A
CAF – caffeine
CEM – cation exchange membrane
CNS – central nervous system
COD – chemical oxygen demand
DC – direct current
DOC – dissolved organic carbon
E2 – estradiol
ED – electrodialytic process
EDCs – endocrine disruptor compounds
EE2 – ethinyl estradiol
EK – electrokinetic process
EPA – environmental protection agency
EU – european union
GAC – granular activated carbon
HPLC – high-performance liquid chromatography
IPCS – international program of chemical safety
LOD – limit of detection
LOQ – limit of quantification
MBPh – oxybenzone
OCs – organic contaminants
OECD – organization of economic and cooperative development
PCBs – polychlorinated biphenyls
PPCPs – pharmaceutical and personal care products
R^2 – coefficient of determination
RSD – relative standard deviation
SPE – solid phase extraction
TOC – total organic carbon
TSS – total suspended solids
WHO – world health organization
WWTP – wastewater treatment plant

1. Introduction

1.1 Considerations and objectives

In the past few decades, environmental research focus has been extended beyond classic environmental pollutants like polychlorinated biphenyls (PCBs), dioxins and pesticides to pharmaceuticals and personal care products (PPCPs) (T. a. Ternes et al. 2004). The latter comprise a wide variety of chemical substances, which includes prescription and therapeutic drugs, veterinary drugs, fragrances and cosmetics. These compounds enter the environment either by their inclusion in the solid wastes and/or via excretions, after their consumption by humans and animals (Rivera-Utrilla et al. 2013).

For this reason, these compounds have been detected in different matrices, including effluents from wastewater treatment plants (WWTPs) (Kosma et al. 2014; Le-Minh et al. 2010; Rivera-Utrilla et al. 2013).

There are two types of wastewater treatment methods. The ones in which physical forces are predominant – *unit operations*, and the methods of treatment in which the contaminants removal is due to chemical or biological reactions – *unit processes.* In the current times, unit operations and processes are combined to achieve different levels of treatment: preliminary, primary, secondary (with or without nutrient removal) and tertiary treatment (Tchobanoglous et al. 2003).

WWTPs are inefficient in the removal of the majority of these compounds due to their complex molecular structure (Bonnineau et al., 2012), wide range of physico-chemical characteristics and low concentrations in the wastewater (Rivera-Utrilla et al. 2013). For example, due to PPCPs limited biological degradability, the activated-sludge treatment process, is inefficient. As so, bioactive and chemical compounds enter the receiving water bodies and soils with no restrictions or ways to know their specific environmental effects (Ternes et al. 2004; Ziylan and Ince 2011; Rivera-Utrilla et al. 2013).

The European Union Water Framework Directive (2000/60/EC) has identified some PPCPs compounds as potential pollutants, but there are no legally regulated maximum concentrations of PPCPs in the environment. Despite PPCPs being discharged at vestigial concentration in effluent water, this may also represent a serious threat to the ecosystem as they have potential to cause, e.g., endocrine disruption in aquatic organisms (Jobling et al. 1998; Rahman et al. 2009).

For all these reasons it is crucial to enlarge the knowledge about methodologies that could efficiently decrease the concentration levels of a broad spectrum of contaminants from effluent, thus preventing their negative effects to the environment.

Electrodialytic process (ED) was successfully used to remove and/or degrade PPCPs from solid matrices (soil and sewage sludge from WWTP) (Guedes et al. 2014; Guedes et al. 2015). It is expected that it has potential to decrease PPCPs levels from effluent from an urban WWTP (up to 94 000 person equivalents in the WWTP horizon), representing an upgrade to conventional WWTP treatments.

The present dissertation aims to answer the following question:

Q – Can the ED process remove PPCPs from WWTPs effluent?

To answer this general question, ED process was applied in two compartment (2C) cells aiming to test:

1. the position where effluent should be put into the cell to provide better removal
2. the type of ion-exchange membrane that is more effective to reduce PPCPs levels, either anionic (AEM) or cationic (CEM)
3. the minimum period of ED treatment that may be applied in a WWTP, to effectively reduce the PPCPs contamination
4. the effect of effluent recirculation on the lower period of time that it was tested
5. the feasibility of applying a sequential set of 6+6 hours without losing effectiveness to remove PPCPs and verifying if it accomplishes the standards established to allow an effluent discharge

It was also performed a study of energetic costs for each cell design and a SWOT analysis about the general process aiming to integrate more information that should help to take the “final decision”.

For this study, 19 laboratorial experiments were carried out with five target PPCPs: caffeine (CAF), bisphenol A (BPA), estradiol (E2), ethinyl estradiol (EE2) and oxybenzone (MBPh). Compounds were extracted from the liquid matrix through Solid Phase Extraction (SPE) and the samples were analysed by High-Performance Liquid Chromatography (HPLC).

1.2 Dissertation structure

This work is organized in seven main chapters:

1. Introduction: scope of the dissertation and its importance, objectives and structure;
2. Literature review: compiled data that support and corroborate the importance of this study, studies already done in this area and description of relevant terms;
3. Materials and methods: description of the used materials and methodologies applied in sampling, extraction, analysis and data processing methods;
4. Results and discussion: results presentation, hypothesis formulation and respective discussion;
5. Conclusions: resume of the main outcomes of the study;
6. Future developments: suggestions for future studies;
7. References.

2. Literature review

2.1 Pharmaceutical and personal care products

Pharmaceuticals are mostly used to treat or prevent human and animal disease, while personal care products are used in daily hygiene tasks and include products such as shampoos, soaps, deodorants, toothpastes, fragrances, sunscreens, make up, etc. (Boxall et al. 2012). In the past few decades, pharmaceutical and personal care products (PPCPs) have received increasing attention as emerging organic contaminants (OCs). They are considered as emerging contaminants because they had not been previously detected or found in far lower concentrations in the water bodies. These contaminants have an associated risk to human health and the environment that is not completely known (Kosma et al. 2014; Le-Minh et al. 2010).

PPCPs can reach the water bodies because they are not entirely eliminated during wastewater treatments (Le-Minh et al. 2010; Rivera-Utrilla et al. 2013; Kosma et al. 2014). The consequent contamination of both surface and ground waters has been recognized as an environmental issue in many countries worldwide (Rivera-Utrilla et al. 2013).

They have characteristics that differentiate them from conventional industrial chemical contaminants. In general, they: (a) can be formed by large and chemically complex molecules that vary widely in molecular weight, structure, functionality and shape; (b) are polar molecules with more than one ionisable group and the degree of ionization and its properties depend on the pH of the medium; they are lipophilic and some of them are moderately soluble in water; (c) can persist in the environment for months (e.g. erythromycin, cyclophosphamide, naproxen and sulfamethoxazole) or years (clofibric acid), and become biologically active through accumulation (Rivera-Utrilla et al. 2013).

There is still no regulation about PPCPs discharges. They have been found in the environment in concentrations within ng L^{-1} to µg L^{-1} and, besides they have been in water for many years, only recently they started to be quantified and accepted as potentially hazardous to ecosystems (Fent et al. 2006). The increasing sensitivity of analytical instruments has allowed the detection of trace amounts. But, on the other hand, these low concentrations make the removal in WWTPs even harder. In addition, PPCPs include a wide variety of chemical classes and so, for effluent treatment, no technology suits well for all compounds at the same time (Yang et al. 2011).

2.1.1 Occurrence and fate in environment

There has been an increasing pollution in surface and ground waters due to PPCPs. It has been acknowledged by many countries as an environmental problem and has led to the establishment of a research field known as pharmaceuticals in the environment (Fatta-Kassinos 2010).

Municipal wastewater is one of the main pathways for the occurrence of PPCPs into the environment. People either excrete pharmaceuticals during the regular course of treatment or improperly dispose of unused or expired drugs in toilets and so, they will reach WWTPs. Hospital wastewater is a minor but relevant extent, that also contributes to the total loads. Personal care products components enter the wastewater via washing, bathing, and showering. Thus, they can go into the receiving waters as dissolved contaminants through the discharges of WWTPs (the ones that do not readily biodegrade). They can also enter in agricultural land when digested sludge is applied as fertilizer or when manure is used as fertilizer. Despite veterinary pharmaceuticals are more likely to directly contaminate soil, the runoff gets into rivers. Point-source discharges from PPCPs manufacturing plants may also be released into the environment, affecting the local area with elevated levels of contamination (Ternes et al. 2004; Boxall et al. 2012; Ziylan and Ince 2011).

After their administration, pharmaceuticals can be excreted without being transformed or they can be metabolized by biochemical reactions in two routines: a first routine in which oxidation, reduction, hydrolysis, and alkylation reactions take place; and a second routine in which glucuronide or sulfate conjugates are formed and excreted by urine or bile in the form of more polar and hydrophilic derivatives, as a metabolite or as a mixture of multiple metabolites (Heberer 2002). The PPCPs most regularly found in WWTPs are: antibiotics, antacids, steroids, antidepressants, analgesics, anti-inflammatories, antipyretics, beta-blockers, lipid-lowering drugs, tranquilizers, and stimulants. They have been identified in the surface and ground waters of Germany, Holland, Switzerland, Italy, Spain, United States, Canada, China and Brazil among others (T. a Ternes 1998; Drewes et al. 2001; T. A. Ternes et al. 1999; Miao et al. 2004; Chen et al. 2011; Yuan et al. 2013; Rivera-Utrilla et al. 2013). Figure 2.1 illustrates the described PPCPs main routes into the environment.

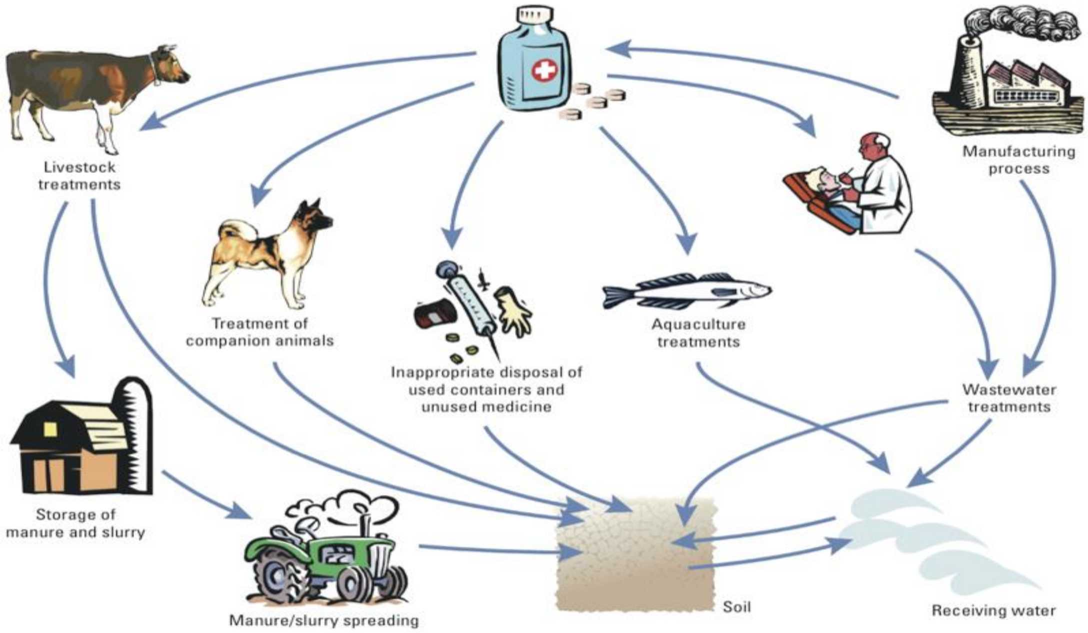


Figure 2.1 - Major pathways of PPCPs release into the environment. Reproduced from Boxall (2004).

Due to elevated lipophilicity (ability of a chemical compound to dissolve in fats, oils, lipids, and non-polar solvents), most PPCPs significantly sorb onto sludge from WWTP (T. a. Ternes et al. 2004; Rivera-Utrilla et al. 2013), which should be efficient in decreasing the concentration of these compounds. However, their structure, the hydrophilic behaviour of some of these compounds, or their degradation products, can result in persistence both during conventional wastewater treatment and after wastewater discharge into the aquatic environment (Drewes et al. 2001). For this reason, it is recognized that municipal wastewater is one of the main pathways for the occurrence of PPCPs in the environment as they can go into the receiving waters as dissolved pollutants through the discharges of WWTPs. Therefore, there is a need to improve WWTPs efficiency to remove PPCP.

European Union (EU) allows the disposal of expired medicines via domestic waste, which may cause leaks from landfill sites that can cause groundwater contamination. Leakage from manure storage tanks or septic tanks, output from sewers and WWTPs, and spray irrigation of raw and treated wastewater onto agricultural land are other possible ways of pharmaceuticals enter groundwater (Fent et al. 2006).

Effects

The occurrence of PPCPs in the environment raises concerns about their potential harm to ecosystems and human health. Although the concentrations of PPCPs are low and difficult to detect, they have potential to promote deleterious environmental effects (Rivera-Utrilla et al. 2013).

The effect of these micro contaminants in the environment depends not only on its concentration, but also on factors such as high lipophilicity or persistence, bioaccumulation, exposition time and mechanisms of biotransformation and elimination. Some substances in the environment suffer biotransformations, which results in metabolites or by-products more harmful than the original compounds. At sufficient concentrations, they have induced negative effects in both animals and some plants, and it is possible that they may have other effects that have not yet been observed (Jones et al. 2004). Meanwhile, chronic effects could not be excluded. The continuous input of PPCPs into the environment may accumulate and cause irreversible harm to wildlife and human beings (Fent et al. 2006; Liu and Wong 2013).

Some PPCPs are comprised in endocrine disruptor compounds (EDC) that have been defined by the organization of economic and cooperative development (OECD) as “an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations”. The presence of EDC in the environment causes effects both in animals and human beings. These effects in animals can be the decrease in the breakage of eggs of birds, fishes and turtles, feminization of male fish, problems in the reproductive system in fishes, reptiles, birds and mammals, and alterations in the immunologic system of marine mammals. Consequently, in some cases, these effects can lead to decays in populations. In human beings, the reported effects so far have been the reduction of the amount of sperm, increase of the incidence of breast, testicle and prostate cancers, and the endometriosis (Esplugas et al. 2007).

Endocrine-active compounds and hormones may interfere with sexual development in humans, once they are highly active compounds that interact with hormone systems. These endocrine disruptors can have a great range of reproductive and development effects, e.g. reduced fertility, feminization of males and intersex phenomena. These hormones possess 10 000 – 100 000 times higher estrogenic potency compared with exogenous endocrine disrupting chemicals (Khanal et al. 2006; Kümmerer 2010). In addition, some anticancer drugs may cause cancer themselves, even at very low doses, one of the threats of modern chemotherapy, and antibiotics may contribute to the selection of bacteria that are resistant against antibiotics. Little knowledge on these issues is available. PPCPs can also act as endocrine disruptors and so, the effects are similar (Liu and Wong 2013).

Nevertheless, the potential effects of these emergent contaminants in water are still uncertain and require further investigation. According to the literature, full environmental risk assessment cannot be performed on the basis of the data available. Currently, different government and non-government organizations such as the European union, the north American environmental protection agency (EPA), the world health organization (WHO), or the international program of chemical safety (IPCS) are considering this problem and setting up directives and legal frameworks to protect and improve the quality of fresh water resources (Esplugas et al. 2007). There is still a lack of fundamental data on the fate and effects of antibiotics resistance genes in the environment. The availability of such data is a prerequisite if proper risk assessment and risk management programs for both humans and the environment are to be undertaken (Kümmerer 2009).

2.1.2 PPCPs in study

Caffeine

Caffeine (CAF), 1,3,7-trimethylxanthine, belongs to the class of organic compounds known as alkaloids and derivatives. These are chemical compounds that contain mostly basic nitrogen atoms. This group also includes some related compounds with neutral and even weakly acidic properties (Fredholm et al. 1999; Ashihara et al. 2008). CAF has great importance in pharmaceuticals because it improves the effect of specific analgesics in cough, cold, and headache medicine. It is used as a cardiac, cerebral, and respiratory stimulant and also as a diuretic (Ogunseitan, 1996). CAF also acts as a central nervous system (CNS) stimulant, temporarily reducing the somnolence and increasing attentiveness (Fredholm et al. 1999). Pure CAF is produced commercially as a by-product from the decaffeination of coffee (Buerge et al. 2003).

It is present in cola drinks, coffee, tea and energy drinks which make this drug one of the most consumed drug in high-developed countries, where 90% of adults consume CAF daily. Coffee, tea, cacao, and cola contain, respectively, about 100, 50, 10, and 40 mg of CAF per serving. The global, average consumption is about 70 mg per person per day, varying in different countries. Thus, exists an important occurrence of this compound into some industrial effluents and domestic wastewaters (Who and Intl. Agency for Research on Cancer 1991; Indermuhle et al. 2013).

Bisphenol A

Bisphenol A (BPA), 4,4′-Isopropylidenediphenol, is a synthetic organic compound which belongs to diphenylmethane derivatives and bisphenols group. The U.S. EPA quotes an unlisted reference which states that BPA has high solubility at alkaline pH conditions because of its dissociation constants, pKa 9.6 to 10.2 (Staples et al. 1998). BPA is a single hydrocarbon molecule that binds with other molecules to form polymers, such as epoxy resins and polycarbonates (Le et al. 2008; U S Environmental Protection Agency 2011). It can also be used in the processing of thermal paper (Shelby 2008) and it has been considered a weak estrogen in a series of in-vitro and in-vivo studies (Morrissey et al. 1987). BPA has well characterized estrogenic and other endocrine disrupting activities that are mediated via multiple molecular mechanisms (Wetherill et al. 2007).

It is currently produced in huge quantities worldwide. On a daily basis, humans are exposed to BPA through a vast range of plastics, “microwave-safe” and metal containers that have plastic and epoxy liners. Some of these products are microwave food products and metal food containers. There are also other kind of products made with BPA, such as compact discs, eyeglass wear, toys, bicycle helmets, and medical devices (Erler and Novak 2010; Staples et al. 1998; Chapin et al. 2008).

Due to this exposure to BPA, scientific community continues to debate about the existence of low-dose effects of BPA and their potential implications for human health (Chapin et al. 2008; Shelby 2008; Commission 2010). Although populations most at risk from exposure to BPA include the developing fetus, infants, children, and pregnant women, there is concern about the effects of BPA in adults (Erler and Novak 2010). Many studies of BPA health effects have focused on well-documented estrogenic activity but there are some reports which have additional modes of action including liver damage, disrupted pancreatic β-cell function, thyroid hormone disruption and obesity-promoting effects (Lang et al. 2008). The most notable effects are evident in fetal development through early childhood development and include secondary sexual developmental changes, neurobehavioral alterations, and immune disorders. BPA has also been found in higher levels in the presence of cardiovascular disease, diabetes, obesity, and liver dysfunction (Erler and Novak 2010).

Estradiol

Estradiol (E2), also known as 17β-estradiol, is a natural steroidal estrogen (produced by the human body). This estrogen is an important female hormone which allows the health maintenance of the reproductive tissues, breasts, skin and brain (Ying et al. 2002). It is an aromatized C18 steroid with two hydroxyl groups and the most active and potent of the natural estrogens (Soto et al. 1995; Delaune and Moore Jr 2013). From its physico-chemical properties it is known that E2 is a hydrophobic organic compound of low volatility. Due to its endocrine disrupting potential it might be harmful for aquatic environment. It may interfere with the normal functioning of endocrine systems and so, affect the reproduction and development in wildlife (Ying et al. 2002; Jobling et al. 1998). The steroids of concern for the aquatic environment due to their endocrine disruption potential are mainly estrogens and contraceptives, which include E2 and EE2, among others (Ying et al. 2002).

Ethinyl estradiol

Ethinyl estradiol (EE2), 17α-ethynyl estradiol, is a synthetic steroid used as contraceptive and for medical treatments of cancer, hormonal disparity, osteoporosis, and other diseases (Yu et al. 2004). It is usually released from conjugated glucuronide or sulphate complexes present in urine because it is metabolised before being excreted (Panter et al. 1999). After being released into the environment, adsorption to natural solids is an important process that affects transport, degradation, biological activity and fate of EDCs (Pignatello and Xing 1996; Sun et al. 2007). Due to their hydrophobic properties, estrogens are strongly sorbed in soils or sediments, potentially restricting the mobility and transport of estrogens from soils to aquatic ecosystems where they seem to cause more damage (Hildebrand et al. 2006; Stumpe and Marschner 2009).

Oxybenzone

Oxybenzone (MBPh), 2-hydroxy-4-methoxybenzophenone, benzophenone-3, is a benzophenone derivative (organic compounds containing a ketone attached to two phenyl groups) used as a sunscreen agent. Once it absorbs UV-B and UV-A rays, the result is a photochemical excitation and absorption of energy. These molecules are designed to absorb UV-B or UV-A radiation and dissipate this energy by re-emission at a less energetic wavelength or by undergoing some cyclic photochemical process and so, decrease skin penetration of radiation which reduces the risk of DNA damage. Sunscreen materials can be either organic or inorganic. Organic sunscreens, where MBPh is included, also called soluble or chemical sunscreens, have been the most extensively employed (US Food and Drug Administration (Department of Health and Human Services) 1999; Chrétien et al. 2010; Coronado et al. 2008).

MBPh is one of the most extensively employed sunscreen compounds, however it is only allowed a maximum of 6% reflecting the frequency with which adverse effects are reported (US Food and Drug Administration (Department of Health and Human Services) 1999). This compound penetrates the skin and can be found in the urine. The amount varies between 0 - 4% (Gonzalez et al. 2006).

2.1.3 Physico-chemical properties

The physico-chemical properties of the studied PPCPs are presented in table 2.1**Erro! A origem da referência não foi encontrada.**. This table includes molecular formula, molecular weight, chemical structure, solubility, ionization constant (pKa), logarithm of the octanol-water partition coefficient (Log K_{ow}) and Henry's law constant of each compound.

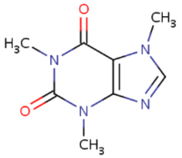
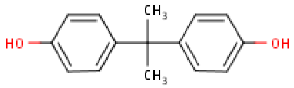
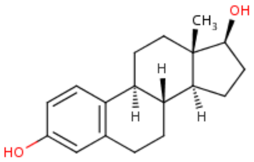
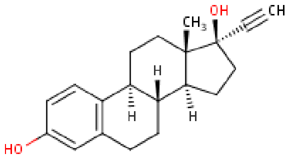
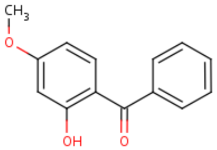
All the PPCPs, except CAF, are fairly hydrophobic (physical characteristic of a molecule that is repelled from a mass of water) and exhibit a low but measurable solubility in water (2.16×10^4 for CAF, 120 for BPA, 3.9 for E2, 11.3 for EE2 and 69 for MBPh). Solubility is the property of a solid, liquid or gaseous chemical substance (solute) to dissolve into a solvent (usually a liquid) to form a solution. The solubility of a substance essentially depends on the physical and chemical properties of the solute and solvent and also on temperature, pressure and the pH of the solution. Solubility is often used to estimate the air-water partition coefficient or Henry's law constant (Rogers and Stovall 2000; IUPAC 1997; Mackay et al. 2006).

PPCPs in study are not volatile. Henry's law is a gas law formulated by William Henry in 1803 and it states that "at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid". Henry's law constant can be considered as a ratio of vapour pressure to solubility, where temperature affects both properties. The temperature dependence of Henry's law constant is related to the temperature-dependence of water density (and consequently molar volume). It is expressed in Pa m^3 mol^{-1} (Lee 2007; Mackay et al. 2006).

The dissociation constant, Ka, or its usually reported negative logarithmic form, pKa, is a quantitative strength measure of an acid in solution. It is the equilibrium constant for a chemical reaction called as dissociation in the context of acid-base reactions. Acid dissociation constant is determined in principle by simultaneous measurement or deduction of the ionic and non-ionic concentrations and the pH of the solution (Mackay et al. 2006). The pKa of BPA, E2, EE2 and MBPh is between 7.6 and 10.7 whereas for CAF is 14.

The octanol-water partition coefficient (K_{ow}) of a compound is defined as a dimensionless concentration ratio of the compound's concentration in a known volume of n-octanol to its concentration in a known volume of water after the octanol and water have reached equilibrium at a specified temperature (Pontolillo and Eganhouse 2001). Water solubility was found to be the major factor affecting the partition coefficient. For many hydrophilic compounds such as the alcohols, K_{ow} is low and can be less than 1.0, resulting in negative values of K_{ow} for this kind of compounds (Mackay et al. 2006). Once K_{ow} can be in a range of many orders of magnitude (10^{-2} to 10^6) it is expressed as its decade logarithm, log K_{ow} (Sangster 1989). The log K_{ow} of BPA, E2, EE2 and MBPh range between 3.3 and 4.0 whereas for CAF it is -0.07.

Table 2.1 - Physico-chemical properties from the PPCPs in study

Compound	*Caffeine*	*Bisphenol A*	*Estradiol*	*Ethinyl Estradiol*	*Oxybenzone*
IUPAC Name	1,3,7-trimethylxanthine	4,4′-Isopropylidenediphenol	17 β-oestradiol	17 α-ethinyloestradiol	2-hydroxy-4-methoxybenzophenone
Chemical Structure					
Category	CSN Stimulant	Plasticizer	Estrogen	Estrogen	Sunscreening agents
Formula	$C_8H_{10}N_4O_2$	$C_{15}H_{16}O_2$	$C_{18}H_{24}O_2$	$C_{20}H_{24}O_2$	$C_{14}H_{12}O_3$
Molecular weight (g mol^{-1})	194.19	228.29	272.38	296.40	228.24
Solubillity[a] (mg L^{-1})	2.16×10^4 (25ºC)	120 (25ºC)	3.9 (27ºC)	11.3 (27ºC)	69 (25ºC)
Ionization constant[b,c,d,e] (pKa) at 25ºC	14.0	9.6 – 10.2	10.7	10.3	7.6
Logarithm of the octanol-water partition coefficient[b] (Log K_{ow})	-0.07	3.32	4.01	3.67	3.79
Henry's law constant[b] (Pa m^3 mol^{-1}) at 25ºC	3.58×10^{-11}	1.0×10^{-6}	3.64×10^{-11}	7.94×10^{-12}	1.5×10^{-8}

[a] Sigma-Aldrich, 2015; [b] Pubchem, 2015; [c] chemicalbook, 2015; [d] Staples et al. 1998; [e] Fontanals et al. 2010

2.2 PPCPs removal in wastewater treatment systems

The present state-of-the-art of wastewater treatment for the removal of PPCPs is based on secondary treatment, which comprises the activated sludge treatment process (AST) preceded by conventional physico-chemical pre-treatment steps and then tertiary treatment. The biological treatment is accepted as the best available technology, although it presents an incomplete removal of a varied range of emerging contaminants, especially polar ones, which are discharged into the final effluent (Petrović et al. 2003).

Therefore, it has become evident that the application of alternative technologies to decrease levels of specific contaminants is needed in order to avoid environmental and human health risks. Is it also expected that legislation regulating effluent discharge starts to include threshold for emerging organic compounds, including PPCPs.

In recent years, there have been studies about the application of new technologies to treat wastewater more effectively. These are the most frequently considered as they might be appropriate for removing trace concentrations of emerging polar contaminants (Petrović et al. 2003). Actually, there are a big variety of possible treatment conjugations to remove wastewater constituents. Some of them include biological systems to remove nitrogen; chemical precipitation to remove phosphorus; distillation to remove volatile organic compounds; liquid–liquid extraction and advanced oxidation processes (AOPs) to remove toxic OCs. Many of these systems are under research and have yet to be applied on an industrial scale (Rivera-Utrilla et al. 2013).

In order to achieve efficient elimination of different contaminants from aqueous system different destructive methods can be chosen. These methods comprise chemical oxidation, incineration or degradation. The non-destructive methods allow the recuperation of the contaminant such as the liquid extraction, absorption and membrane processes. The application of either of them will be based on the concentration in the effluent, the properties of the present compounds and volume flows of the effluent to be treated which will affect the cost of the process (Esplugas et al. 2007).

2.2.1 Conventional systems

In general, the WWTPs in Europe, comprise preliminary treatment, primary treatment, secondary treatment (with or without nutrient removal) and tertiary treatment. These are the so-called conventional systems.

Preliminary treatment involves the screening of raw sewage through bar screens to remove large objects and other wastewater constituents such as floatables, grit and grease. Primary treatment mainly removes suspended solids and organic matter by gravity. Secondary treatment involves the removal of biodegradable organic matter (in solution or suspension), suspended solids and, when it includes nutrient removal, also nutrients (phosphorus, nitrogen or both phosphorous and nitrogen) (Tchobanoglous et al. 2003; Khanal et al. 2006).

The most used biological treatment of municipal and industrial WWTPs is the AST process which is based on microorganisms to break down the organic matter. This process consists in three basic components: a reactor where the microorganisms responsible for the treatment are kept in suspension and aerated (aeration tank), sedimentation tank for liquid-solid separation and a recycling system for returning solids removed from the liquid-solids separation unit back to the reactor. It is formed flocculent settable solids that can be removed by gravity settling in sedimentation tanks. The tertiary treatment is the removal of residual suspended solids (after secondary treatment), usually by granular medium filtration or micro screens (Tchobanoglous et al. 2003).

Disinfection is also typically a part of tertiary treatment, which refers to the partial destruction of disease-cause organisms and destruction of some organic (and most of the times, recalcitrant) compounds. Disinfection can be achieved by (i) chemical agents, such as chlorine, chlorine dioxide, ozone, among others and (ii) physical agents, like heat and UV radiation (Tchobanoglous et al. 2003). Chlorine dioxide, ClO_2, is a more potent oxidant than chlorine and can degrade numerous organic compounds by oxidation. ClO_2 reacts selectively with functional groups with high electron density, such as tertiary amines and phenoxides. In comparison to ozone, ClO_2 reacts slower and with fewer compounds; in comparison to chlorine, it reacts faster with sulfonamides, macrolides, and estrogens (Huber et al. 2005). Various studies on the chlorination of aromatic compounds revealed that the chlorine reaction rate can be strongly affected by the presence of different functional groups in the benzene ring. The reaction is usually rapid in pharmaceutical products containing amines (Adams et al. 2002).

The WWTP with conventional treatment systems have a limited capacity to remove PPCPs from urban wastewaters, once most of the compounds cannot be metabolized by microorganisms and may even inhibit their activity or produce their bioaccumulation in the food chain. The great difficulty in conventional systems is to find a treatment process that assures the removal of all types of compounds.

In short, conventional treatment systems are unable to completely remove a large amount of the organic micro contaminants present in urban wastewaters. More effective and specific treatments are required to reduce the environmental and potential impact of effluents and comply with increasingly strict legislation (Rivera-Utrilla et al. 2013).

Effluent used in the study

The effluent used in this study is from Quinta do Conde WWTP (a portuguese parish that belongs to the county of Sesimbra). This WWTP has a conventional treatment system. At first, there is a fine screen to retain the solids that come with the wastewater and then, the tank where grit and grease are removed. The solids and grit removed in this phase are sent to proper destination and the grease is sent to the anaerobic digesters. After that, primary treatment is comprised by covered lamellar primary settling tank. Secondary treatment is carried out by aeration reactors with suspended biomass (oxidation ditches) where the wastewater is biologically treated by microorganisms and then, goes to secondary settling tank to solid-liquid separation. The liquid phase (effluent) is disinfected by UV radiation before it is released in Ribeira de Coina. The sludge originated from primary and biological treatment are thickened and equalized by hot anaerobically digestion. After digestion, sludge is mechanically dehydrated and stored in silos of dewatered sludge (Águas de Lisboa e Vale do Tejo 2007).

2.2.2 Technologies based on advanced oxidation processes

There is a group of chemical-oxidative processes called advanced oxidation processes (AOP), which refer to a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials from water and wastewater by oxidation through reactions with hydroxyl radicals ($^{\bullet}OH$). This radical is highly unstable and reactive because of its high oxidation potential. Thus, it is able to oxidize and mineralize almost ever organic molecule into CO_2 and inorganic ions. AOPs are based on in-situ production of $^{\bullet}OH$ and there are different techniques to generate them. Once formed, they attack the most part of organic molecules causing their breakdown. Subsequent attacks by $^{\bullet}OH$ would lead to ultimate mineralization (Andreozzi 1999; Rudder et al. 2004; Rivera-Utrilla et al. 2013).

These $^{\bullet}OH$ are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). The most commonly applied AOPs are photocatalysis, namely O_3/UV, H_2O_2/UV, TiO_2/UV and solar photocatalysis, anodic oxidation (AO), ozonation, Fenton's reagent, ultrasound (US) and wet oxidation, (Brillas et al. 2009).

Photocatalysis generate hydroxyl radicals through photochemical ways. In nature, it is common to find compounds that can decompose by photochemical reactions from UV radiation application. This degradation depends on the radiation wavelength, compound molar absorption capacity, and quantum yield. Photocatalytic processes use a semiconductor metal oxide as catalyst and oxygen as oxidizing agent. In this process, the initiating event is the absorption of the radiation, which will cause the formation of electron-hole pairs. The considerable reducing power of formed electrons allows them to reduce some metals and dissolved oxygen with the formation of the superoxide radical ion O_2^- whereas remaining holes are capable of oxidizing adsorbed H_2O or OH^- to reactive $^\bullet OH$ (Rivera-Utrilla et al. 2013; Andreozzi 1999).

There has been an increasing attention to AOPs based on ozone, which is based on the combined application of O_3: O_3/OH^-, O_3/H_2O_2 and O_3/activated carbon systems for the removal of PPCPs from wastewater. Ozonation corresponds to approximately 90% of the oxidation treatments found in the scientific literature (Esplugas et al. 2007). Generally, the reaction of ozone with organic chemicals can be considered based on direct reactions of ozone with the target molecule and on hydroxyl radical mediated reactions. The direct reactions of ozone consist on specific additions to unsaturated hydrocarbons and electron transfer reactions (e.g., reactions with phenolate ions). The radical mediated reactions start with the generation of $^\bullet OH$ initiated by the reaction between hydroxide ions and ozone, according to a chain reaction proposed by Staehelin and Hoigné (1982, 1985). The combined application of ozone and hydrogen peroxide enhance the degradation efficiency which can be attributed to the oxidation effect of the produced $^\bullet OH$. However, (Zwiener and Frimmel 2000) concluded that the so-called radical scavengers compete with the pharmaceuticals for the hydroxyl radicals and by this decrease the degradation kinetics of the PPCPs. Bicarbonate and carbonate ions, as well as the dissolved organic carbon (DOC), are examples for scavengers. In order to increase the degradation kinetics of the PPCPs in river water, the $^\bullet OH$ concentration has to be increased, which can be done by increasing the applied oxidant concentrations. (Zwiener and Frimmel 2000), also noted that significant degradation efficiency was obtained when the applied ozone concentration was equal to the DOC value of the river water (3.7 mg L^{-1}). With the obtained results, it was assumed that the ozone is consumed by the DOC. Consequently, sufficient ozone for reactions with hydrogen peroxide was only available at an initial ozone concentration similar to the DOC value of the investigated river water. The oxidant concentration needed depends on both the reaction kinetics of the pharmaceuticals and the $^\bullet OH$-scavenging capacity of the matrix of the treated water (Zwiener and Frimmel 2000).

The most common technique used at industrial level is the Fenton process, which only uses iron salt and hydrogen peroxide at acidic conditions (Esplugas et al. 2007). It has been demonstrated that Fenton's reagent is able to destroy toxic compounds in wastewaters such as phenols and herbicides. Production of $^\bullet OH$ by Fenton reagent happens by adding H_2O_2 to Fe^{2+} salts. This is a simple way to produce $^\bullet OH$ once there is no need of neither special reactants nor special apparatus. This reactant is a viable oxidative system for wastewater treatment considering that iron is very abundant and a nontoxic element and hydrogen peroxide is easy to handle and environmentally safe. The rate of degradation of organic contaminants with Fenton–Fenton as reagents is strongly accelerated by irradiation with UV-VIS light. This is an extension of Fenton process which takes advantage from UV-VIS light irradiation at wavelength values higher than 300 nm. In these conditions, the photolysis of Fe^{3+} complexes allows Fe^{2+} regeneration and the occurrence of Fenton reactions due to the presence of H_2O_2 (Andreozzi 1999).

Anodic oxidation, also called electro-oxidation, represent the environmental friendly aspect in using electricity. It is flexible and has the capacity to react with contaminants by both the direct and indirect effects of electricity. Direct oxidation can be achieved through mineralization with $^{\bullet}OH$ produced by dimensionally stable anodes with high oxygen over voltages. In fact, hydroxyl radicals are exclusively generated on anodes from the oxidation of water, and organic compounds can be completely transformed or degraded by reaction with adsorbed $^{\bullet}OH$. Indirect oxidation can be achieved through the electrochemical generation of a mediator in solution (such as HClO, HBrO, H_2O_2, $H_2S_2O_8$, and others) to convert toxic organics to less harmful products by using graphite or noble-metal anodes (Zaviska et al. 2012).

Ultrasound (US) has been used as an AOP for degradation of organic contaminants, which, compared to conventional methods, can assure several benefits once it is environment friendly (no toxic chemical is used or produced). The organic contaminants can be destroyed through pyrolysis or oxidation by strongly oxidative free radicals that are generated during ultrasonication (Pham et al. 2009)

Wet oxidation makes use of oxygen or air to achieve pollutant oxidation at high temperatures (130 – 300 ºC) and pressure (0.5–20 Mpa). Since oxidation is an exothermic process, simple thermal balance shows that wastes with COD contents higher than approximately 20 g/l undergo auto thermic wet oxidation, whereas fuel consumption should be taken into account to achieve combustion temperatures for leaner wastewaters (Andreozzi 1999).

By-products of the reactions between oxidants and organics must always be considered. However, most oxidation by-products of known EDCs and their cumulative estrogenicity profiles are largely unknown (Alum et al. 2004).

These technologies, all based on compounds oxidation, are used nowadays to remove more demanding contaminants from the physico-chemical point of view. However, due to the associated costs or even danger related to the formation of by-products, there is still a need to investigate new ways and approaches to remove them from WWTPs effluent and water bodies.

2.3 Electrodialytic Process

The electrodialytic process (ED) was developed at the Technical University of Denmark in 1992 and it is a remediation technique which can also be used for the recovery of elements with environmental and socio-economical value. This process is based on the electrokinetic principle (EK) but uses ion exchange membranes. The EK remediation is a process in which a low-voltage direct current is applied across a section of contaminated soil to move contaminants. The electrodes (cathode and anode) cause the mobilization of the particles (e.g., ions) due to the applied electric current. In this technique, a low-level direct current (DC) passes between electrodes and acts as a cleaning agent and transports the contaminants out of the soil towards one of the electrode compartments, from where they can be removed (Ribeiro and Maroto 2006; USAEC 1997).

ED process consists in applying a low level DC to induce contaminants migration from the sample to electrode compartments using an ion-exchange membrane in order to either facilitate or block the movement of the contaminants, depending on their charge (Ribeiro and Maroto 2006). For that, it uses an electric current density of the order of milliamps per square centimetre (mA cm^{-2}) applied to the cross-sectional area of a contaminated matrix which is placed between the electrode compartments, creating electric potential drops of the order of Volts per centimetre (V cm^{-1}). This type of contaminants extraction from the contaminated matrix requires the simultaneous flows of fluid, electricity and chemicals under the combined influences of hydraulic, electrical and chemical gradients. The electrodes are placed in opposite positions and ionic exchange membranes are used to separate contaminated matrix from the electrode ends (Ribeiro and Maroto 2006).

2.3.1 Transport mechanisms

The EK process invokes three main mass-transport mechanisms: electroosmosis, electromigration and electrophoresis. There are also other types of mass-transport usually present in some extension like diffusion and hydraulic convection. In ED process, there is also electrodialysis.

Electroosmosis

Electroosmosis is the movement of liquid induced by an applied electric potential gradient. When an electric field is applied to a wet matrix, cations are driven to the anode and the anions towards to the cathode and, as the ions move, they carry their water of hydration and exert a viscous drag around them. This kind of mass-transport is the major mechanism of removal of uncharged and/or weakly dissociated organic contaminants. It is also the dominant transport process for both organic and inorganic contaminants that are dissolved, suspended, emulsified or in similar forms. However, it only occurs in electrokinetic process (EK), not in ED process (Ribeiro and Maroto 2006; Reddy and Cameselle 2009). The electroosmotic flux, J_{eo}, is described by the equation 2.1:

$$J_{eo} = -k_e c \phi_e \qquad \text{(equation 2.1)}$$

Where:
k_e – electroosmotic permeability
c – concentration of species
ϕ_e – gradient of electric potential.

Electromigration

Electromigration is the movement of individual ions in a solution under an applied electric field. The direction of the ionic electromigration is towards the electrode with opposite charge – positive ions will be driven towards the cathode and the negative ions towards the anode (Ottosen and Rörig-Dalagard 2006). The electromigration transport, Jm, is given by the equation 2.2:

$$Jm = -u{*}c\phi_e \qquad \text{(equation 2.2)}$$

Where:
u* and c – ionic mobility and concentration of species;
ϕ_e – gradient of electric potential.

Electrophoresis

Electrophoresis (also known as cataphoresis) is the movement of charged particles of colloidal size under an applied electric field. The charged particles are attracted to one of the electrodes and repelled from the other (Ribeiro and Maroto 2006; Reddy and Cameselle 2009).

Electrodialysis

Electrodialysis is a selective transport technique based on electrical potential to drive the separation and where an ion-selective membrane works as physical barrier through which ions are transported away from a feed solution. Electrodialysis is ruled by an electrical potential difference across a cation or anion exchange membranes between an anode and a cathode. The cation exchange membranes (CEM) allow the transfer of cations but inhibit the transfer of anions.

On the other hand, anion exchange membranes (AEM) allow the transfer of anions and impede the transfer of cations.

Diffusion

Diffusion is the movement of ionic species under a chemical concentration gradient. Ionic and molecular constituent forms of the contaminants move from areas of higher concentrations to areas of lower concentration. In free solutions it is usually expressed by Fick's law. In the latter case, the effective diffusion coefficient must be obtained correcting the diffusive coefficient, to take into account the porosity and the tortuosity effects, which can decrease this transport in more than one order of magnitude (Ribeiro and Maroto 2006; Reddy and Cameselle 2009). The diffusive flux in soil can be obtained by the equation 2.3:

$$J_d = -D*\nabla c \qquad \text{(equation 2.3)}$$

Where:

D* – effective diffusion coefficient

∇c – concentration gradient.

In general, in the usual conditions for the electrokinetic treatment this is a secondary transport (Ribeiro and Maroto 2006).

Electrode reactions

Usually, the applied electric current leads to electrolysis of water at the electrodes. The hydroxyl ions (OH^-) and protons (H^+) generated by electrolysis reactions (equations 2.4 and 2.5) move towards the opposite charged electrode. Due to the formation of hydrogen ions in the anode there is a pH decrease near the anode and, at the same time, an increase in the pH near the cathode. Thus, it is generated an acid medium at the anode and an alkaline medium at the cathode. There is also a possibility of chlorides occur in the solution and chlorine gas can be produced (equation 2.6) (Reddy and Cameselle 2009; Ribeiro and Maroto 2006; Guedes, Couto, et al. 2014).

$$\text{Cathode: } 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \qquad \text{(equation 2.4)}$$

$$\text{Anode: } 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{(equation 2.5)}$$

$$\text{Anode: } 2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(equation 2.6)}$$

2.3.2 Applicability of ED process

The ED process, using a 2C cell, has already been tested in the removal of: (i) PCBs (Gomes et al. 2015) and heavy metals (Pedersen et al. 2014) from soil. There were achieved removals of 83% for PCBs and 81-92% for Cu, Pb and Zn; (ii) PPCPs, phosphorus (Guedes et al. 2015) and metals (Lisbeth M. Ottosen et al. 2007) from sewage sludge. For PPCPs, it was achieved a removal of Ibuprofen between 46 - 97% and CAF between 20 - 47%. In the case of total P, there were a recovery of 78 ± 2% and for metals it was achieved a removal of 40% of Ni and 76% of Zn; (iii) metals (Kirkelund et al. 2015) from sewage sludge ash, with a percentage of Cd removal up to 56% and (iv) phosphorus and microcystins (Couto et al. 2015) recovering 84% of phosphorus and reducing microcystins concentration from water.

2.4 PPCPs analysis and determination

2.4.1 Extraction methods

Solid phase extraction

Solid-phase extraction (SPE) is a commonly used sample-preparation technique for the isolation of certain analytes, usually from a mobile phase (gas, fluid or liquid). The analytes, compounds or chemical constituents that are of interest in an analytical procedure, are retained in the solid phase of the cartridge during the sampling process. Then, the analytes are recovered by elution using a liquid or fluid. The main goals of SPE are trace enrichment (concentration), matrix simplification (sample clean-up) and medium exchange (transfer from the sample matrix to a different solvent or to the gas phase) (Poole 2003).

The analytes are retained in the solid phase sorbent which is generally either silica or chemically modified silica similar to the bonded phases used in high-performance liquid chromatography (HPLC). Silica with chemically bonded alkyl chains such as C18 or C8, phenyl, amino, ion exchange groups or unmodified silica are the most widely-used, although polymeric resins (polystyrene/divinyl benzene copolymers), florisil (activated magnesium silicate), alumina and charcoal also find applications. SPE sorbents are chosen based on the predominant interaction mechanism for each one. Sorbents can be classified according to the polarity of the surface (Fifield and Kealey 2000).

Most SPE is carried out using a small packed bed of sorbent (25–500 mg) contained in a cartridge usually made from a polypropylene syringe barrel, the sorbent stays in the middle of polyethylene fritted discs. The sorbent generally occupies only the lower half of the cartridge, leaving space above to accommodate several millilitres either of the sample solution or washing and eluting solvents. Depth filters can also be positioned immediately above the sorbent bed to remove particulate matter from sample solutions (Poole 2003; Fifield and Kealey 2000). Figure 2.2 (a) shows the cartridge used in this study, with two filters and the sorbent in the middle (bed sorbent of 200mg); (b) shows the look of the cartridge during the sample loading step.

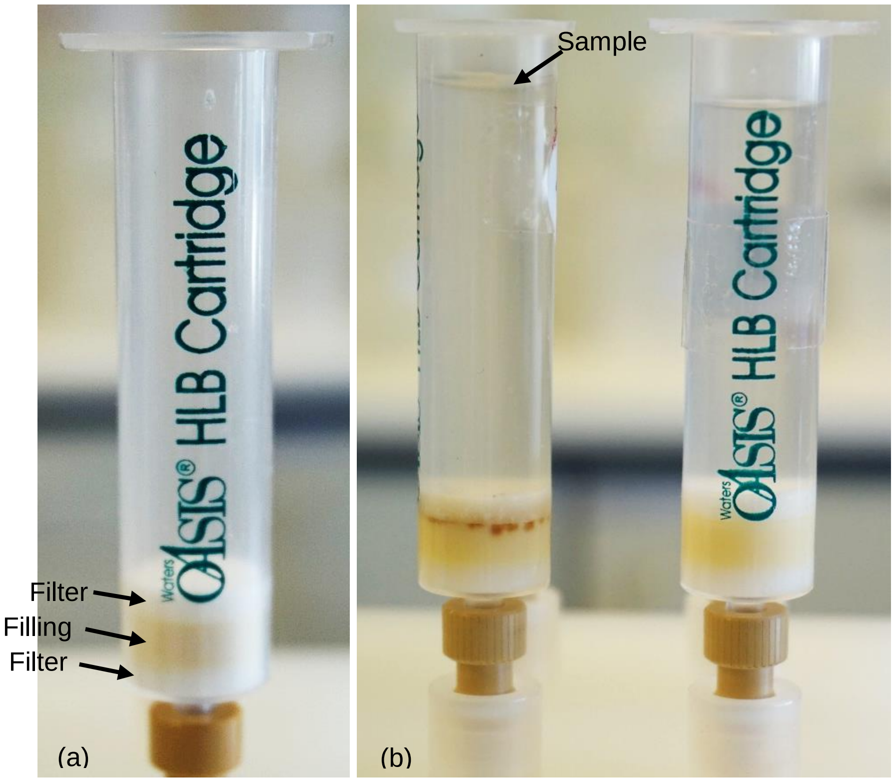


Figure 2.2 - (a): Cartridge used for SPE; (b): Sample loading.

A typical SPE procedure, aiming analyte enrichment, comprises four distinct steps: (1) sorbent conditioning and re-equilibration, (2) sample loading, (3) washing (to remove unwanted sample components) and (4) elution of analytes (in this study there were only taken steps 1, 2 and 4). In the first step, the cartridge is flushed through with strong solvent(s) to remove impurities and to ensure that the sample solution and their analytes will be properly in contact with the surface of the sorbent particles. Re-equilibration with sample solvent (usually an aqueous matrix) turns the phase "environment" compatible with that of the sample solution, avoiding unwanted chemical changes when loading the sample and improving method efficiency and reproducibility.

The second step, sample loading, is when the sample solution is passed through the cartridge with the purpose of retaining the analytes of interest while the sample passes through. For the success of retention, the sample solvent should have a weak power of elution compared to the affinity of the sorbent. The sample volume must be taken into account so as to be well within the capacity of the sorbent bed for whichever components are to be retained, and the flow rate of the solvent should not be extreme (normally no more than 10 $cm^3 min^{-1}$) otherwise retention efficiency will be compromised.

Third step, washing, if 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. These could either be analyte(s) or matrix components, depending on which are not retained by the sorbent.

Finally, fourth step, elution, is to recover retained analytes (Fifield and Kealey 2000).

2.4.2 Analytical methods

The analysis of OCs is a real analytical challenge, not only because of the diversity of chemical properties of these compounds, but also because of generally low concentrations and the complexity of matrices. One of the major limitations in the analysis of emerging contaminants remains the lack of methods for quantification of low concentrations (Petrović et al. 2003).

High performance liquid chromatography

High performance liquid chromatography (HPLC) is a technique used for the physical separation, identification and quantification of components present in a mixture/sample. The separation of mixtures is made with volume of sample in a scale of a microgram to gram. It is based on a stationary phase and a mobile phase. The sample is injected in the HPLC system into the mobile phase (eluent) and then passes through the stationary phase (a column containing an absorbent material) by means of a pressurized flow of eluent. Typically, the eluent (also called solvent) is pumped at pressures up to about 200 bar. It can achieve flow rates of 1–5 $cm^3 min^{-1}$ through 10 – 25 cm columns packed with particles of 3 μm diameter. Normally, the eluent is a water-based solvent, organic solvent or both, which drags the sample components. The components separation occurs into the column. Components migrate through the column at different rates due to different relative affinities for the stationary and mobile phases based on adsorption, size or charge. After leaving the column, the sample passes through a detector which sends the signals to a computer software and it is converted in chromatograms. Figure 2.3 shows a representative scheme of the HPLC system and its main components (Fifield and Kealey 2000).

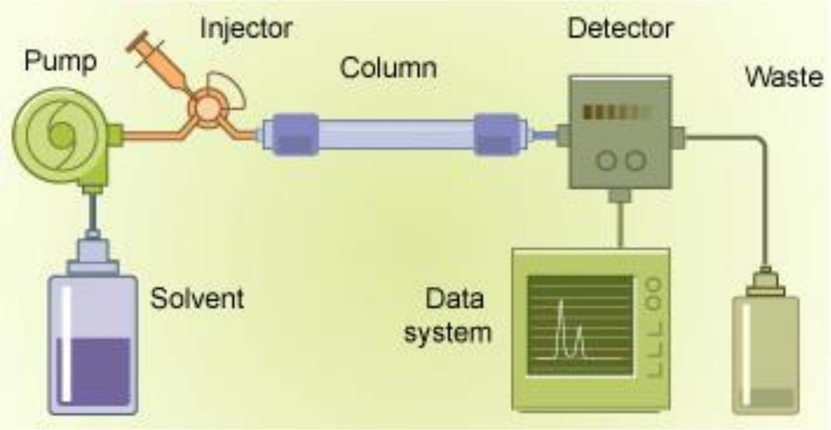


Figure 2.3 - Scheme of HPLC system. (Source: http://www.chromedia.org/).

Calibration

The calibration of the instrument is a crucial step in most measurement procedures. It is based on a set of operations that establish the relationship between the output of the measurement system i.e., the instrument response and the known concentrations of the calibration standards i.e., the amount of analyte present. There is a big variety of analytical methods that require the calibration of an instrument, namely the ones used in this study. It usually involves the preparation of standards containing a known amount of the analyte of interest. Then it is measured the instrument response for each standard and established the relationship between the instrument response and analyte concentration. This relationship is then used to transform measurements made on test samples into estimates of the amount of analyte present (Prichard and Barwick 2003).

Limit of detection and limit of quantification

When the analyte concentrations starts to decrease the standard deviation, at first decreases proportionally, but then remains constant in concentration units. At some point, the analyte response will become equal to or even smaller than the standard deviation and so, the response can no longer be distinguished from random variations. This represents the approaching to the limit of detection (LOD). The lowest concentration at which the analyte can both be reliably detected and at which some predefined goals for bias and imprecision are met is called the limit of quantification (LOQ). The LOQ may be equivalent to the LOD or it could be a much higher concentration but it cannot be lower than the LOD (Armbruster and Pry 2008).

Method recovery

The method recovery of an analyte in an experimental procedure is the detector response obtained from an amount of the analyte added to and then extracted from the matrix, compared to the detector response for the true concentration of that analyte. It may also be understood as the percentage of the analyte originally in the matrix that reaches the end of the procedure (United Nations Office On Drugs and Crime (UNODC) 2009). It is similar to accuracy but includes the extraction efficiency of an analytical method. Recovery of the analyte doesn’t have to be 100%, but the extent of recovery of an analyte should be consistent, precise, and reproducible (Prichard and Barwick 2003).

The method recovery is calculated considering the ratio between the initial (PPCPs concentration spiked in the effluent before ED experiments) and final (PPCPs concentration detected after the ED experiments) concentration and presented as a percentage (equation 2.7).

$$\text{Recovery (\%)} = \frac{\text{PPCPs concentration after analytical determination } \left(\text{mg L}^{-1}\right)}{\text{PPCPs initial concentration } (\text{mg L}^{-1})} \times 100 \qquad \text{(eq. 2.7)}$$

3. Material and methods

3.1 Experimental procedures

For this study, 19 ED experiments were performed using WWTP effluent spiked with five PPCPs: CAF, BPA, E2, EE2 and MBPh. Figure 3.1 shows the main steps taken before the experiments and figure 3.2 represents the main steps taken after the ED experiments (for C.AEM.24 it was not possible to measure the conductivity).

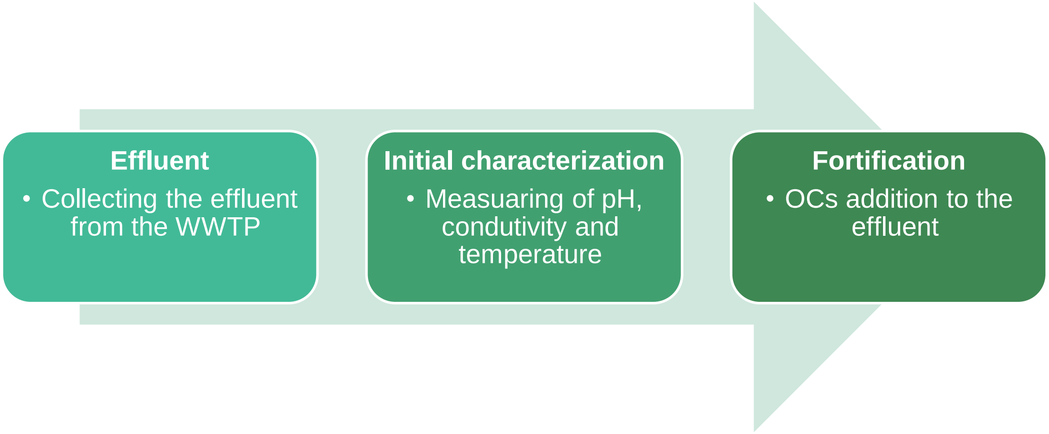


Figure 3.1 - Experimental procedures made before each experiment.

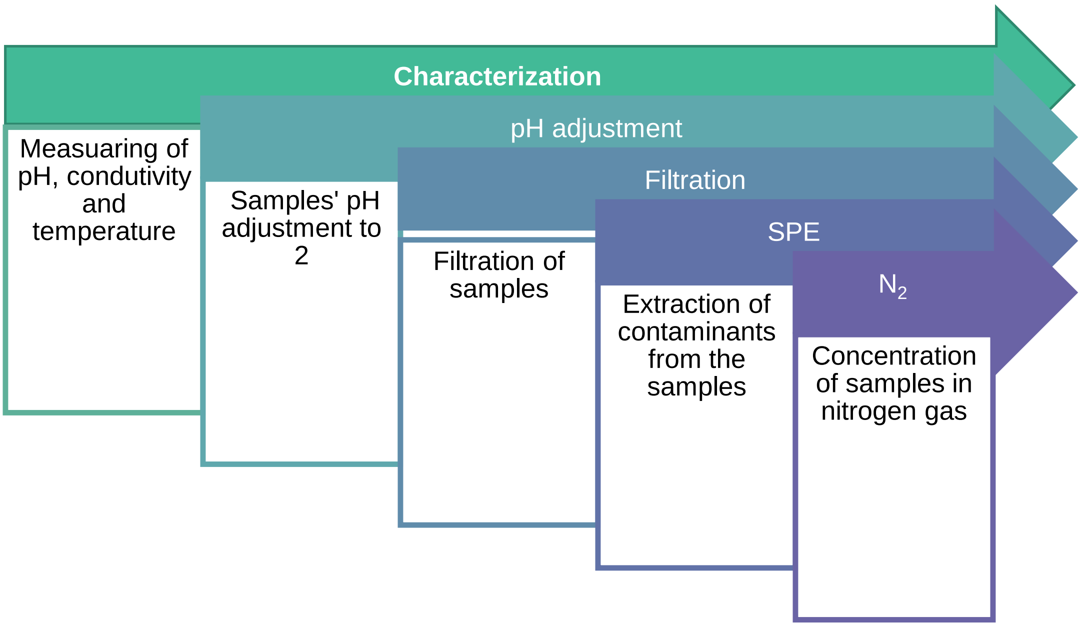
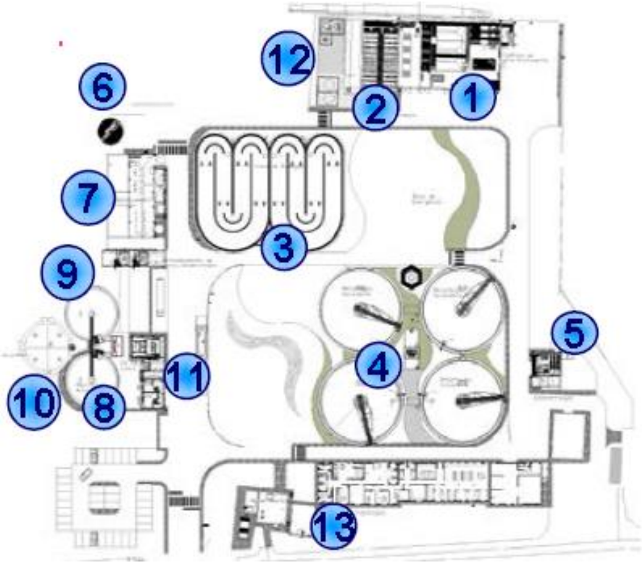


Figure 3.2 - Experimental procedures made after each experiment.

3.1.1 Effluent collection site

The effluent used in this study was collected at the output of the secondary settling tank, at Quinta do Conde WWTP, as described in a subsection from section 2.2.1. In figure 3.3 it is shown the plan and respective treatments of the WWTP of Quinta do Conde, where the liquid phase treatment comprises the preliminary treatment, primary sedimentation, aeration tank, secondary sedimentation and disinfection (through UV radiation). The solid phase (sludge) treatment includes gravity thickener, anaerobic sludge digestion, dewatering and storage in proper containers. Samples were collected at the output of secondary settling tank (represented by number four in figure 3.3). The initial and final values of effluent characterization (TSS, pH, BOD_5, COD, P_T, NO_3, NO_2, NH_4,) were determined in the lab of Quinta do Conde WWTP.



1 – Preliminary treatment
2 – Primary settling tank
3 – Aeration reactor
4 – Secondary settling tank
5 – UV disinfection
6 – Gravity thickener
7 – Sludge treatment building
8 – Sludge digestion
9 – Silos of dewatered sludge
10 – Gasometer
11 – Co-generation
12 – Deodorization
13 – Exploitation building

Figure 3.3 - Wastewater treatments applied in WWTP of Quinta do Conde. Source: (Águas de Lisboa e Vale do Tejo, 2007).

3.1.2 Effluent sampling

Effluent was collected weekly, in a plastic flask and kept cooled until the arrival to the laboratory, where the temperature is controlled. In the laboratory, it was stored in the hotte till it would be spiked to be used in the experiments.

3.2 Reagents and material

CAF (≥97%), BPA (≥99%), E2 (≥97%), EE2 (≥98%) and MBPh (≥97%) were purchased from Aldrich (Steinheim, Germany). All used solvents were from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). Acetonitrile (ACN), methanol (MeOH) and acetone (Ace) were Gradient Grade. The water used for SPE and HPLC eluent was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA).

Besides the laboratorial material used for the experiments and samples preparation it was used glass volumetric flasks Linex class A (10 mL), glass measuring pipettes Linex class A (1 mL, 2 mL and 5 mL), micropipettes LabNet (10µL to 1000µL), glass beakers (10 mL to 1000 mL), glass funnels 60º short stem, glass Pasteur pipettes, glass measuring cylinders (10 mL to 1000 mL), glass graduated tubes (10 mL and 15 mL) and glass stoppered bottles (2 mL, 6 mL and 22 mL). All material was washed with a specific soap (Teepol) and then passed three times through deionized water (conductivity < 0.1 µS cm^{-1}) and one time through MeOH.

3.3 Electrodialytic experiments

The ED laboratory cell used (figure 3.4) had two compartments (2C). The cell was made of glass with an internal diameter of 8 cm and length of 10 cm. The ion exchange membranes separating the two 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. Electrolyte and effluent (in some experiments, further on explained) was circulated by use of a peristaltic pump (4 mL min^{-1}). The temperature was constant and controlled by air conditioning (about 22/23 ºC).

All the results obtained for the removals of OCs during the experiments were based on the recovery of each compound for each period of time (equation 3.1).

$$\text{Removal (\%)} = \left(1 - \frac{\text{PPCPs concentration after analytical determination } (\text{mg L}^{-1})}{\text{PPCPs mean concentration recovery } (\text{mg L}^{-1})}\right) \times 100 \qquad \text{(eq. 3.1)}$$

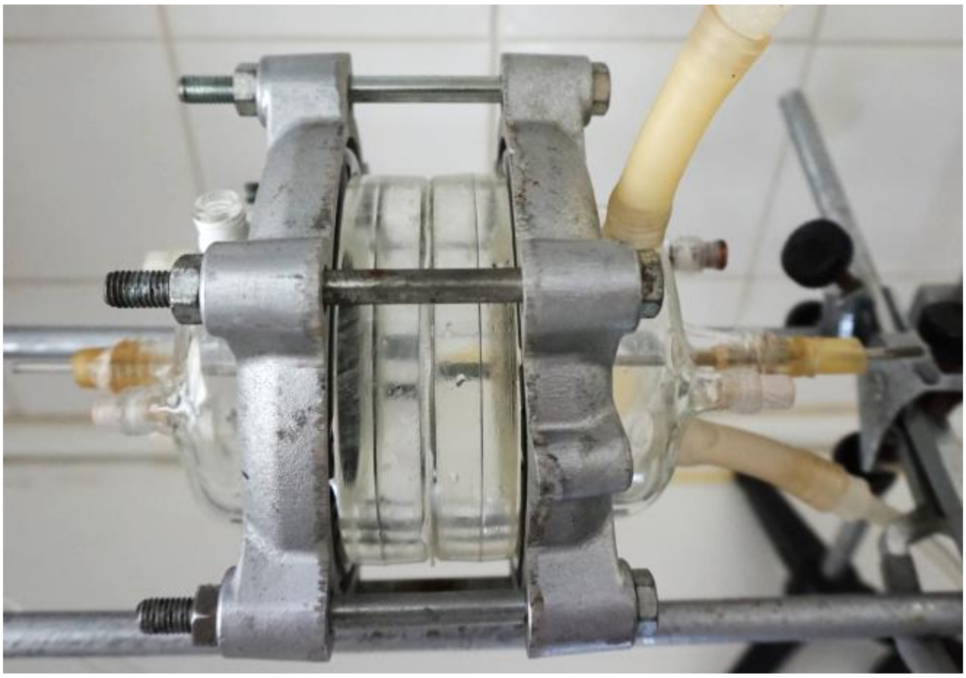


Figure 3.4 - ED laboratory cell.

Different ED cell set-ups were used varying the membrane used (AEM or CEM) and the compartment in which the effluent was placed (cathode or in anode end) and all of them with electrolyte recirculation. Figure 3.5 shows a schematic representation of the experimental designs used during the study. The described experiments are resumed in table 3.1.

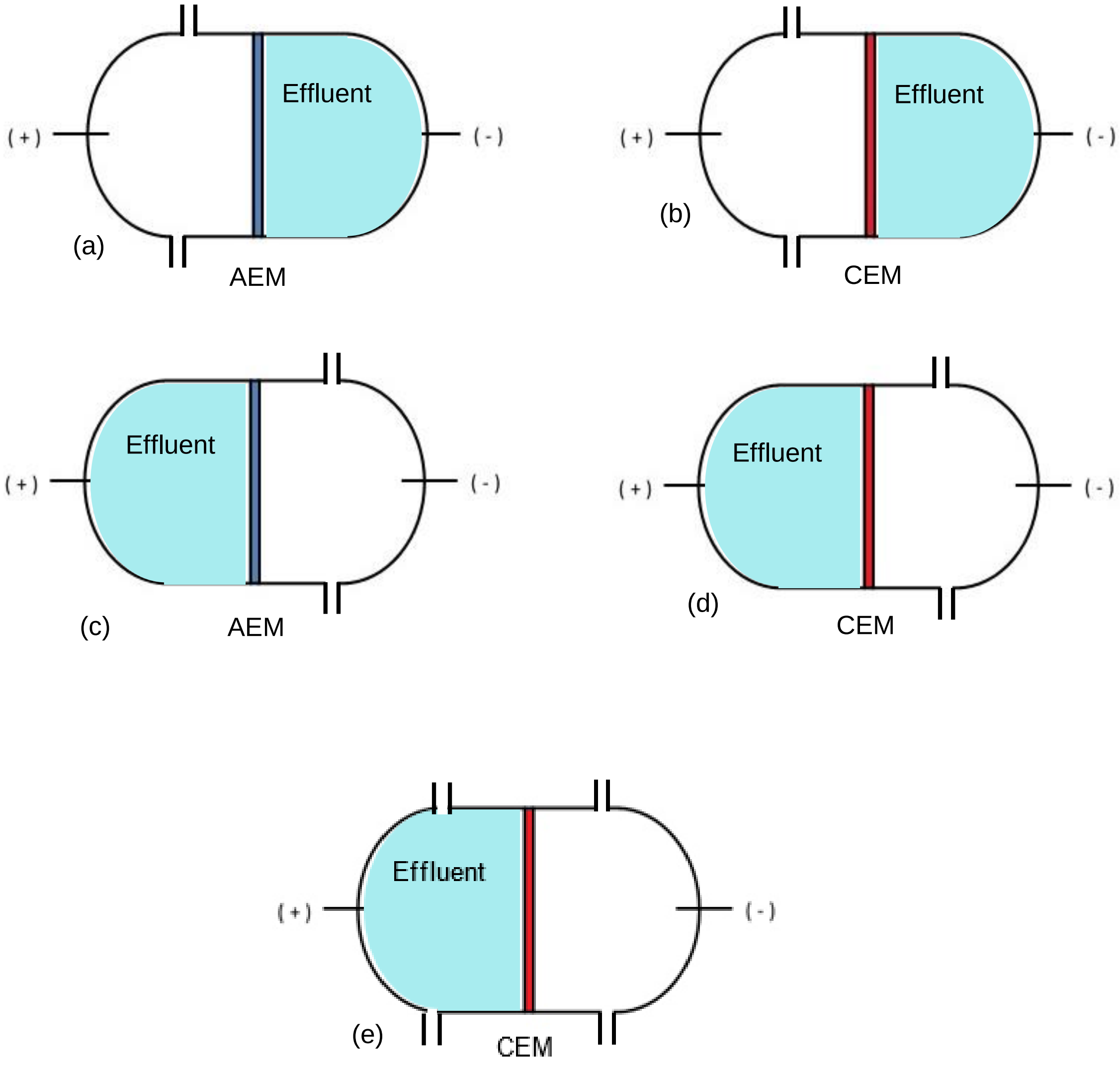


Figure 3.5 – Schematic representation of the five laboratory cell set-ups used in which the effluent was placed at the: (a) cathode end with AEM; (b) cathode with CEM; (c) anode with AEM; (d) anode with CEM and (e) anode with CEM with both electrolyte and effluent recirculation.

Table 3.1 - Experimental conditions

Experiment	*Effluent compartment*	*Membrane*	*Current (mA)*	*Time (h)*	Effluent circulation	*Scheme (Figure 3.5)*
Control 1	-	AEM	0	24	No	
Control 2	-	CEM	0	24	No	
A.AEM.24	Anode	AEM	20	24	No	(c)
C.AEM.24	Cathode	AEM	20	24	No	(a)
A.CEM.24	Anode	CEM	20	24	No	(d)
C.CEM.24	Cathode	CEM	20	24	No	(b)
A.AEM.12	Anode	AEM	20	12	No	(c)
C.AEM.12	Cathode	AEM	20	12	No	(a)
A.CEM.12	Anode	CEM	20	12	No	(d)
C.CEM.12	Cathode	CEM	20	12	No	(b)
A.AEM.6 *n=3*	Anode	AEM	20	6	No	(c)
C.AEM.6 *n=3*	Cathode	AEM	20	6	No	(a)
A.CEM.6 *n=3*	Anode	CEM	20	6	No	(d)
C.CEM.6	Cathode	CEM	20	6	No	(b)
A.AEM.6 (20,40,60)	Anode	AEM	20-40-60	6	No	(c)
C.AEM.6 (20,40,60)	Cathode	AEM	20-40-60	6	No	(a)
A.CEM.6 (R)	Anode	CEM	20	6	Yes	(d)
A.AEM.6+6	Anode	AEM	20	6+6	No	(c)
A.CEM.6+6	Anode	CEM	20	6+6	No	(d)

Meaning of the experiment code:

X.YEM.Z – X is the compartment where the effluent is placed (A - Anode or C - Cathode); Y is the membrane used (C - Cation or A - Anion); Z is the duration of experiment, in hours and R means the recirculation of the effluent.

Initially, twelve experiments at 20 mA were conducted along 6, 12 and 24 hours altering between the use of an AEM or CEM and effluent in the anode or cathode compartment. Two control experiments (no current) using an AEM (Control 1) and CEM (Control 2) were also carried out. After, two experiments of 6 hours with a current gradation (20, 40, 60 mA) were made using an AEM and placing the effluent in the cathode and anode end. It was also carried out one experiment of 6 hours with recirculation of both electrolyte and effluent and two experiments of 6 plus 6 hours in which the effluent was renewed after the first 6 hours. Summarizing, a total of 19 ED experiments were carried out, all run in dark conditions, for different periods of time (6, 12 and 24 hours) and experimental designs.

It was used 300 mL of effluent and 500 mL of electrolyte (a 10^{-2} M $NaNO_3$ solution). In order to assess the contaminants mobilization and remediation/degradation by ED, the effluent was spiked with 3 ppm of a mixture containing the OCs in acetone and deionized water. The effluent had to be spiked with a known concentration in order to calculate the percentage of removal/degradation.

At the end of the experiments both electrolyte and effluent samples (catholyte and anolyte, depending on the set-up used) were collected and hydrogen peroxide measured. Hydrogen peroxide was determined using semi-quantitative test strips Quantofix Peroxide25 (Macherey-Nagel, Germany). Then, their pH and volume were registered and pH adjusted to 2 (in both effluent and electrolyte samples). After, effluent was filtrated under vacuum and the analytes were extracted by SPE. Membranes were soaked in HNO_3 (1M) for 24 h, to assure the decontamination, and then in deionized water to allow membranes re-equilibration.

3.4 PPCPs analysis

3.4.1 Sample preparation

Aqueous samples

After the ED experiments, the liquid matrices (effluent and electrolyte) were collected, their volume was registered and pH adjusted to 2, using nitric acid. After, the effluent was filtered by 0.45 µm filters (glass fibre). The total P content was determined by inductively coupled plasma - atomic emission spectrometer (ICP-AES, Varian 720-ES). The extraction of the organic analytes present in both effluent and electrolyte was performed by 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 MeOH, followed by re-equilibrium with 3×6 mL of Milli-Q water. The aqueous samples, 200 mL of the electrolyte and 300mL of effluent, 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. 2 min by vacuum. The retained analytes were eluted with 6 mL of MeOH.

All the extracts were concentrated under a gentle stream of nitrogen from 4 mL to 2 mL. Samples were transferred to a vial and kept at -20ºC until analysis in HPLC. Figure 3.6 shows the steps described earlier.

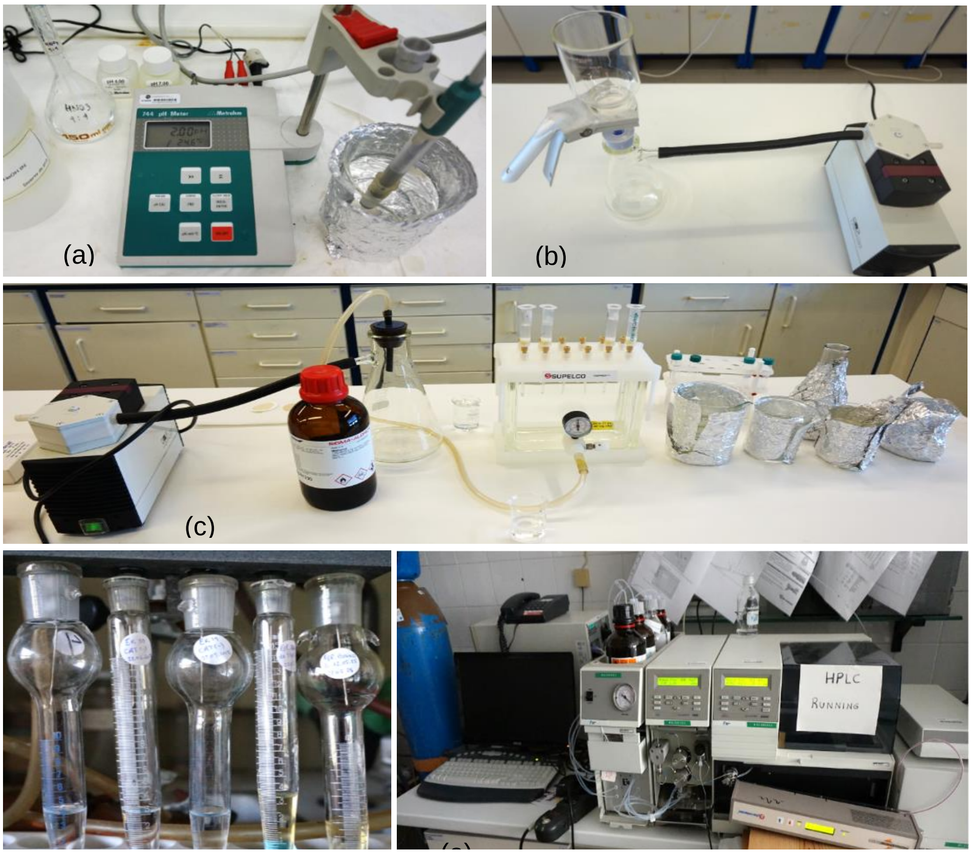


Figure 3.6 - Sequential analytical procedures for the aqueous samples: (a) pH adjustment; (b) Filtration; (c) SPE; (d) N_2 concentration; (e) HPLC analysis.

3.4.2 HPLC conditions

HPLC was performed on a Finnigan MAT HPLC system (ThermoScientific, USA) equipped with a SP P4000 Pump, a AS 3000 Auto-sampler, the diode array detector (DAD) was a TSP Spectra SYSTEM UV6000LP with the wavelength set between 200 and 800 nm and a TSP SN 4000 Interface. The contaminants separation was carried out using Chromolith High Resolution RP-18e column with 100 mm × 4.6 mm from VWR (Darmstadt, Germany) and Onyx Security Guard C18 cartridges (5 × 4.6 mm) from Phenomenex (Torrance, USA). All HPLC runs were performed at a constant flow rate of 1 mL min^{-1}, in gradient mode, with the oven set to 38 ºC. The eluents used were a mixture of ACN/Mili-Q water/Formic acid (eluent A: 5/94.5/0.5%; eluent 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. The samples analysed in HPLC had a total volume range between 200 µL and 1000 µL, depending on the concentration/dilution needed. All operations and data analysis were processed by the Xcalibur software v.1.3. (Thermo Scientific, USA). These conditions were adopted according to the ones used by (Guedes et al. 2015).

3.4.3 Calibration curve and recovery of the analytical procedure

The linearity of the method was evaluated for the analytes using standard solutions with different concentrations (0.5, 2.0, 3.5, 5.0, 6.5 and 8.0 mg L^{-1}). The standard solutions were dissolved in MeOH from a stock solution, composed by the compounds under study (CAF, BPA, E2, EE2 and MBPh) in a concentration of 400 ppm diluted in MeOH:Eluent A (1:1, v:v). The effluent was spiked with the five compounds under study (CAF, BPA, E2, EE2 and MBPh), at a concentration of 3 ppm, in order to determine the extraction recoveries. Non-spiked effluent was also extracted and analysed to check possible interfering compounds and the specificity of the method.

3.4.4 Statistical analysis

The statistically significant differences in removal percentages of OCs among replicates for 5% level of significance were analysed through ANOVA tests followed by Tukey tests using GraphPad Prism software.

4. Results and discussion

4.1 Analytical analysis

4.1.1 Calibration

Standard solutions of CAF, BPA, E2, EE2 and MBPh were initially analysed by HPLC, to determine the retention time of each compound. It was used an HPLC analysis in gradient mode, which consisted in the usage of more than one eluent for the mobile phase, resulting in alteration gradient of the mobile phase composition during the analysis. The gradient is formed by increasing the percentage of organic solvent (in this case ACN). This represents the best suited type of analysis once the compounds under study highly differ in their physico-chemical properties. Two eluents were used, A and B, as described in section 3.4.2. The first eluent, A, was the weaker solvent, in this case, 5% of ACN / 94.5 % of Mili-Q water / 0.5% of formic acid and eluent B was the stronger solvent, 94.5% of ACN / 5 % of Mili-Q water / 0.5% of formic acid. This gradient affects the retention time, which is measured from the time at which the sample is injected to the point at which the display shows a maximum peak height for that compound, indicating how long it takes for a compound to leave the HPLC column (Chromacademy 2010).

Chromatograms were obtained for each standard solution with peaks corresponding to the different PPCPs. Figure 4.1 shows an example of an obtained chromatogram.

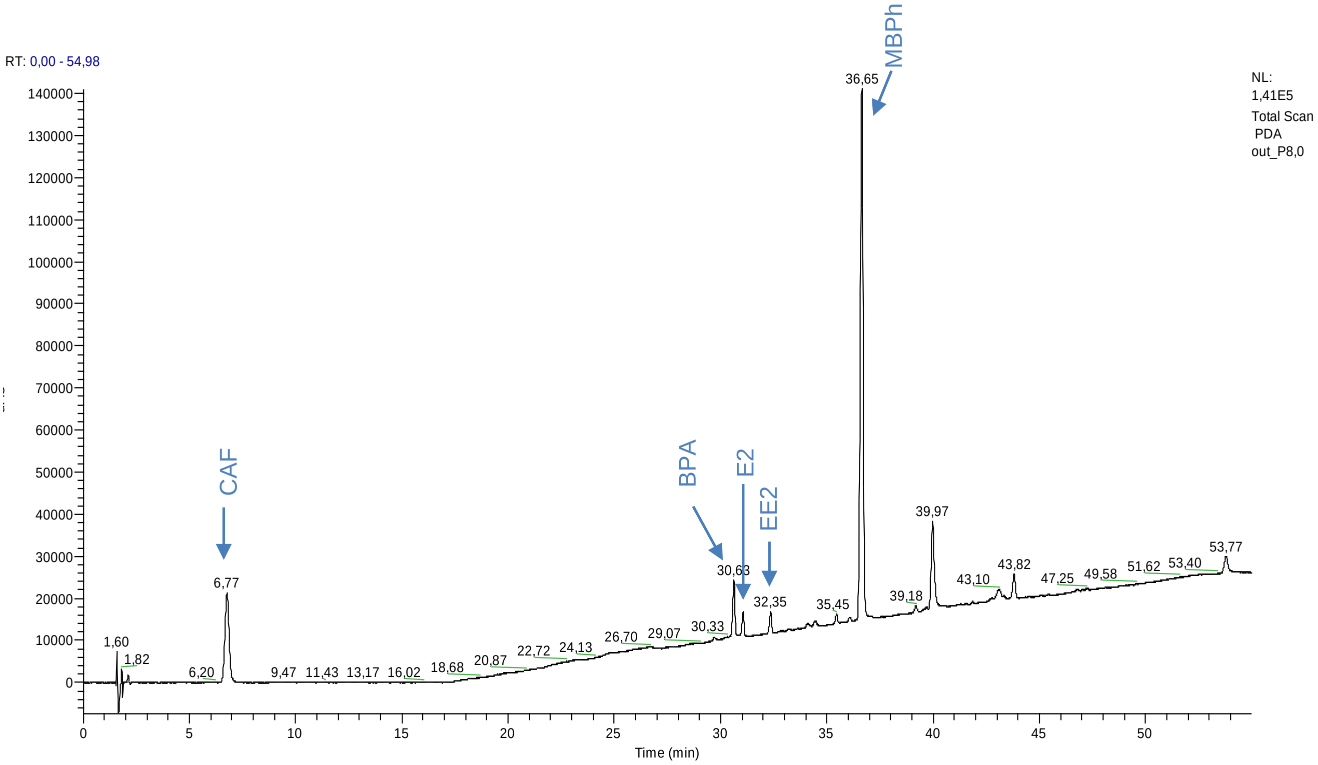


Figure 4.1 - Example of a chromatogram obtained for a standard solution (8 mg L^{-1}).

CAF has the lowest retention time (6.8 min), followed by BPA (30.6 min), E2 (31.1 min), EE2 (32.4 min) and MBPh (36.7 min). This fact can be explained by the eluent gradient. The first eluent used is mostly (94.5%) composed by water and CAF is the compound with lower log K_{ow} and higher solubility in water (-0.07 and 2.16×10^4 mg L^{-1}, respectively) which results in a higher affinity to the mobile phase, being the first to leave the HPLC column.

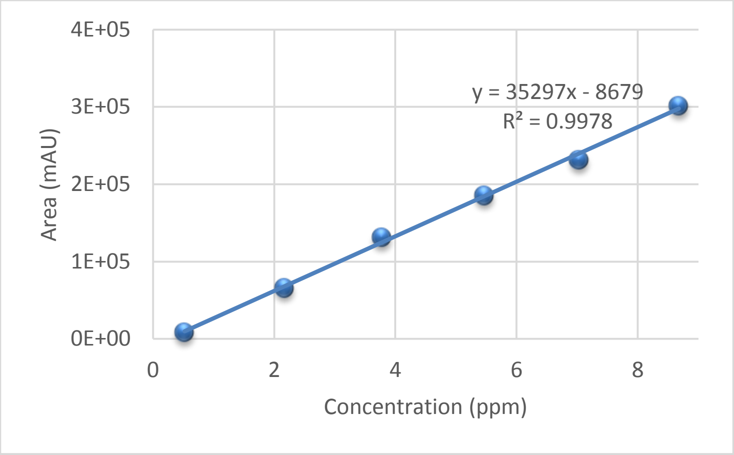
BPA, E2 and EE2 have close retention times. BPA has high solubility in water (120 mg L^{-1}), when compared to E2 and EE2 (3.9 and 11.3 mg L^{-1}, respectively) and that might be an explanation for their output order. On the other hand, these three compounds have similar log K_{ow} values (3.32 for BPA, 4.01 for E2 and 3.67 for EE2) which might explain the similar retention times.

MBPh has the highest retention time from the compounds in study which might be due to its high solubility in organic solvents and so, it will have more affinity to the mobile phase when it has a higher percentage of ACN.

This knowledge of the retention time will allow to identify the chemicals of interest in an experimental sample. That can be done by comparing chemicals retention time and obtained UV spectrum (signature produced by each chemical in the detector) with those of each compound from the calibration standard solution. If the retention time of a compound present in an experimental sample match the retention time of a compound present in the standard solution, it might be the same compound. However, retention time can varies and so, both retention time and UV spectrum are used to identify the compound.

After the analysis of the chromatograms and identification of each compound, the peak areas were calculated in order to determine the calibration curve. Calibration curve, by interpolation, will allow the determination of a compound concentration present in an experimental sample. The calibration curve of this study was performed through standards with concentrations of 0.5, 2.0, 3.5, 5.0, 6.5 and 8.0 mg L^{-1}. The obtained data fitted a linear regression, $y = mx + b$, where y is the area, in (mAU), x is the concentration of the compound, in ppm, m the slope and b the y-intercept.

Figures 4.2 to 4.6 represent the calibration curves obtained for CAF, BPA, E2, EE2 and MBPh, respectively. It is observed that the point corresponding to the concentration of 6.5 ppm is out of the calibration curve, comparing to the other points. This could be due to some kind of error in the solution but it does not affect the strength of the curve.



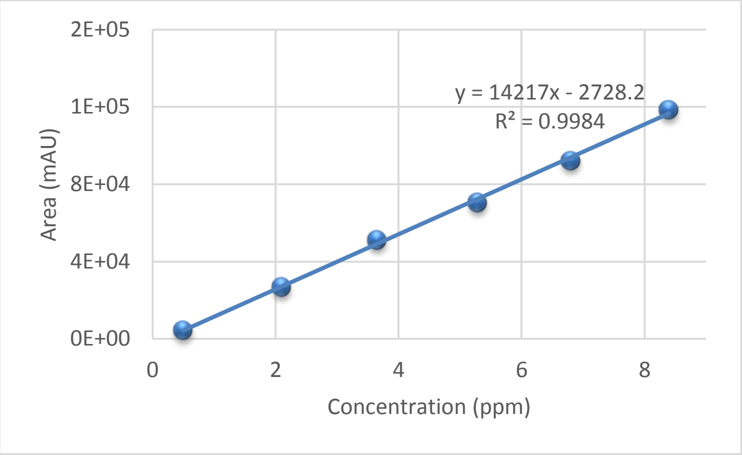
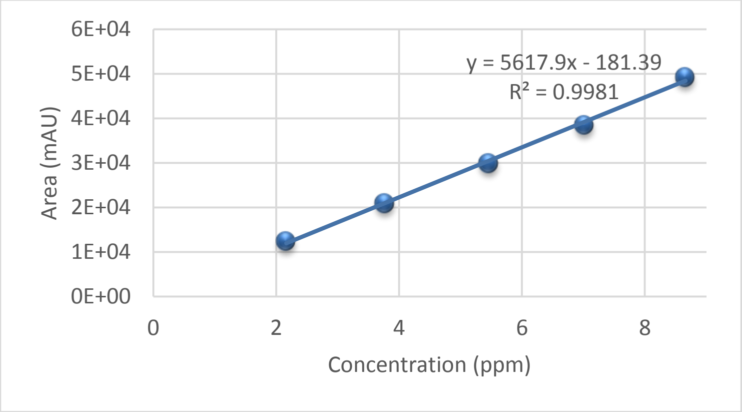


Figure 4.2 - CAF calibration curve.

Figure 4.3 - BPA calibration curve.



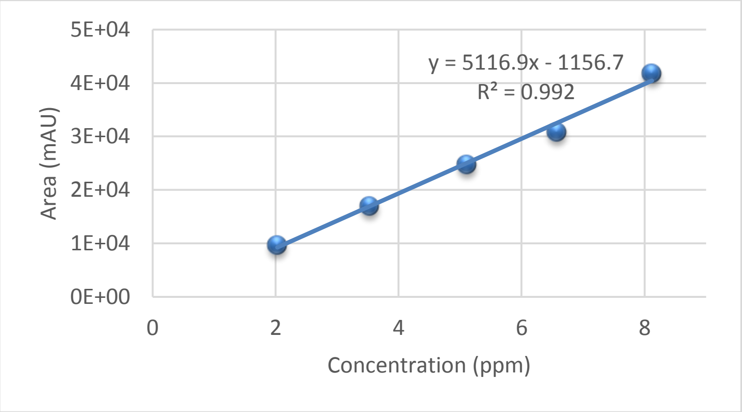


Figure 4.4 - E2 calibration curve.

Figure 4.5 - EE2 calibration curve.

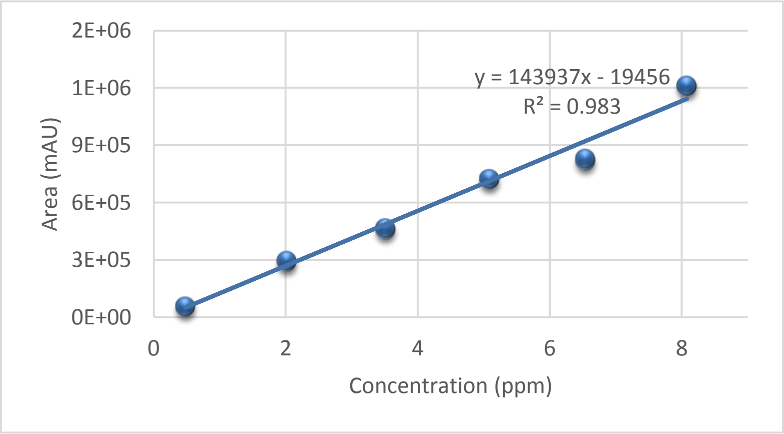


Figure 4.6 - MBPh calibration curve.

The coefficient of determination (R^2) is used to determine how well a set of observed data values fit a mathematical model. Low values of R^2 represent a dispersion of data values in relation to the mathematical model. Thus, to express a good adjustment of data values to the calibration line, R^2 values should be as close to 1 as possible and should not be lower than 0.990 (International Organization for Standardization, 1990). In this case, except for MBPh, which presents an R^2 of 0.9830, all the calibration curves equations have R^2 values bigger than 0.990. The R^2 value of MBPh indicates a lower linearity of results comparing to the other compounds, even though with an acceptable R^2 value.

The relative standard deviation (RSD) aims to describe the dispersion of the variable in a way that does not depend on the variable's measurement unit and is defined as the ratio of the standard deviation to the mean. It basically expresses the precision and repeatability of an assay and is commonly expressed as a percentage. The higher the RSD, the bigger the dispersion in the variable. In this case, CAF, BPA, E2, EE2 and MBPh present a RSD in a range of 0 – 6%, 0 – 6%, 0 – 5%, 0 – 5% and 0 – 2%, respectively. The bigger range is 0 – 6%, for CAF and BPA, and the lower range of RSD is presented for MBPh, being the compound with lower variation relatively to the predicted value.

The calibration curves also give the working range, which represents the interval experimentally established and statistically proved by the calibration of the method, between the lowest and highest mass concentration. This is the range of concentration that can be adequately determined by the instrument, by providing an useful signal that can be related to the concentration of the analyte (International Organization for Standardization 1990). It is clear that E2 and EE2 have a similar R^2 and, at the same time, lower working range, 2.03 – 8.12 mg L^{-1} and 2.05 – 8.20 mg L^{-1}, respectively, comparing to the other compounds. CAF, BPA and MBPh also present a working range very similar between them 0.49 – 8.24 mg L^{-1}, 0.48 – 8.00 mg L^{-1} and 0.56 – 9.40 mg L^{-1}, respectively.

4.1.1 Limit of detection and limit of quantification

The analytical thresholds of the method were defined based on the calculation of LOD, calculated using the equation 4.1, and LOQ, calculated using the equation 4.2.

$$LOD = 3 \times S_0 \qquad \text{(eq. 4.1),}$$

$$LOQ = 3 \times LOD \qquad \text{(eq. 4.2)}$$

Where:

S_0 is the residual standard deviation of the calibration curve. Using the equations presented, there were obtained the values for LOD and LOQ, for each compound, presented in table 4.1.

Table 4.1 – LOD and LOQ values for HPLC analysis.

	HPLC method	
Compound	*LOD (ppm)*	*LOQ (ppm)*
CAF	0.11	0.34
BPA	0.14	0.42
E2	0.28	0.84
EE2	0.60	1.8
MBPh	0.16	0.47

The use of other techniques such as liquid chromatography coupled with mass spectrometry LC-MS could provide lower LOD and LOQ values. However, the HPLC LOD and LOQ values were considered sufficient for the purpose of this study.

4.1.2 Method recovery

The experiments carried out to assess the recoveries for each contaminant, were based on the fortification of effluent (with a solution containing the contaminants, ACE and deionized water) followed by analytes extraction using SPE method. The spiked effluent was left in dark conditions, during the same time as the experiments (6, 12 and 24 hours; n=2). The recovery was calculated considering the ratio between the initial and final OCs concentration and presented as a percentage, as described in section 2.4.2. Figure 4.7 shows the recovery results achieved for each contaminant in study, for three different periods of time: 6, 12 and 24 hours, and the respective standard deviation (n=2).

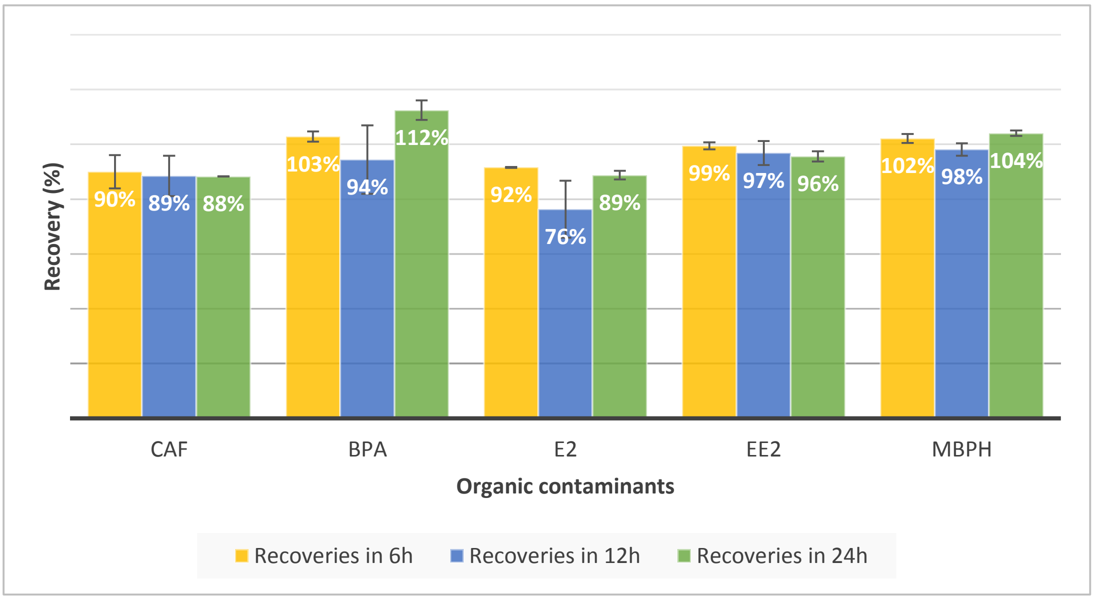


Figure 4.7 - Graphic representation of the percentage recoveries for each contaminant and respective standard deviation (n=2), for 6, 12 and 24 hours.

It is observed that there is no relation between time and recovery. This means that besides the time (6, 12 or 24 hours), the recovery percentages were in the same order of magnitude, with small deviations: CAF had a mean recovery of 89 ± 1%, BPA 103 ± 9%, E2 86 ± 8%, EE2 97 ± 2% and MBPh 101 ± 3%.

Recovery percentages were between approximately 80 and 110%. Recovery should be within 100 ± 20% in order to assure analytical quality of the results, which in this case is verified for all compounds except for E2 (at 12 hours). Even though, the higher standard deviation observed for E2, puts the compound inside the analytical error of the accepted range. A statistical analysis was carried out between the different periods and compounds and there were no statistically significantly differences between achieved the recoveries at $p < 0.05$.

CAF had a recovery percentage of 88 ± 0% in 24h, 89 ± 7% in 12h and 90 ± 6% in 6h. In general, CAF presented lower percentage of recovery (88 – 90%), comparing to the other tested contaminants. CAF is more polar, has a lower log K_{ow} value being more soluble in water. The extraction capacity of sorbents in the SPE bed depends on the bed capacity, the volume of sample loaded, the nature and volumes of conditioning solvents and eluents. One important parameter is the breakthrough volume, which determines the maximum volume of sample which can be introduced into the sorbent. Once the breakthrough volume is exceeded, contaminants might pass through the sorbent bed. Once CAF is more soluble in water and presents a low K_{ow}, it might have reached its breakthrough volume and passed through the cartridge, thus presenting lower recovery percentages. Additionally, it could also be influenced by the capacity factor, which is a mean of measuring the retention of an analyte on the sorbent. A low capacity factor value indicates that the analyte is poorly retained (Scientific 2014).

E2 presented recovery percentages in a range of 76 – 92%, and a higher variation within the different periods of time compared to the BPA, EE2 and MBPh. BPA also showed variation between the recoveries of 6, 12 and 24 hours. EE2 and MBPh have the highest percentages of recovery (96 – 99% and 98 – 104%, respectively) which can be related to their, e.g., good solubility in MeOH, used in SPE as final step for the dissolution of the OCs.

4.2 ED experiments results

Initial characteristics of the effluent used on ED experiments are presented in table 4.2. Some parameters such as pH, TSS, BOD_5 and COD were measured in each sampling period, while Nt, P_T, NO_3, NO_2 and NH_4, were measured only on specific times. These parameters were measured in the Quinta do Conde WWTP laboratory and the conductivity was measured in the laboratory where this study took place, right after the arrival of the effluent. The presented parameters are essential to characterize the effluent about its quality. It is also presented in table 4.3 the initial main characteristics of electrolyte.

Table 4.2 - Initial characteristics of the effluent used in the ED experiments

Date	*TSS (mg/L)*	*pH*	*BOD_5 (mg/L)*	*COD (mg/L)*	*P_T (mg/L)*	*NO_3 (mg NO_3/L)*	*NO_2 (mg NO_2/L)*	*NH_4 (mg NH_4/L)*	*Conductivity (µS/cm)*
05.05.15	<10	6.94	<6	27	4.7	*	*	4.8	*
12.05.15	<10	7.70	<6	37	*	*	*	*	885
19.05.15	<10	6.84	<6	37	7.8	*	*	*	829
02.06.15	<10	6.89	4.9	34	4.1	*	*	0.1	859
16.06.15	17	7.31	6.1	47	11.5	*	*	*	947
30.06.15	<10	7.54	<6	37	3.1	*	*	*	849
21.07.15	5	7.31	<6	40	3.2	<4	<4	7.6	840

* not available / not determined

Table 4.3 - Initial characteristics of electrolyte used in the ED experiments

Date	*pH*	*Conductivity (µS/cm)*
05.05.15	6.02	*
12.05.15	6.28	1 188
19.05.15	6.13	1 342
02.06.15	7.45	1 179
16.06.15	6.42	1 146
30.06.15	6.37	1 195
21.07.15	6.21	1 213

* not available / not determined

All samples presented TSS below 10 mg L^{-1}, except the sample collected on June 16th that contained 17 mg L^{-1} of TSS. This samples also presented the highest BOD_5, COD, P_T, and conductivity. These differences may be explained by WWTP influent characteristics as well as biological reactor conditions which affect the properties of the effluent at the secondary settling tank. The weather conditions of the sampling date may have also influenced these results. There were also analysed each effluent samples, without fortification, and it was not detected any of the OCs in study.

4.2.1 pH, conductivity and voltage

Figure 4.8 represents the pH values measured at the end of each ED experiment for electrolyte and effluent samples, represented as anolyte and catholyte, according to the experimental design used.

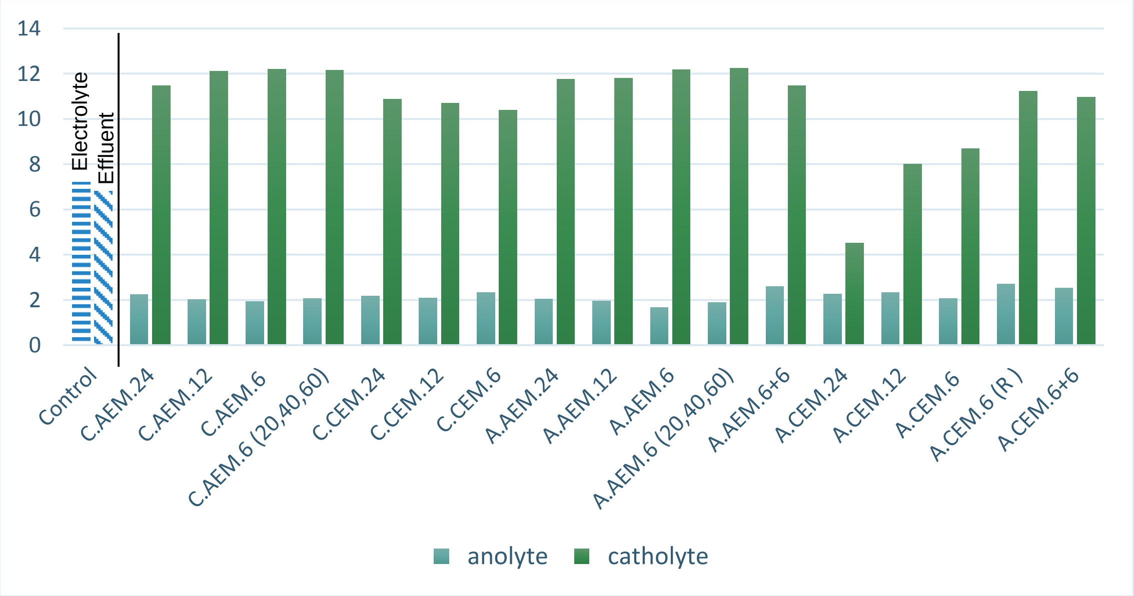


Figure 4.8 - Values of pH for both anolyte and catholyte after each ED experiment.

Both effluent and electrolyte have a similar initial value of pH, approximately 7 (see table 4.2 and table 4.3). It can be observed that in control experiments (when there is no current applied) the pH value is maintained throughout the experimental period, being similar to the initial value. After the ED experiments, values of pH in the cathode are higher than the pH values in the anode. Anolyte pH was around 2.2 ± 0.3 which is explained by the water electrolysis and consequent formation of H^+ ions in the anode compartment, causing the pH decrease in this compartment (eq. 2.4 – please see section 2.3.1). Catholyte values of pH were around 10.9 ± 1.9 which is explained by the production of OH^-, due to water electrolysis, in the cathode end (eq. 2.4 – please see section 2.3.1). These decrease and increase of pH is detected in both effluent and electrolyte, when placed in anode and cathode compartment, respectively.

There is no significant differences in anolyte and catholyte pH values among the different periods of time, pulse current or the compartment where electrolyte and effluent are placed (RSD of 12 and 19%, for anolyte and catholyte, respectively).

However, in some experiments such as A.CEM.24, A.CEM.12 and A.CEM.6, catholyte pH values are slightly low (4.5, 8.0 and 8.7, respectively, with an R^2 of 0.97), comparing to the other set-up values of pH in the catholyte. This might suggest that, in this set-up, CEM influenced the variation of pH during the experiments. This membrane will allow the migration of H^+ ions from the anode (effluent) to the cathode (electrolyte), resulting in a pH decrease in the electrolyte (Reddy and Cameselle 2009).

The conductivity was also measured after each ED experiment for both effluent and electrolyte. They are represented as anolyte and catholyte, according to the experimental design used, in figure 4.9.

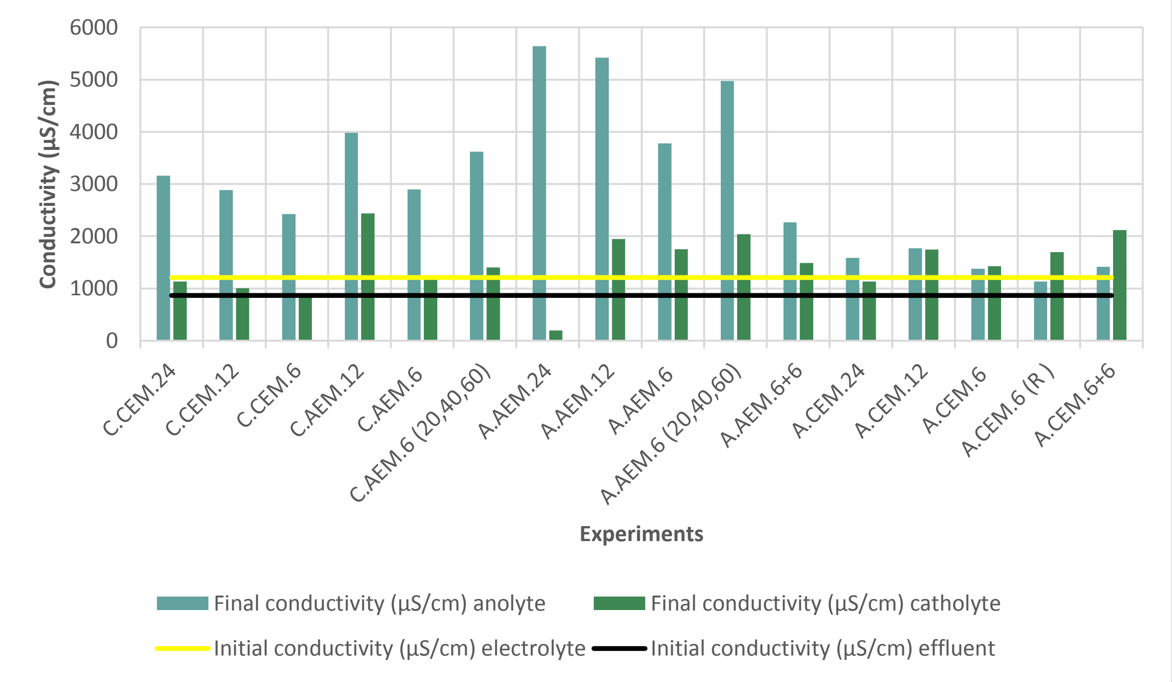


Figure 4.9 - Measured conductivity for each experiment (anolyte and catholyte).

Final values of conductivity, either for effluent and electrolyte, are higher than the initial ones (comparing to their initial mean value, which was included in the graphic for easier comparison). This fact might be due to the degradation of the compounds once there will be more ions present in solution, causing an increase of conductivity.

Conductivity is higher in the anolyte than in the catholyte, in A.AEM set-up (effluent placed in the anode compartment and AEM). This might be due to the oxidation processes, which occurs in the anode compartment. When a compound is degraded it can generate more compounds and so more ions are present in the solution, increasing the conductivity, as described before. Additionally, the anions from the electrolyte (NO_3^-) can pass through the membrane and reach the anode end.

For C.CEM and C.AEM set-ups, the conductivity in the anolyte (electrolyte) is also higher than in the catholyte (effluent). In the cathode end, reduction reactions or reactions with other compounds may promote the electromigration of ions, e.g. PPCPs intermediates or by products, towards the electrolyte which might explain the higher conductivity in the anode compartment.

In A.CEM set-up (electrolyte placed in the cathode and use of a CEM), the conductivity after the experiments is higher on the anode (effluent) only for 24 hours of experiment. In other way, conductivity is higher in the cathode compartment than in the anode, for 6 hours experiments, and equal, for 12 hours experiments. This fact might suggest that, as time passes, and as the degradation of PPCPs increases, also increases their intermediates or by-products, which have a negative charge. But the presence of a CEM, does not allow their migration towards the electrolyte, increasing the effluent conductivity.

During the ED experiments initial and final voltage was also measured. The results are presented in figure 4.10

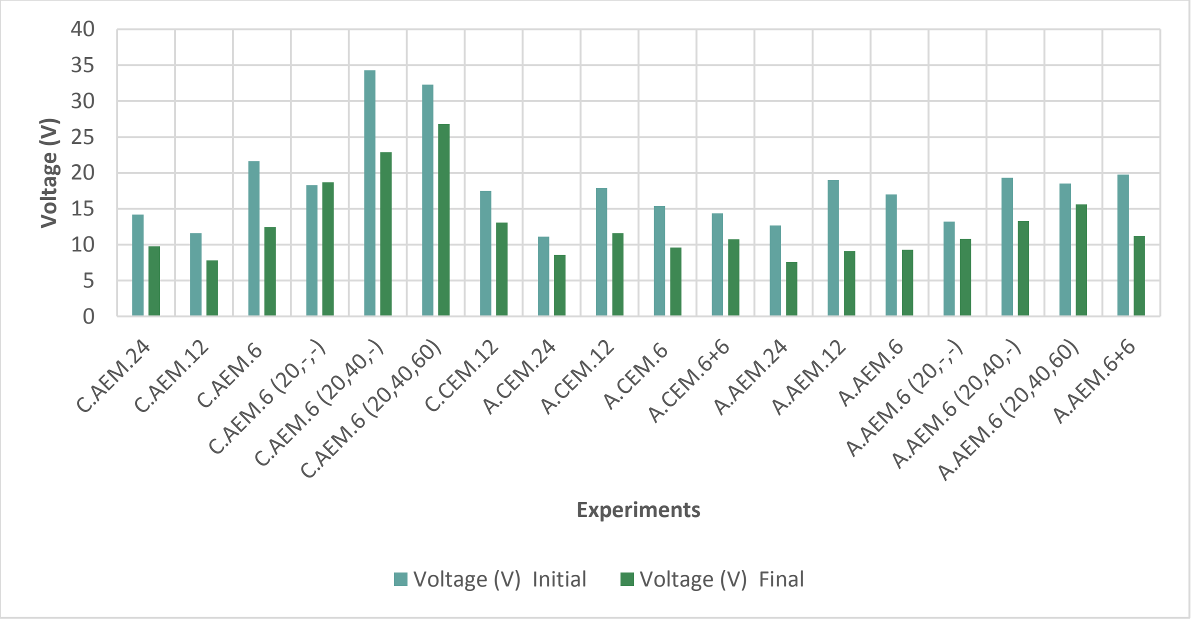


Figure 4.10 - Voltage drop between the working electrodes for each experiment (initial and final).

It is seen that voltage before ED treatment is higher than at the end of each experiment. According to the Ohm’s law (equation 4.3):

$$I = \frac{\Delta V}{R} \qquad \text{(equation 4.3)}$$

Where:

I – applied current, in units of amperes (A)

ΔV – potential difference, in units of volts (V)

R – resistance, in units of ohms (Ω)

To a fixed current (20 mA), only a difference in the resistance could make the voltage differ. If the voltage decreased it means that the resistance decreased. That might be explained with the compounds migration and/or degradation. The OCs can migrate from one compartment to another and be degraded or be degraded in the compartment where they are place. The degradation cause the presence of more ions in solution, and consequently higher conductivity (as proved with the previous results of conductivity) and that reduced the resistance to conduct the same current.

4.2.2 PPCPs removal

In order to assess if the ED process can remove PPCPs from WWTPs effluent there were made 19 ED experiments whose results are presented in table 4.4

Table 4.4 - Percentage of contaminants removed in each ED experiment

		Compound				
		CAF	*BPA*	*E2*	EE2	*MBPh*
Control 1		-2	36	26	33	25
Control 2		16	43	48	45	39
A.AEM.24		95	97	99	99	92
C.AEM.24		55	95	84	85	88
A.CEM.24		>96	>96	>89	>79	>95
C.CEM.24		39	61	92	92	96
A.AEM.12		80	93	97	98	90
C.AEM.12		68	81	74	77	78
A.CEM.12		63	77	86	90	77
C.CEM.12		21	13	12	22	22
A.AEM.6 *n=3*	$\bar{X}$	$60^{a,b,c,d,e,f,g,h}$	$85^{l,i,j,k}$	$91^{i,j,k}$	$89^{j,k}$	76^{k}
	SD	11	8	3	4	15
C.AEM.6 *n=3*	$\bar{X}$	$17^{a,b,l,d,e,i,f,g,j,h,k,m}$	$56^{d,e,f,g,h}$	$46^{f,g,h,m}$	$44^{h,m}$	47
	SD	12	2	2	1	2
A.CEM.6 *n=3*	$\bar{X}$	$88^{c,i,j,k,l}$	$94^{l,i,j,k}$	$96^{i,j,k}$	$96^{j,k}$	94^{k}
	SD	12	3	3	3	1
C.CEM.6		33	49	23	50	45
A.AEM.6 (20, 40, 60)		92	95	99	>80	>95
C.AEM.6 (20, 40, 60)		14	72	60	59	64
A.CEM.6 (R)		30	61	56	71	94
A.AEM.6+6 (1)		80	93	94	94	89
A.AEM.6+6 (2)		81	95	94	95	91
A.CEM.6+6 (1)		73	74	85	86	85
A.CEM.6+6 (2)		82	82	86	88	87

LEGEND:
Experiment code:
X.*Y*EM.*Z*h (*T*), where
X – compartment with effluent (A - anode or C - cathode)
Y – ion exchange membrane (A - anion or C - cation)
Z – duration of experiment (24, 12 or 6 h or a sequence of 6+6 h)
T – additional information (current intensity steps (20, 40, 60), effluent recirculation (R), first and second part of the experiment (1) and (2), respectively)

Statistics – removal statistically significantly different at p<0.05 comparing to:
a - BPA A.AEM.6
b - BPA A.CEM.6
c - CAF C.AEM.6
d - E2 A.AEM.6
e - E2 A.CEM.6
f - EE2 A.AEM.6
g - EE2 A.CEM.6
h - MBPh A.CEM.6
i - E2 C.AEM.6
j - EE2 C.AEM.6
k - MBPh C.AEM.6
l - BPA C.AEM.6
m - MBPh A.AEM.6

Removal calculations: $\left(1-\frac{\text{PPCPs concentration after analytical determination }(\text{mg L}^{-1})}{\text{PPCPs mean concentration recovery }(\text{mg L}^{-1})}\right)\times 100\%$

The amount of each compound missing in the effluent after ED experiment, was considered as removed. For the removal calculations, it was considered the final concentrations (after ED experiments) and the recoveries percentages for each compound at each period of time.

In control experiments, with no applied current, (Control 1 and Control 2) the removal of PPCPs was mainly attributed to diffusion or to sorption to the membranes. Comparing both membranes, the concentration of PPCPs decreased more when the CEM was used. In both cases, CAF had the lowest removal percentage (-2% for Control 1 and 16% for Control 2) and the highest were for BPA (36%) in Control 1 and E2 (48%) in Control 2. For both Control 1 and 2, the percentage of contaminants present in the electrolyte was below LOQ, suggesting that compounds should be mainly adsorbed to the membranes instead of crossing it (table 8.1 in appendix section).

In all cases, the amount of contaminants not detected was considered as degraded.

Four ED experiments were done for 24 hours, one for each set-up. The results showed higher removals for A.AEM design (effluent placed in the anode compartment and AEM separating the two compartments, see figure 3.4)), with a degradation percentage ranging from 92 to 99%. MBPh was the contaminant with the lowest removal (92%) whereas E2 and EE2 had the highest removals (99%). C.AEM (effluent placed in the cathode compartment and AEM separating the two compartments, see figure 3.4) and C.CEM (effluent placed in the cathode compartment and CEM separating the two compartments, see figure 3.4)) set-up had degradation percentages in a range of 55 – 95% and 39 – 96% respectively, wherein CAF was the compound least removed in both cases. Like in A.AEM, also in C.CEM set-up the MBPh was the contaminant more removed (96%). In C.AEM set-up, BPA was the compound with higher removal percentage (95%).

Figure 4.11 shows the effluent chromatogram obtained after ED treatments, A.CEM.24, A.AEM.24, C.CEM.24 and C.AEM.24, respectively. The A.CEM.24 set-up (effluent placed in the anode compartment and CEM separating the two compartments, see figure 3.4)) presented new peaks at the end of experiment, in the effluent.

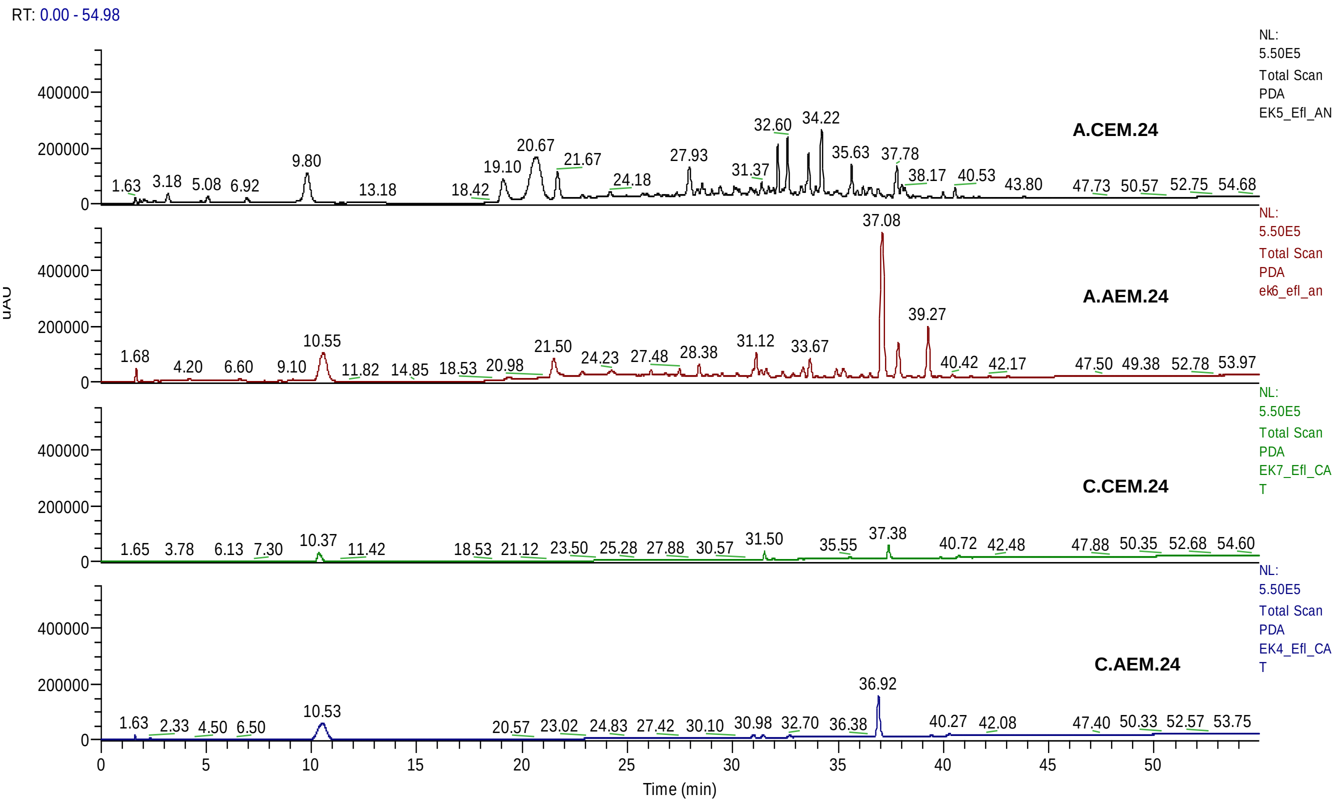


Figure 4.11 - Comparison of the obtained chromatograms for effluents of the experiments A.CEM.24, A.AEM.24, C.CEM.24 and C.AEM.24, respectively.

These peaks present in A.CEM.24 may be intermediates or by-products generated in the anode compartment (when oxidation occurred) remaining in this compartment due to their electrical charge and consequent presence of CEM. The formation of new peaks was also detected on electrodegradation experiments conducted with electrolyte spiked with the studied contaminants and placed in the anode compartment, using a CEM (Guedes et al. 2015). In this work, the main goal was to assess applicability of the ED process for remediation of six emerging contaminants (CAF, BPA, E2, EE2, Ibuprofen and MBPh) from sewage sludge.

In the electrolyte, the higher percentage of contaminants was found in A.CEM.24 (4% for CAF, 1% for BPA, E2 and MBPh and bellow LOQ for EE2) and C.CEM.24 (3% for CAF and bellow LOD for the other compounds), meaning that PPCPs passed from the effluent to the electrolyte though CEM. This means that a part of contamination still remained un-degraded either in cathode or in anode compartment. In C.AEM electrolyte, all contaminants were below the LOD and in A.AEM it was detected 1% of CAF, 2% of MBPh and <LOQ of the other contaminants (table 8.1, in appendix section). The presence of these small concentrations of contaminants in the electrolyte suggests that either the PPCPs were degraded in the compartment where the effluent was placed or moved towards the electrolyte where degradation occurred.

The results proved that, in 24 hours, it was possible to remove (and even degrade) PPCPs from WWTPs effluent with considerable efficiency.

Four more experiments of 12 hours were made in order to assess the suitability of decreasing effluent' residence time and in which set-up this would be more efficient. In this case, the results showed higher removal percentages with A.AEM set-up, 80 – 98%. CAF had the lowest percentages of removal for A.AEM, C.AEM and A.CEM, 80%, 68% and 63%, respectively. EE2 was the most removed for A.AEM and A.CEM, 98% and 90%, respectively, and BPA showed the highest percentage of removal in C.AEM, 81%. In this set of 12 hours experiments there were also noticed the formation of new peaks for the same set-up (A.CEM).

Like in 24 hours experiments, C.CEM.12 design, revealed to be less efficient in compounds removal, comparing to the other designs, with a percentage of degradation in a range of 12 – 22%. In this case, E2 was the compound with lower removal percentage, 12%, and EE2 and MBPh were the most removed, 22% for both. Regarding the presence of PPCPs in the electrolyte, CAF (2%) and MBPh (6%) were the ones found in the A.AEM experiment. In the other experiments the percentage of PPCPs in electrolyte were bellow LOQ (table 8.1 in appendix section).

Due to the satisfactory removals achieved in the 12 hour experiments, it was also tested a treatment period of 6 hours aiming to find a process that could reduce treatment periods that could be implemented in a WWTP. The four designs were tested again but the number of replicates was lower for the set-up with lower removal efficiency for the 12-hour period (A.AEM.6 n=3, A.CEM.6 n=3, C.AEM.6 n=3 and C.CEM.6 n=1). In 6 hours, the A.CEM set-up demonstrated higher degradation, 88±12 to 96±3%, with statistically significantly differences ($p<0.05$). CAF was the less removed, 88±12%, being statistically significantly different from all the compounds from C.AEM set-up. E2 and EE2 were the most removed, 96±3%, with statistically significantly differences ($p<0.05$) comparing to E2, EE2 and MBPh from C.AEM set-up. BPA had a removal of 94±3%, with statistically significantly differences ($p<0.05$) comparing to BPA, E2, EE2 and MBPh from C.AEM set-up. MBPh had a removal of 94±1% being statistically significantly different ($p<0.05$) from MBPh from C.AEM set-up. In the electrolyte, CAF and MBPh were below the LOQ and BPA, E2 and EE2 were below LOD (table 8.1, in appendix section).

For C.AEM.6, removals were in a range of 17±12% to 56±2%, with statistically significantly differences ($p<0.05$). CAF had the lowest removal, 17±12%, being statistically significantly different ($p<0.05$) from all the compounds from A.AEM.6, A.CEM.6 and C.AEM.6 set-ups. BPA had the highest removal, 56±2%, with statistically significantly differences ($p<0.05$) comparing to E2, EE2 and MBPh from A.AEM.6 and A.CEM.6 set-ups. E2 was removed in 46±2%, being statistically significantly different ($p<0.05$) from EE2 and MBPh from both A.CEM.6 and A.AEM.6. EE2 had percentages of removal of 44±1%, being statistically significantly different ($p<0.05$) from MBPh from both A.CEM.6 and A.AEM.6. MBPh had percentages of removal of 47±2%, with no statistically significantly differences (*p*<0.05). In the electrolyte, it was only detected CAF (1%) and MBPh (1%) (table 8.1, in appendix section).

The A.AEM.6 set-up had percentages of removal in a range of 60±11% to 91±3% with statistically significantly differences (*p*<0.05). CAF was the less removed, 60±11%, being statistically significantly different (*p*<0.05) from BPA, E2 and EE2 from A.AEM.6 and A.CEM.6 and also from MBPh from A.CEM.6 and CAF from C.AEM.6 set-up. E2 was the most removed, 91±3%, with statistically significantly differences (*p*<0.05) comparing to E2, EE2 and MBPh from C.AEM.6 set-up. BPA had a removal of 85±8%, with statistically significantly differences (*p*<0.05) comparing to BPA, E2, EE2 and MBPh from C.AEM set-up. EE2 was removed in 89±4% with statistically significantly differences (*p*<0.05) comparing to EE2 and MBPh from C.AEM.6 set-up. MBPh had a removal of 76±15% being statistically significantly different (*p*<0.05) from MBPh from C.AEM set-up. In the electrolyte, it was only detected CAF (2%) and MBPh (2%) (table 8.1, in appendix section).

For the C.CEM.6 set-up, the most and less removed were EE2 (50%) and E2 (23%). In the electrolyte, none of the compounds were detected (table 8.1 in appendix section).

After the study of experimental time and cell set-up, it was tested the change of current intensity. There were made two experiments of 6 hours (once it demonstrated considerable good removal efficiency results), where the current intensity increased 20 mA every 2 hours (20, 40, 60 mA). It was only tested the C.AEM and A.AEM designs to compare with the previous experiments. Degradation percentages were higher in A.AEM set-up, comprising a range of degradation percentage between 92 – 95%, wherein MBPh was the most removed, CAF the less removed (92%) and EE2 was not detected (which presupposes a removal higher than 80%, according to the corresponding percentage of LOD). C.AEM presented degradation percentages in a range of 14 – 72% where, once again, CAF has the lowest degradation percentage and BPA the highest. For both experiments, in electrolyte, BPA, E2 and EE2 were below LOD and CAF and MBPh were below LOQ.

Volatilization is not expected to be an important removal process based upon the estimated Henry's Law constant of the here studied compounds (table 2.1). It is also not expected that the missing quantities of OCs be due to retention on the material once it was used only glass materials. From the obtained results, it can be concluded that the most important removal process is electrochemical migration followed by PPCPs degradation (it was not possible to assess if it is a complete process, mineralization, or if part of the process including the presence of by-products and /or intermediates).

It can be concluded that independently of the time (6, 12 and 24 hours) the compartment with higher removal efficiencies is the anode compartment. Two situations may happen: (i) PPCPs are degraded in the cell compartment where effluent is, where the main removal mechanism is, most likely, anodic oxidation and/or (ii) the PPCPs may move towards the cathode compartment, through ion exchange membrane, and then be removed/degraded. This hypothesis is also corroborated by the low concentration of PPCPs found in the electrolyte (cathode compartment). However, intermediates and/or by-products may also pass to the electrolyte or remain in the effluent, according to their charge and the used membrane. The presence of new peaks in the obtained chromatograms strongly suggests that this was the case. The A.AEM set-up run for 24 h-experiment was the most prominent situation suggesting that intermediates and/or by-products were found in the effluent, for two possible reasons: the positive electrical charge with AEM acting as a barrier or the high and continuous generation of ions that did not have enough time to migrate towards the electrolyte. Hydrogen peroxide was <LOD (0.5 mg/L H_2O_2) in all experiments (effluent either in cathode or anode compartment).

Regarding the behaviour of studied PPCPs, CAF was the least degraded contaminant for all the set-ups while BPA, E2, EE2 and MBPh achieved higher degradation removals, for different experiments. CAF had a mean removal of 81±12% for A.AEM set-up, 72±24% for A.CEM, 39±27% for C.AEM and 31±9% for C.CEM. BPA had a mean removal of 93±4% for A.AEM set-up, 81±13% for A.CEM, 76±16% for C.AEM and 41±25% for C.CEM. E2 had a mean removal of 96±3% for A.AEM set-up, 83±14% for A.CEM, 66±17% for C.AEM and 42±42% for C.CEM. EE2 had a mean removal of 93±7% for A.AEM set-up, 85±9% for A.CEM, 66±18% for C.AEM and 55±35% for C.CEM. MBPh had a mean removal of 90±8% for A.AEM set-up, 89±7% for A.CEM, 69±18% for C.AEM and 54±38% for C.CEM.

As the main removal process is hypothesized to be degradation in the electrode compartment, this will be dependent of, e.g., the reactive group of each compound. CAF belongs to the amides, amines and imides reactive groups. Its functional group is classified as weakly basic due to its pKa value of 14.0 (Fontanals et al. 2010). During all the ED experiments, the maximum pH value observed was around 12 (cathode compartment) and so, pH solution was always lower than CAF pKa, which means that CAF would be protonated (behave like a base and accept protons, according to the Brønsted–Lowry definition). The reactive group of the other contaminants (BPA, E2, EE2 and MBPh) is a phenol (Rahman, Yanful, and Jasim 2009). Phenols are weak acids that liberate protons. When the effluent was placed in the cathode compartment, solution pH in the cathode end is higher than the contaminants pKa, meaning that they will mostly be in their ionized forms. This negative charge will allow their passage towards the electrolyte if an AEM is being used. When effluent is in the anode compartment, the compounds are not ionized and, according to their electrical charge, they will electromigrate towards the cathode compartment (electrolyte) depending on the used membrane.

According to log K_{ow} values of the compounds under study, CAF is the most hydrophilic (log K_{ow} < 1) and soluble ($2.16\text{x}10^4$ mg L^{-1}) compound whereas BPA, E2, EE2 and MBPh are highly hydrophobic (log K_{ow} > 3) and have less ability to be dissolved in water (120, 3.9, 11.3 and 69 mg L^{-1}, respectively). These characteristics that group the compounds in two main clusters would be of extreme importance in the case of having two different phases (e.g. soil and/or sludge and water (Guedes et al. 2014; Guedes et al. 2015) where the contaminant would be more in the liquid or solid fraction according to these physico-chemical properties. In this study, this is not determinant as there is only the liquid phase (either effluent or electrolyte). However, the lipophilic PPCPs may have been influenced by the organic content of the effluent, namely by adsorption to the suspended organic matter. Two options were considered in this case. Additionally, these compounds may have also been retained in the ion exchange membranes.

Considering the obtained results and comparing to the studies that have already been made it is clear that oxidation is an effective way to degrade/remove PPCPs from WWTP's effluent. Specifically in the electrode compartment, PPCPs may have been oxidized by direct anodic electrochemical oxidation. PPCPs may have also be removed by indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation. Most likely, these effluents contained chloride ions that could be transformed into active chlorine (Mussa and Othman 2015; Chiang et al. 1995).

Esplugas et al. (2007) reviewed the removal of some pollutants like E2, EE2 and BPA using oxidation processes, such as ozonation and photocatalysis. It was reported that they were able to remove them with efficiencies above 90% and also remove the estrogenic activity significantly. However, in some cases, a residual activity still remains after the treatment. Removals higher than 98% were obtained for BPA, E2 and EE2 using TiO_2 photocatalysis. In order to achieve high removals, large irradiation times were required compared with dark ozonation processes.

Huber et al. (2005) also made a study about the oxidation of pharmaceuticals during ozonation of municipal wastewater effluents where EE2 (among others) was efficiently oxidized (>90%) in the three effluents considered for O_3 doses $\geq$ mg 2 mg L^{-1} with higher fraction oxidized by O_3 than by $^{\bullet}OH$. It was also investigated the effect of suspended solids on micro pollutant oxidation and for that were used three effluents that varied in the concentration of suspended solids. Another study carried out by Lubliner, Redding, and Ragsdale (2010) demonstrated that ozone is a highly effective oxidant for removing the majority of organic contaminants from wastewater, achieving percentages of removal higher than 80% for CAF, MBPh (among others). Hollender et al. (2009) also obtained removal percentages higher than 84%, using ozone oxidation for removal of MBPh.

As the degradation efficiency of an AOP is limited by the radical scavenging capacity of the matrix the use of ozone have some premises. It was reported (Zwiener and Frimmel 2000; Petrović et al. 2003) that for satisfactory degradation of pharmaceuticals (>90%) from wastewater, the ozone concentration has to be equal to the dissolved organic carbon (DOC) value which means that economic considerations have to underpin the feasibility of the process for wastewater treatment. From this, it can be inferred that, besides the good removal efficiencies achieved by the use of ozone, this technique may be considered expensive and not accessible to WWTP, becoming more expensive to be applied in influents/effluents with a strong organic matter content.

The next step was to adapt the cell design to a WWTP *in situ* context. Therefore, the lab scale experiments were conducted by promoting effluent recirculation using the cell set-up that presented higher degradation percentages, A.CEM. With degradation percentages in a range of 30 – 94% (see table 4.4), this set-up proved to be less efficient than the other options tested. Also here, CAF had the lowest degradation percentage and MBPh the highest. This results suggest that, for an effective contaminants degradation, the retention time of the effluent in electrode compartment should be higher as, most likely, the time was not sufficient to promote the removal and consequent degradation of PPCPs.

Final experiments

According to the results obtained with effluent recirculation and still trying to replicate what would happen in a WWTP, two final experiments were made (with replicates) to test the addition of fresh effluent (after 6 hours, giving a cycle of 6 plus 6 hours), maintaining the electrolyte (for 12 hours). Given that A.AEM and A.CEM proved both to represent efficient set-ups in contaminants removal for 6 hour-period, the experiments were carried out for both designs. This time, the A.CEM set-up showed lower degradation percentages, 73 – 86% in the first 6 hours (A.CEM.6+6 (1)) and 82 – 88% in the second 6 hours (A.CEM.6+6 (2)). The A.AEM set-up represented higher degradation percentages, 80 – 94% in the first 6 hours (A.AEM.6+6 (1)) and 81 – 95% in the second (A.AEM.6+6 (2)), which suggest that renewing the effluent and maintaining the electrolyte does not affect the degradation efficiency and so, it is doable in a WWTP. Only CAF and MBPh were detected in the electrolyte in a percentage range between <LOD to 1% and <LOD to 3%, respectively (table 8.1 in appendix section).

For these final experiments WWTP effluent parameters were also assessed, after the ED experiments, with the aim of compare with the initial values. The obtained results are presented in table 4.5.

Table 4.5 - Characteristic WWTP parameters values, after the final ED experiments

Experiment	*TSS (mg/L)*	*pH*	*BOD_5 (mg/L)*	*COD (mg/L)*	*P_T (mg/L)*	*NO_3 (mg NO_3/L)*	*NO_2 (mg NO_2/L)*	*NH_4 (mg NH_4/L)*
A.CEM.6+6	4	3	>50	3205	3.2	19.2	<4	<5
A.AEM.6+6	3	3	>50	3308	2.7	562.2	<4	8

It is clear the increase of both BOD_5 and COD, comparing with the initial effluent values. The values exceeded the legislation threshold of effluent discharge, limiting the application of the technique in a WWTP, in the here tested conditions. Two reasons are suggested for this increase: (i) the organic load of the matrix spiking (even though PPCPs had higher removal efficiencies, the presence of intermediates or by-products is also considered); (ii) ions such as NOx may influence the determination as they can also be oxidized. There was also observed a decrease of TSS. Membrane clogging was not observed so it is suggested that either the acidic pH influenced their dissolution or the electrical current enhanced their solubilization/disaggregation. Additionally, also in A.AEM set-up, the NO_3, NO_2 and NH_4 values are higher than A.CEM set-up and higher than before the experiment. Once the electrolyte used was a $NaNO_3$ solution, the ions will dissociate (as $NaNO_3$ is a salt), with NO_3^- passing through the anionic membrane but not through the cationic membrane, due to its charge. The increase of NO_2 and NH_4 seems to be a consequence of reduction of NO_3 in the cathode compartment.

4.2.3 Phosphorus removal

Phosphorus analysis was never the main goal of this study, especially since it is not expected to find a concentration of phosphorus over 2 mg L^{-1}, according to the Portuguese law (DL 348/98, November 9th). Nevertheless, due to its economic value and utilization in agriculture as fertilizer, it was assessed its recovery in these experiments.

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 exposed in equations 4.4, 4.5 and 4.6. For each dissociation reaction, there is a different acid dissociation constant (Ka), pKa_1, pKa_2, and pKa_3.

$$H_3PO_{4(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + H_2PO^-_{4(aq)} \qquad pKa_1 = 2.12 \qquad \text{(equation 4.4)}$$

$$H_2PO^-_{4\,(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + HPO^{2-}_{4(aq)} \qquad pKa_2 = 7.21 \qquad \text{(equation 4.5)}$$

$$HPO^{2-}_{4\,(aq)} + H_2O \rightleftharpoons H_3O^+_{(aq)} + PO^{3-}_{4(aq)} \qquad pKa_3 = 12.67 \qquad \text{(equation 4.6)}$$

Table 4.6 shows the percentage of total phosphorous (P_T) present in the effluent and electrolyte samples, according to the initial value.

Table 4.6 - Results of phosphorus analysis for each sample

Sample	*P_T final in the effluent (%)*	*P_T final in the electrolyte (%)*
Control 1	63	18
Control 2	97	2
C.CEM.12	95	4
A.AEM.12	77	4
A.CEM.12	95	4
A.AEM.6	76	5
A.CEM.6	95	3
C.AEM.6	17	64
A.CEM.6 (R)	94	4
A.AEM.6+6	77	4
A.CEM.6+6	95	4

A considerable high percentage (19%) of P_T was retained in the AEM, comparing to the percentage retained in the CEM (1%). When the control experiments were performed, 18% of P diffused to the electrolyte when the AEM was used (Control 1).

Between experiments, P_T only electromigated to the electrolyte in the set-up where the effluent was placed at the cathode and AEM was used, recovering 64% in the electrolyte. In this set-up the basic pH puts P in the forms HPO_4^{2-}/PO_4^{3-} that are able to electromigrate towards the anode compartment, in the presence of an AEM. When effluent is at the anode compartment, the acidic pH puts P in a dynamic equilibrium between H_3PO_4/ $H_2PO_4^-$, which will move towards phosphoric acid as pH decreases. In this case, the presence of a CEM inhibited the electromigration of the anion whereas the presence of an AEM allowed the removal of 23% of P from the effluent. This topic is discussed under the light of P removal from effluent to be discharge aiming to avoid a nutrient upload to the fresh water bodies, which may contribute to, e.g., eutrophication. But, besides it was the scope of this study, there is also a perspective of effluent re-use for, e.g., crop irrigation. In this case, the A.CEM set-up would be the most adequate as the effluent would be clean (with vestigial concentrations of PPCPs) and act as a P-source.

4.2.4 Other results

After collection, effluent was analysed in a microscope in order to evaluate microorganism content. In effluent sample from 16.06.2015 a live microorganism was detected (figure 4.12), being considered vestigial and very unlikely to happen. The microorganism found seems to be a free-living ciliate due to its cilia and ability to swim. The sample was analysed again after the ED experiment and some crystals were observed, figure 4.13 (the real colours might be different from those presented in the images). These findings occurred in C.AEM.6 (20, 40, 60 mA) set-up. The effluent was placed in cathode compartment and, as described earlier in this work, in the cathode compartment happens the increase of pH.

This pH increase would allow to the formation of phosphate and with additional research based mainly on the appearance of the crystals (figure 4.14), it is believed that the crystals may be triple phosphate (hypothesis based on its main characteristics like color and shape). Triple phosphate crystals (also called struvite crystals) usually exist in an alkaline or sometimes a neutral solution and are soluble in acetic acid. This solubility was not possible to assess due to the low amount of crystals (not visible at naked eye). These crystals have a characteristic “coffin lid” appearance and are colourless and shaped like three to six-sided rectangular prisms. They are composed of magnesium ammonium phosphate (Brown 2004; Mikesh 2015).

Figure 4.12 - Microscopic observation of a microorganism present in effluent. Photo amplification: 1160x.

Figure 4.13 - Microscopic observation of the crystals. Photo amplification: 290x.

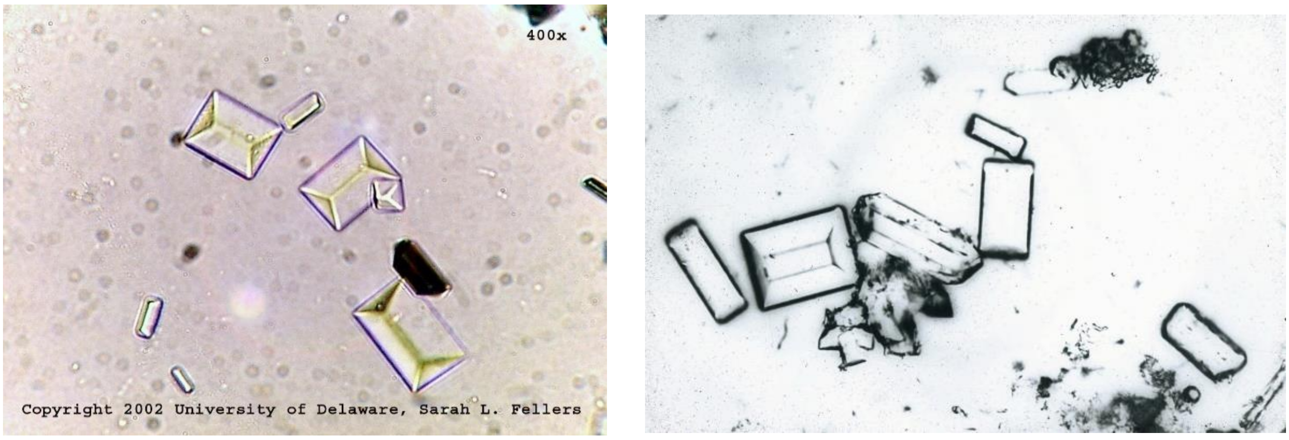


Figure 4.14 - Images found for triple phosphate. Sources: University of Delaware, 2002 and Beth Israel Deaconess Medical Center, Inc., 2004, respectively.

4.3 Energy costs

The main goal of this study was to assess whether the ED process was effective in the removal of contaminants from effluent and if so, evaluate its applicability in a WWTP. Once the ED process revealed positive results in the contaminants removal, as described earlier, it is believed that it could be set in a WWTP as a complementary treatment. For that purpose, the associated energy costs were evaluated using equation 4.7 (Tran and Drogui 2013) and considering an energy price of 0.15 € / kWh.

$$E_c = \frac{U_c \times I \times t}{1000} \qquad \text{(equation. 4.7)}$$

Where:
Ec – Energy consumption (KWh)
Uc – Cell voltage (V)
I – Applied current (A)
t – Treatment time (h)

In table 4.7 it is presented the energy costs (in €/m^3 of treated effluent) of each experiment.

The costs are in a range of 0.7 – 2.9 €/m^3 and, it is supposed that, the higher costs correspond to the experiments of longer duration. It is detected an increase of approximately 62% in the energy costs comparing 6 hours to 12 hours of experiment and about 70% when comparing 6 hours to 24 hours. Neither the compartment nor the used membrane seem to have a considerable and direct implication on energy costs. However, there is a significant cost increase (40%) when the current was increased during the experiments (C.AEM.6 (20, 40, 60) and A.AEM.6 (20, 40, 60). C.AEM.6 (20, 40, 60 mA) has an energy cost 40% higher than A.AEM.6 (20, 40, 60 mA). According to the Ohm's law, when the current was increased, the voltage also increased significantly and that unnecessarily increases the energy consumption.

Table 4.7 - Energy costs associated to each experiment

Experiment	*Energy costs (€/m^3)*
Control 1	-
Control 2	-
A.AEM.24	2.4
C.AEM.24	2.9
A.CEM.24	2.4
C.CEM.24	2.1
A.AEM.12	1.6
C.AEM.12	1.1
A.CEM.12	1.6
C.CEM.12	1.8
A.AEM.6	0.8
C.AEM.6	0.8
A.CEM.6	0.7
C.CEM.6	*
A.AEM.6 (20,40,60)	0.9
C.AEM.6 (20,40,60)	1.5
A.CEM.6 (R)	*
A.AEM.6+6	1.8
A.CEM.6+6	1.5

* Voltage not measured

The A.AEM and A.CEM set-ups achieved higher percentages of removal (>88%) and it proved to be efficient for 6 hours of treatment. Thus, for the implementation on a WWTP, this treatment would cost approximately 0.80 € (only considering the energy costs). Comparing to other treatments, also based on compounds oxidation, namely AOPs, the associated costs are in a range of 21.0 €/m^3 for UV/US/O_3 to 3 660.5 €/m^3 for US alone, 5.90 €/m^3 to 21.4 €/m^3 for US + UV treatment and US alone, respectively and 15.3 €/m^3 for US + UV + H_2O_2 to 3 346.4 €/m^3 for US alone. Also considering only the energy costs (Mahamuni and Adewuyi 2010).

4.3.1 SWOT analysis

To assess if the ED process would be a suitable technique for implementation in a WWTP, a SWOT (strengths, weaknesses, opportunities and threats) analysis was carried out, table 4.8.

Table 4.8 - SWOT analysis

Strengths	**Weaknesses**
- Effective removal of PPCPs - *In situ* treatment - Can be applied to different contaminants at the same time	- Electrolyte renovation - Electrolyte might also need to be treated after the ED process - Membranes washing
Opportunities	**Threats**
- growing concern about PPCPs accumulation in the environment - Can be combined with other treatment processes	- Possible formation of harmful by-products during treatment

PPCPs are now widely used and on a daily basis. Due to the difficulty of completely remove these contaminants from wastewater, the concentrations released to the environment, due to effluent discharge, will imply either deposition and accumulation in the aquatic environment, or bioaccumulation and biomagnification. This also represents an associated risk to human health increasing concern about the need to effectively decrease PPCPs levels from effluent discharge. Thus, ED process can be considered as an alternative to remove those contaminants. It can also be combined with other treatment processes, which is an opportunity to better suit the different kinds of treatment needs.

The obtained results in this study proved that the ED process is effective in the removal of PPCPs from a WWTP effluent. The set-ups with higher percentages of removal, A.AEM and A.CEM, achieved efficient removals, despite the very different physico-chemical properties of the five PPCPs in study (CAF, BPA, E2, EE2 and MBPh), showing that ED process can be applied to different contaminants at the same time. Once the main components needed to apply this process are electrolyte, effluent and current, there is a possibility for this process to be carried out as an *in situ* treatment.

However, there are some limitations in this process that might need further studies for improvement. The electrolyte used for the ED process will need to be renovated at some point.

That might be a weakness of the process once it will demand the stop of the operation. There is another aspect about the electrolyte that will affect the whole process that is the need to be treated. During the experiments that was not studied but according to the obtained results, there are some compounds that manage to pass from the effluent to the electrolyte. It was also suggested that a part of some compounds can be retained in the membrane which will require the membranes washing.

During the ED experiments it was noticed the formation of intermediates and/or by-products in A.CEM set-up, especially for 12 and 24 hours experiments. The presence of these compounds is a possibility in the other tested set-ups. This may be considered a threat as the intermediates and/or by-products can be more harmful than the initial contaminants and so, it is important to study and assess this problem in order to avoid it.

5. Conclusions

Nowadays, WWTPs are not completely efficient in removing different types of contaminants with low concentrations, as it is the case of PPCPs. Even in vestigial concentrations, the release of these contaminants associated to effluent discharge can lead to environmental and human health risks. Alternative solutions to face this problem are needed.

In this study, it was possible to prove the effectiveness of ED process in the removal of these contaminants. The effluent placed in the anode compartment achieved higher removal rates than when placed in the cathode compartment, this being more visible for lower treatment periods. The main removal mechanism of PPCPs in the anode compartment is degradation through oxidation. For a treatment of 6 hours, the presence of anion an AEM and effluent placed in the anode compartment, led to removal percentages between 76 and 91% for all the compounds, except CAF (removal of 60%). The presence of a CEM led to removals between 88 and 96% for all compounds under study. In the tested conditions, this was the most suitable set-up to decrease effluent PPCPs levels. Nevertheless, the presence of intermediates and/or by-products was also observed.

The test of the current steps was also effective in removing contaminants for the A.AEM set-up (6 hours). The recirculation of effluent experiment suggests that, for effective contaminants degradation, it is essential to increase effluent retention time in the ED cell.

The sequential set of 6+6 hours revealed to be a suitable option as removal percentages were between 80 - 94% and 81 – 95% for the first and second ED treatment cycles, respectively when an AEM was used and between 73 – 86% and 82 – 88% for the CEM. The main removal process seems to be oxidation in the anode compartment and not electromigration towards the cathode compartment. An increase of BOD_5 and COD was observed and might be explained by the effluent spiking. Regarding the decrease of P levels for effluent discharge (if P-levels are outside the legislation threshold) the most effective treatment in this set-up would be the use of an AEM as 23% was removed from the effluent.

The associated costs for the most effective set-up, 6 hours treatment, is approximately 0.8 € to treat each cubic meter of wastewater. Compared to other treatment processes with the same objective, this value is considerable lower (only considering the energetic cost and not the maintenance).

It is clear that organic contaminants, especially the ones under study (CAF, BPA, E2, EE2 and MBPh), are not easy to remove due to different behaviours under different conditions. The results showed that CAF, comparing to the other contaminants in study, had lower removal percentages. Along the ED experiments, the differences found in the degradation percentages are mainly attributed to their chemical structures, reactivity and mechanisms formerly studied by different authors.

6. Future developments

This study contributed to increase knowledge about the potential of ED process to be applied as an alternative technique to remove PPCPs. But, during this study, other questions appeared, motivating other studies to make improvements to the process.

The presence of either intermediates or by-products in effluent placed in the anode compartment (mainly due to oxidation processes) needs more research, including their identification and effective risk to the environment and human health.

The time of the experiments can be optimized in order to understand if a lower duration is still effective. It was also found the formation of crystals. It might be interesting to investigate what they really are and in what conditions they are formed.

The increase of BOD_5 and COD was an unexpected result that could compromise the ED applicability. For the implementation of the ED process in a real WWTP, it is crucial to understand why it happened and how BOD_5 and COD levels can decrease.

It would be also useful to study how long the electrolyte could be used, in continuous, before being replaced. During these experiments the electrolyte was always renewed at each experiment, except for the last experience. However, the maximum period tested was 24 hours, and is important to understand the duration in which electrolyte is effective (e.g. conductivity, presence of contaminants/intermediates or by-products, etc).

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8. Appendix

Table 8.1 - Percentage of contaminant detected in the effluent and electrolyte after the ED experiments, in relation to the initial amount

		Compound				
		CAF	*BPA*	*E2*	EE2	*MBPh*
Control 1	Effluent	102	64	74	67	75
	Electrolyte	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Control 2	Effluent	84	57	52	55	61
	Electrolyte	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
A.AEM.24	Effluent	5	3	1	1	8
	Electrolyte	1	<LOQ	<LOQ	<LOQ	2
C.AEM.24	Effluent	45	5	16	15	12
	Electrolyte	<LOD	<LOD	<LOD	<LOD	<LOD
A.CEM.24	Effluent	<LOD	<LOD	<LOD	<LOD	<LOD
	Electrolyte	4	1	1	<LOQ	1
C.CEM.24	Effluent	61	39	8	8	4
	Electrolyte	3	<LOD	<LOD	<LOD	<LOD
A.AEM.12	Effluent	20	8	4	2	11
	Electrolyte	2	<LOQ	<LOD	<LOD	6
C.AEM.12	Effluent	32	19	26	23	22
	Electrolyte	<LOD	<LOD	<LOD	<LOD	<LOD
A.CEM.12	Effluent	37	23	14	10	23
	Electrolyte	1	<LOD	<LOD	<LOD	1
C.CEM.12	Effluent	79	87	88	78	78
	Electrolyte	<LOQ	<LOQ	<LOD	<LOD	<LOQ
A.AEM.6 *n=3*	Effluent	40	16	9	11	24
	Electrolyte	2	<LOQ	<LOD	<LOD	2
C.AEM.6 *n=3*	Effluent	83	44	55	56	53
	Electrolyte	1	<LOD	<LOD	<LOD	1
A.CEM.6 *n=3*	Effluent	12	6	6	5	6
	Electrolyte	<LOQ	<LOD	<LOD	<LOD	<LOQ
C.CEM.6	Effluent	67	51	77	50	55
	Electrolyte	<LOQ	<LOQ	<LOD	<LOD	<LOQ
A.AEM.6 (20,40,60)	Effluent	8	5	1	<LOD	<LOD
	Electrolyte	<LOQ	<LOQ	<LOD	<LOD	<LOQ
C.AEM.6 (20,40,60)	Effluent	86	28	40	41	36
	Electrolyte	<LOQ	<LOD	<LOD	<LOD	<LOQ
A.CEM.6 (R)	Effluent	70	39	44	29	6
	Electrolyte	1	<LOD	<LOD	<LOD	<LOQ
A.AEM.6+6 (1)	Effluent	20	7	6	6	11
	Electrolyte	-	-	-	-	-
A.AEM.6+6 (2)	Effluent	19	5	6	5	9
	Electrolyte	1	<LOD	<LOD	<LOD	3
A.CEM.6+6 (1)	Effluent	27	26	15	14	15
	Electrolyte	-	-	-	-	-
A.CEM.6+6 (2)	Effluent	18	18	14	12	13
	Electrolyte	1	<LOQ	<LOQ	<LOQ	2