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Ciências

Electrochemical treatment of sanitary landfill leachates

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Dedictory

Choose a job you love, and you will
never have to work a day in your life.

Confucius

This thesis is dedicated to my mentor,
Prof. Doutora Ana Carreira Lopes

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Resumo alargado

Os lixiviados de aterros sanitários são um dos principais problemas ambientais existentes no que se refere a poluição aquática, uma vez que são efluentes muito complexos que contêm diferentes metais pesados, compostos orgânicos e inorgânicos, alguns deles tóxicos e refratários e que possuem cor e odor. Atualmente, o tratamento eficiente de lixiviados é um desafio, uma vez que os métodos convencionais de tratamento utilizados não são suficientes para atingir o nível de purificação necessário. Assim sendo, tem sido estudada a aplicação de várias “tecnologias avançadas” no tratamento de lixiviados de aterros sanitários e, entre elas, os métodos eletroquímicos têm recebido especial ênfase. De facto, as tecnologias eletroquímicas têm mostrado elevada eficiência na eliminação de poluentes persistentes e vários estudos têm descrito a sua aplicação no tratamento de águas residuais.

No trabalho descrito nesta tese, foi estudada a aplicação de dois métodos eletroquímicos, a eletrocoagulação e a oxidação eletroquímica, no tratamento de lixiviados de aterros sanitários. O principal objetivo do trabalho consistia em apresentar uma solução eletroquímica eficiente para o tratamento de lixiviados de aterros sanitários. De entre os métodos eletroquímicos existentes, a oxidação eletroquímica é, de acordo com a literatura, aquele que apresenta maior eficiência na eliminação de poluentes persistentes, sem a desvantagem da produção de lamas e, por essa razão, foi selecionado para a realização deste trabalho. Contudo, uma vez que a maioria dos lixiviados contêm grandes quantidades de matéria suspensa e coloidal, que condicionam a eficiência do processo de oxidação eletroquímica, foi decidido avaliar o efeito da introdução de um pré-tratamento de eletrocoagulação antes da aplicação do processo de oxidação eletroquímica.

Considerando as soluções de tratamento atualmente implementadas e as características e variabilidade das águas lixiviantes, foram estabelecidos vários objetivos secundários, que a seguir se enumeram.

1. A maioria das estações de tratamento de águas lixiviantes inclui processos biológicos, que são eficazes na remoção da matéria orgânica biodegradável. De forma a otimizar os recursos já existentes, foi estudada a aplicação do processo de oxidação eletroquímica na remoção dos compostos orgânicos persistentes após os tratamentos biológicos. Deste modo, pretendeu-se avaliar a eficiência do processo de oxidação eletroquímica quando aplicado como pós-tratamento ao efluente de um processo biológico, para eliminar os compostos orgânicos persistentes ainda remanescentes.
2. Tendo em conta que a maioria dos lixiviados de aterros sanitários apresentam baixos índices de biodegradabilidade e que os processos biológicos são pouco eficazes quando a razão entre carência bioquímica de oxigénio e a carência química de oxigénio é inferior a

0,5, foi decidido usar a oxidação eletroquímica no tratamento de lixiviados brutos, para estudar a aplicação do processo de oxidação eletroquímica no tratamento de lixiviados sem qualquer tipo de pré-tratamento, determinando as condições experimentais que conduzem a eficiências de tratamento mais elevadas.

3. Sabendo que a matéria suspensa e coloidal existente nos lixiviados torna o processo de oxidação eletroquímica menos eficiente, foi avaliada a introdução de um processo de eletrocoagulação, anterior ao processo de oxidação eletroquímica, com o objetivo de remover as partículas suspensas e coloidais existentes nos lixiviados brutos. Deste modo, pretendeu-se avaliar o incremento na eficiência do tratamento eletroquímico decorrente da introdução de um processo de eletrocoagulação, aplicado como pré-tratamento ao processo de oxidação eletroquímica.
4. Apesar das propriedades excepcionais dos elétrodos de diamante dopado com boro (BDD) e dos bons resultados obtidos com este material de elétrodo, o seu custo é muito elevado, o que condiciona a sua aplicação a nível industrial. Assim, foi decidido estudar a aplicação de um material de elétrodo mais económico e comparar o seu desempenho com o dos elétrodos de BDD. Foi escolhido o Ti/Pt/PbO₂, uma vez que este material foi preparado e utilizado com sucesso pelo nosso grupo de investigação na degradação de vários fármacos. O objetivo deste estudo foi o de avaliar a viabilidade de utilização de ânodos de Ti/Pt/PbO₂ no processo de oxidação eletroquímica para o tratamento de lixiviados, e comparar o seu desempenho com os ânodos de BDD.

No sentido de concretizar os objetivos propostos, foram realizados vários ensaios laboratoriais, utilizando diferentes amostras de lixiviados e aplicando diferentes condições experimentais. O estudo foi dividido em quatro partes, de acordo com os quatro objetivos estabelecidos, apresentando-se, em seguida, um resumo dos ensaios realizados e das principais conclusões obtidas.

Parte 1: Aplicação do processo de oxidação eletroquímica como pós-tratamento

Estudo 1 - Aplicação do processo de oxidação eletroquímica a lixiviados biologicamente tratados: ensaios em escala laboratorial com agitação

Este estudo foi realizado à escala laboratorial, utilizando uma célula eletroquímica com modo de operação descontínuo, com agitação. Foram ensaiadas amostras de lixiviado recolhidas numa estação de tratamento de águas lixiviantes após o tratamento biológico por lamas ativadas, utilizando um ânodo de BDD uma vez que, de acordo com a literatura, este material de ânodo apresenta propriedades únicas e os melhores resultados na oxidação eletroquímica de poluentes persistentes. Foi estudada a influência da carga orgânica inicial e da densidade de corrente aplicada.

Estudo 2 - Aplicação do processo de oxidação eletroquímica a lixiviados biologicamente tratados: ensaios em escala semi-piloto com recirculação

A finalidade deste estudo foi avaliar o efeito do *scale-up* do processo na eficiência do tratamento de oxidação eletroquímica. Os ensaios foram realizados numa instalação semi-piloto, em modo descontínuo, com recirculação, utilizando uma célula eletroquímica DiaCell 100 com ânodo e cátodo de BDD, com uma área de 70 cm² cada. Foi estudada a influência da densidade de corrente aplicada e do caudal de recirculação.

Parte 2: Aplicação do processo de oxidação eletroquímica no tratamento de lixiviados brutos

Estudo 3 - Aplicação do processo de oxidação eletroquímica no tratamento de lixiviados brutos: agitação vs. recirculação

As amostras de lixiviado utilizadas neste estudo foram recolhidas num aterro sanitário de idade intermédia e apresentavam um índice de biodegradabilidade muito baixo. Os ensaios foram realizados em escala laboratorial, em modo descontínuo, utilizando duas células eletroquímicas distintas, uma com recirculação e outra com agitação, de forma a estudar a influência da hidrodinâmica da célula no desempenho da eletrodegradação. Também neste estudo foram utilizados ânodos de BDD. Foi avaliada a influência da densidade de corrente aplicada, tendo sido realizados estudos em que a densidade de corrente foi reduzida ao longo do ensaio com o objetivo de aumentar a eficiência energética do processo.

Estudo 4 - Aplicação do processo de oxidação eletroquímica no tratamento de lixiviados brutos: ensaios em escala semi-piloto com recirculação

Com a finalidade de avaliar o efeito do *scale-up* do processo na eficiência do tratamento de oxidação eletroquímica, foram realizados ensaios na instalação semi-piloto, em modo descontínuo, com recirculação, utilizando a célula eletroquímica DiaCell 100. Foi avaliada a influência do caudal de recirculação e da densidade de corrente aplicada, tendo sido realizados estudos em que a densidade de corrente foi reduzida ao longo do ensaio com o objetivo de aumentar a eficiência energética do processo.

Parte 3: Aplicação de um processo combinado de eletrocoagulação seguido de oxidação eletroquímica no tratamento de lixiviados

Estudo 5 - Aplicação de um processo combinado de eletrocoagulação seguido de oxidação eletroquímica no tratamento de lixiviados: uso do processo combinado como pré-tratamento vs. tratamento de afinação

Este tratamento combinado (eletrocoagulação + oxidação eletroquímica) foi estudado em lixiviados brutos e em lixiviados biologicamente tratados, a fim de avaliar a aplicabilidade do processo e as condições da sua máxima eficiência. Os ensaios

decorreram em escala laboratorial, em modo descontínuo. No processo de eletrocoagulação foram utilizados elétrodos consumíveis de ferro, uma vez que na literatura estes são identificados como sendo os mais adequados para o tratamento de lixiviados. A influência do pH inicial, da carga orgânica inicial, do tempo de eletrólise e do potencial/intensidade de corrente aplicados foi avaliada no processo de eletrocoagulação e, posteriormente, foi estudado o seu efeito no processo de oxidação eletroquímica posterior. Nos ensaios de oxidação eletroquímica foi utilizado um ânodo de BDD.

Estudo 6 - Aplicação de um processo combinado de eletrocoagulação seguido de oxidação eletroquímica no tratamento de lixiviados: efeito na biodegradabilidade do lixiviado

Neste estudo foi avaliada a aplicação do tratamento eletroquímico combinado como um pré-tratamento aos processos biológicos, a fim de otimizar os recursos existentes e reduzir os custos associados ao tratamento. Foi ainda avaliada influência da densidade de corrente aplicada no processo de oxidação eletroquímica.

Parte 4: Utilização de ânodos de Ti/Pt/PbO₂ no processo de oxidação eletroquímica, aplicado ao tratamento de lixiviados

Estudo 7 - Ânodos de Ti/Pt/PbO₂ vs. ânodos de BDD no tratamento de lixiviados biologicamente tratados e amostras simuladas

Neste estudo foram utilizadas amostras de lixiviado biologicamente tratado de um aterro sanitário classificado como novo. Os ensaios decorreram à escala laboratorial, em modo descontínuo, com agitação. Foram também realizados ensaios com amostras de efluente simulado, a fim de estudar a influência das condições experimentais no mecanismo de degradação.

Estudo 8 - Ânodos de Ti/Pt/PbO₂ vs. ânodos de BDD no tratamento de lixiviados e amostras simuladas: estudo da influência da densidade de corrente aplicada e da concentração de íons cloreto

Para este estudo, foram recolhidas amostras num aterro sanitário classificado como velho, sem qualquer tipo de tratamento. Foi estudada a influência da densidade de corrente aplicada e da concentração de íons cloreto, uma vez que a concentração inicial de íons cloreto presente no lixiviado era bastante mais baixa comparada com os outros lixiviados estudados e, de acordo com a literatura, não era suficiente para potenciar a oxidação indireta. Com o intuito de estudar a influência das condições experimentais no mecanismo de degradação, foram realizados ensaios utilizando amostras de efluente simulado.

Os objetivos propostos foram atingidos e os resultados mostraram que os tratamentos eletroquímicos podem ser aplicados eficientemente no tratamento de lixiviados de aterros sanitários. Dependendo das características do lixiviado a tratar, as metodologias eletroquímicas podem ser aplicadas como pré-tratamento ou como tratamento de afinação aos processos biológicos. Os processos biológicos são referenciados com especial ênfase na integração com os processos eletroquímicos, pois estão entre os processos de tratamento mais económicos e encontram-se implementados na maioria das estações de tratamento de águas lixiviantes. Assim sendo, a integração dos processos biológicos com as metodologias eletroquímicas surge como a solução mais eficiente e económica.

Para lixiviados provenientes de aterros sanitários “novos”, com elevada carga orgânica biodegradável, o processo de oxidação eletroquímica mostrou ser eficiente quando aplicado após o tratamento biológico, removendo a matéria orgânica refratária remanescente do tratamento biológico. Nos estudos realizados neste âmbito foram obtidos consumos energéticos de 15 e 21 W h (g COD)⁻¹, para ensaios realizados em escala laboratorial e semi-piloto, respetivamente.

Para lixiviados designados por “velhos” ou com baixo índice de biodegradabilidade, o processo de oxidação eletroquímica mostrou ser mais eficiente quando aplicado ao lixiviado bruto, sem qualquer tipo de tratamento, tendo sido obtidas remoções da carência química de oxigénio acima de 90% com consumos energéticos na ordem dos 78 W h (g COD)⁻¹.

Nas situações em que os lixiviados a tratar apresentam uma grande quantidade de sólidos, a introdução de um processo de eletrocoagulação anterior ao de oxidação eletroquímica torna o tratamento mais eficiente. De facto, os ensaios de eletrocoagulação realizados conduziram a reduções da carga orgânica na ordem dos 50% com consumos energéticos de 2 W h (g COD)⁻¹. O tratamento combinado de eletrocoagulação seguido de oxidação eletroquímica, quando aplicado a lixiviados brutos, conduz ao aumento da biodegradabilidade dos poluentes orgânicos, potenciando assim a posterior aplicação de processos biológicos. Um aumento no índice de biodegradabilidade de 0,3 para 0,9 foi observado nos ensaios combinados realizados, com remoções da carência química de oxigénio de 95%. Este tratamento combinado apresenta ainda a vantagem de poder utilizar a redução catódica simultânea para remover os metais pesados existentes nos lixiviados, uma vez que estes processos reduzem os iões metálicos, depositando-os sobre o cátodo.

Quando a quantidade de sólidos no lixiviado é baixa, é preferível a aplicação apenas do processo de oxidação eletroquímica, uma vez que este não apresenta a desvantagem da produção de lamas. Apesar dos bons resultados obtidos neste processo utilizando ânodos de diamante dopado com boro, os estudos realizados utilizando ânodos de Ti/Pt/PbO₂ mostraram que este material de ânodo pode ser utilizado no tratamento de lixiviados de aterros sanitários, conduzindo a consumos energéticos inferiores aos observados com os ânodos de

BDD. Foi também observado que os dois materiais de ânodo apresentam cinéticas de remoção da carência química de oxigênio similares e que, apesar de os ânodos de BDD conduzirem a índices de mineralização superiores, os ânodos de Ti/Pt/PbO₂ potenciam remoções de azoto total e amoniacal superiores.

Palavras-chave

Lixiviados de aterros sanitários; Eletrocoagulação; Oxidação eletroquímica; Oxidação anódica; Eléttodos de BDD; Eléttodos de Ti/Pt/PbO₂; Eléttodos de ferro

Abstract

Sanitary landfill leachate is one of the major environmental problems concerning water pollution, since it is a very complex wastewater containing different heavy metals, organic and inorganic compounds, some of them refractory and toxic, which possesses colour and odour. Optimal leachate treatment, in order to fully reduce the negative impact on the environment, is today a challenge, since the conventional treatment methods used are not enough to reach the level of purification needed. For this reason, several advanced technologies have been studied for the treatment of sanitary landfill leachates and among them electrochemical methods have received great attention. In fact, electrochemical technologies have shown high efficiency in the elimination of persistent pollutants and several studies have reported its application in wastewater treatment.

The objective of the work described in this thesis was to evaluate the application of two electrochemical methods, electrocoagulation and electrochemical oxidation, in the treatment of sanitary landfill leachates. Studies were performed with different leachate samples, collected at different sanitary landfill facilities, at different points of the treatment plants existed and in different seasons of the year. Different cell configurations and electrode materials were experimented. Operational variables such as applied current/potential, stirring, flow rate and electrolysis time were studied. Pollutants removal, mineralization and biodegradability indexes and energetic costs were also assessed.

The results obtained demonstrated that electrocoagulation and electrochemical oxidation are effective technologies to treat leachates from sanitary landfills. Depending on the leachate characteristics, electrochemical treatments can be applied as pre-treatment or post treatment of biological processes. For leachates with high content in organic matter, electrochemical oxidation was more effective when applied after the biological treatment, eliminating the refractory organic matter remaining. Energy consumptions of 15 and 21 W h (g COD)⁻¹ were achieved at laboratory and semi-pilot scales experiments, respectively.

For leachates designated as “old” or with low biodegradability index, electrochemical oxidation process was more efficient when applied to the raw leachate, without any kind of pre-treatment. Chemical oxygen demand removals above 90% were achieved with energy consumptions of 78 W h (g COD)⁻¹.

For leachates with a high amount of solids, the application of an electrocoagulation process before the electrochemical oxidation enhanced the treatment efficiency. Electrocoagulation assays performed led to reductions in organic load of 50% with energy consumptions of 2 W h (g COD)⁻¹. Furthermore, the combined electrocoagulation/ electrochemical oxidation

treatment, when applied to raw leachates, enhances the biodegradability of the organic pollutants, improving the performance of the subsequent biological process. An increase in the biodegradability index from 0.3 to 0.9 was attained for the combined assays performed, with chemical oxygen demand removals above 95%. Moreover, this combined treatment has the advantage of being able to use the simultaneous cathodic reduction to remove heavy metals from the leachate, since these processes reduce the metal ions by depositing them onto the cathode. However, when solids content is low, it is preferable to apply only the electrochemical oxidation process, since it does not have the disadvantage of sludge production.

The experiments using Ti/Pt/PbO₂ anodes showed that this material can be successfully used for the treatment of sanitary landfill leachates, leading to lower energy consumptions than those obtained with boron doped diamond anodes. Both anode materials presented similar chemical oxygen demand removal kinetics and, despite boron doped diamond anodes yields higher mineralization indexes, Ti/Pt/PbO₂ promotes higher levels of total and ammonia nitrogen removals.

Keywords

Sanitary landfill leachate; Electrocoagulation; Electrochemical oxidation; Anodic oxidation; BDD electrode; Ti/Pt/PbO₂ electrodes; Iron electrodes

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List of symbols and acronyms

A	Electrode area
Abs	Absorbance
Abs ₀	Absorbance before electrolysis
Abs _t	Absorbance after an electrolysis time t
AN	Ammonia nitrogen
AN ₀	Ammonia nitrogen before electrolysis
BDD	Boron-doped diamond
BOD	Biochemical oxygen demand
BOD ₅	Five-day biochemical oxygen demand
(BOD ₅) ₀	Five-day biochemical oxygen demand before electrolysis
CE	Current efficiency
[Cl ⁻] ₀	Initial chloride concentration
COD	Chemical oxygen demand
COD ₀	Chemical oxygen demand before electrolysis
COD _{cr}	Critical chemical oxygen demand
COD(t)	Chemical oxygen demand at electrolysis time t
Cond.	Conductivity
DC	Dissolved carbon
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
DOC ₀	Dissolved organic carbon before electrolysis
DS	Dissolved solids
DSA	Dimensionally stable anodes
E	Energy consumption
EC	Electrocoagulation
EO	Electrochemical oxidation
E _{sp}	Specific energy consumption
F	Faraday constant
FAAS	Flame atomic absorption spectrometry
Fe _{sp}	Specific iron consumption
HPLC	High-performance liquid chromatography
I	Applied current intensity
ICE	Instantaneous current efficiency
IE _{sp}	Instantaneous specific energy consumption
j	Current density
j _{lim}	Limiting current density

j_{lim}^0	Initial limiting current density
k_m	Mass transport coefficient
M_x	Anode metal molar mass
n	Number of electrons
NA	Not applied
ND	No detectable
NDIR	Non-dispersive infrared
NS	Not specified
pH_0	Initial pH
Ref.	Reference
SPR	Ternary Sn-Pd-Ru oxide coated titanium
SS	Stainless steel
t	Electrolysis time
t_{cr}	Critical time
TKN	Total Kjeldahl nitrogen
TKN_0	Total Kjeldahl nitrogen before electrolysis
TOC	Total organic carbon
TN	Total nitrogen
TN_0	Total nitrogen before electrolysis
U	Cell voltage
UV-vis	Ultraviolet-visible
V	Sample volume
X_{sp}	Specific anode consumption
α	Ratio between current density and initial limiting current density
ΔCOD	Chemical oxygen demand decay
Δm_{anode}	Anode mass dissolved
λ_{max}	Wavelength of maximum absorbance
φ	Current efficiency of electrocoagulation process

Chapter 1

Introduction

This chapter presents an overview on the motivation to develop this work. It describes also the objectives defined and the strategy followed to attain those objectives. A description of the content of this thesis is also presented at the end of the chapter.

1.1 Environmental context

Population growth and new patterns of consumption have been leading to the production of huge amounts of municipal solid wastes that are usually discarded in sanitary landfills, since this is a relatively simple procedure with low cost [1]. However, as a result of rainwater percolation through the wastes, extracting and bringing with it several pollutant materials, a very complex wastewater is produced, usually named as sanitary landfill leachate.

Several types of pollutants can be found in sanitary landfill leachates composition, such as all types of organic and inorganic compounds, some of them refractory and toxic, and heavy metals [1,2].

The composition of sanitary landfill leachates varies depending on the landfills characteristics, such as [3,4]:

- the waste type received at the disposal site and its degree of decomposition;
- the seasonal weather variation during the waste disposal;
- the filling process regarding waste compaction, landfill cover and height of landfill layers;
- the landfill environment - waste degradation phase, humidity, precipitation, temperature, etc..

These aspects are interconnected and their combination contributes to the overall variance in the leachate quality and characterization.

According to the age, the sanitary landfill can be classified as young (less than 5 years), medium age (5-10 years) and old (more than 10 years) [5]. As the landfill age increases,

leachates parameters such as chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD₅), BOD₅/COD ratio and pH vary considerably [5]. In Table 1.1, a compilation of the main landfill leachate characteristics according to landfill age is presented. Additionally, Figure 1.1 represents the trend in the variation of the main parameters that characterize sanitary landfill leachates over the age. It can be seen that COD and BOD₅ concentration decrease, as time proceeds and leachate organic waste degradation goes through the successive aerobic, acetogenic, methanogenic, and stabilization stages. In fact, most of the biodegradable organic matter, which can be evaluated by BOD₅ value, is decomposed in the stabilization process and so BOD₅/COD ratio decreases with time, because the non-biodegradable organic matter that contributes to the portion of COD will largely stay unchanged in this process [6]. On the contrary, pH increases with age. In sum, young leachates are characterized by high COD concentrations (> 10000 mg L⁻¹) and BOD₅/COD ratios (0.5 - 1), whereas old leachates present COD concentrations below 4000 mg L⁻¹ and BOD₅/COD ratios below 0.1 [5].

Table 1.1 - Landfill leachate characteristics according to sanitary landfill age.

Landfill age	pH	COD / mg L ⁻¹	BOD ₅ /COD	Reference
Young < 5 years	5.6 - 9.1	1870 - 70900	0.05 - 0.70	[3]
	< 6.5	> 10000	0.5 - 1	[5]
	4.5 - 7.5	6000 - 60000	0.58	[7]
	6	3000 - 60000	0.6 - 1.0	[8]
	< 6.5	> 15000	0.5 - 1	[9]
Medium 5 < years < 10	6.9 - 9.0	1180 - 9500	0.07 - 0.33	[3]
	6.5 - 7.5	4000 - 10000	0.1 - 0.5	[5]
	6.5 - 7.5	3000 - 15000	0.1 - 0.5	[9]
Old > 10 years	7.0 - 11.5	100 - 10000	0.01 - 0.37	[3]
	> 7.5	< 4000	< 0.1	[5]
	7.5 - 9.0	500 - 4500	0.06	[7]
	6.6 - 7.5	100 - 500	0 - 0.3	[8]
	> 7.5	< 3000	< 0.1	[9]

Despite the landfill leachates composition varies with the landfill age, it also varies from place to place. Besides the represented parameters in Table 1.1 and Figure 1.1, which are the most common in the characterization of the leachates, there are more than 200 compounds that have already been identified in sanitary landfill leachates, such as aromatic and halogenated compounds, phenols, pesticides and several heavy metals [1,2,4].

In addition to organic compounds, ammonia nitrogen (AN) is of great environmental concern in landfill leachates [8]. It is released from wastes mainly by decomposition of proteins and has been found in leachates at concentrations ranged from 0.2 to 13000 mg L⁻¹ [3]. Ammonia

nitrogen does not have an obvious decreasing trend in concentration with time, except due to dilution by leaching, and may disrupt biological units for leachate treatment due to its toxicity. Therefore, AN has been identified as the most significant component in leachate in a long term [7].

Due to its complex, recalcitrant and varied composition, as displayed above, sanitary landfill leachates represent a significant source of pollution, presenting an accumulative, threatening and detrimental effect to the survival of aquatic life forms and ecology balances [5]. An inadequate leachate management involves serious risks, particularly the contamination of water resources, at the surface and groundwater, and soils, and consequently, induces genome damage in the population that consumes the contaminated water [1,2,5,10].

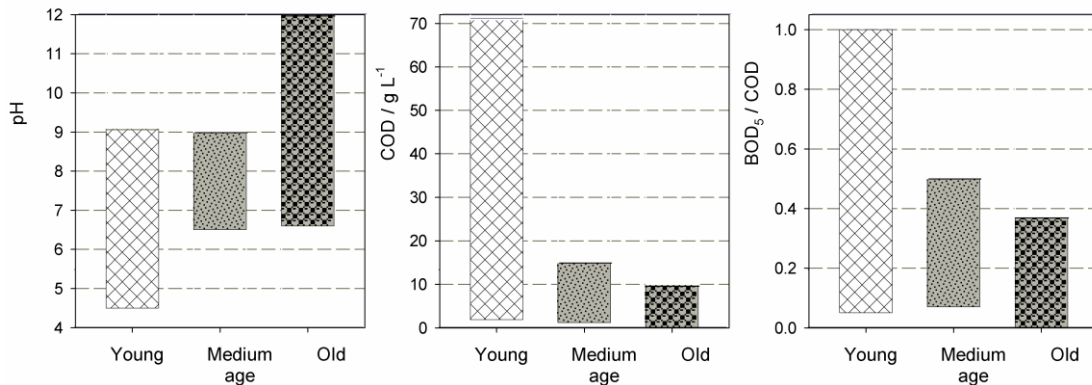


Figure 1.1 - Variation of the main parameters that characterize sanitary landfill leachates over the age [3,5,7-9].

Nowadays, biological reactors, with nitrification/denitrification steps, followed by membrane technologies, are commonly used to treat leachates. However, due to the variability in the quality and quantity of the leachate throughout the life span of the treatment plant, these conventional treatments may become ineffective. Thus, it is very important to apply reliable and effective treatment technologies, capable of deal with such complex effluents.

In this context, electrochemical treatments have been showing high efficiency in the elimination of persistent pollutants and several studies have described the application of these methods in the treatment of complex effluents [7,11-15]. In fact, electrochemical technologies provide several advantages, being the inherent advantage the environmental compatibility as it uses a clean reagent, the electron. Other advantages include the use of simple equipment, easy operation, robustness, versatility and amenability to automation [16,17].

There are several papers describing the application of electrochemical technologies in sanitary landfill leachates, with promising results [18-55]. In fact, these treatment methods have shown high potential to treat efficiently sanitary landfill leachates, despite the high operating costs pointed as the main drawback to its full-scale implementation.

1.2 Global aims

The main goal of this work was to search for an efficient electrochemical solution for sanitary landfill leachates treatment, which could complement or partially replace the existing treatment systems. With this purpose and taking into account that the composition and characteristics of this kind of wastewaters can significantly vary, even in the same landfill facility, the following secondary goals were established:

1. Evaluate the feasibility of an electrochemical oxidation (EO) treatment applied as a polishing step, after a biological process, to eliminate the remaining dissolved persistent organic compounds.
2. Study the application of an electrochemical oxidation treatment to raw sanitary landfill leachates, determining the best operational conditions that lead to higher treatment efficiencies.
3. Evaluate the introduction of an electrocoagulation (EC) process before the EO treatment.
4. Study the application of Ti/Pt/PbO₂ anodes for EO treatment of sanitary landfill leachates and evaluate its performance when compared with boron-doped diamond (BDD) anodes.

1.3 Strategy

In order to achieve the goals proposed, several sets of experiments were performed with different leachates samples and at different operational conditions. Leachate samples were collected from three sanitary landfills with different ages.

Since most of the leachate treatment sites comprise biological processes, first it was studied the application of electrochemical technologies as a biological step post-treatment. In fact, the biological processes are effective in removal of biodegradable organic substances and, mainly for leachates from a young landfill, high degradation levels can be achieved, leaving only the persistent organic compounds, which can be easily oxidized by EO.

The EO was chosen to perform this study because, among the electrochemical technologies, it allows the highest treatment efficiencies without the disadvantage of sludge production. EO experiments were performed using a BDD anode since, according to literature, it presents the best results. Samples of a leachate treated on site by a biological nitrification and denitrification process were used in this study. In a first set of experiments, a laboratory scale cell, in batch mode with stirring, was employed and the influence of the initial organic load and of the applied current density on the EO performance was assessed, in order to determine the optimal conditions for the application of EO as a post treatment of a biological step. Then, in order to study the effect of the scale up of the process in EO treatment efficiency, a second set of experiments was performed applying a semi-pilot plant operating in batch mode with recirculation using a BDD DiaCell 100 electrochemical cell, with an electrode area of 70 cm². Different current densities and flow rates were tested.

Considering that most of the sanitary landfill leachates present low biodegradability indexes, and that the biological processes have limited effectiveness when the BOD₅/COD ratio is lower than 0.5, the application of EO as a first treatment to a sanitary landfill leachate with low biodegradability index was evaluated. Again, the choice of EO was due to its ability to remove organic pollutants without carrying out the accumulation of refractory organics. Samples used in this study were collected at a medium age sanitary landfill that presented a very low BOD₅/COD ratio. BDD anodes were used in all experiments and different operational conditions were assessed, including cell configurations, applied current densities and flow rates, in order to evaluate the feasibility of the application of EO as a single treatment and the best operational conditions. Experiments were conducted at laboratory scale in batch mode, using two different electrochemical cells, one with recirculation and the other with stirring, with the aim of studying the influence of the hydrodynamics inside the electrochemical cell on the electrodegradation rate. The influence of the applied current density was also investigated and experiments where the current density was decreased by steps were performed, in order to study this effect on the current efficiency of the process. After determining the most favourable conditions at laboratory scale, an attempt to scale up the process was made and experiments were performed using a semi-pilot plant, operating in batch mode with recirculation, using a BDD DiaCell 100 electrochemical cell, with an electrode area of 70 cm². Different current densities and flow rates were tested. The influence of the current density decreased by steps during the degradation process was also assessed.

With the aim of reducing the operational costs that EO of landfill leachates involves, especially when it is used as a single treatment the possibility of combining this technology with other techniques, as pre-treatment or polishing step, was studied.

For sanitary landfill leachates with a high biodegradability index, the combination of biological processes with EO post-treatment seems to be a feasible solution. But when leachate presents low biodegradability, biological processes are not effective. Thus, as mentioned before, most of the landfill sites had already made the investment on biological treatments, and a possible solution to avail that investment was the introduction of an EO process as a pre-treatment, to convert initially recalcitrant and non-biodegradable organic substances into more readily biodegradable intermediates. Even so, and taking into account that generally sanitary landfill leachates present high amounts of colloidal and suspended particles, the application of EO as a first treatment still would get costly. In an attempt to overcome this drawback, the application of a combined EC/EO process to treat sanitary landfill leachates was evaluated. The use of such integrated treatment was investigated either as a pre-treatment or as a polishing step. EC was applied as a first step, in order to remove colloidal and suspended particles, and it was followed by EO either to completely oxidize the dissolved persistent organic compounds or to convert them into more readily biodegradable intermediates. Experiments were performed using raw and pre-treated leachate samples and several operational conditions were tested. In EC assays, iron consumable electrodes were used, since they were identified in literature as the most suitable for leachate treatment, and variables such as initial pH, stirring, leachate dilution, electrolysis time and applied potential/current intensity were investigated. The influence of the EC pre-treatment experimental conditions on the EO performance was assessed. The application of combined EC/EO processes to improve the biodegradability of leachates was evaluated. Again a BDD anode was used in the EO assays and the influence of the EO applied current density on the EC/EO process efficiency was also studied.

At last, and still in an attempt to reduce EO costs, studies were performed with a different anode material. Despite the exceptional properties of BDD electrodes and the good results obtained when this electrode is used, their large-scale utilization is very costly. Thus, the use of a different electrode material that is less expensive than BDD was investigated. A Ti/Pt/PbO₂ anode was chosen, since this electrode material have been successfully prepared and used by our research group in the electrochemical degradation of several pharmaceutical drugs. The evaluation of the ability of this anode compared with BDD anode was assessed for two different types of leachates from a young and an old sanitary landfill. The first set of assays was performed using a biologically pre-treated sanitary landfill leachate from a young landfill site. A leachate collected from an old landfill site was used in the second set of assays, where the effects of the applied current density and of the addition of extra chloride ion were investigated, since the initial concentration of Cl⁻ present in leachate was quite low

comparing with other leachates studied and, according to literature, was not enough for an effective indirect oxidation. Moreover, to better understand the influence of the experimental conditions on the degradation rate and its mechanism, both sets of assays were also performed with simulated samples.

1.4 Thesis overview

This thesis is structured in eight main chapters. In the first chapter, the motivations to perform this work and the context in which it is inserted are presented. The global aims of the work are identified and a description of the strategy followed to achieve those goals is made.

Subsequently, the second chapter consists in a concise literature review related with the application of the electrochemical technologies used in this work, namely electrocoagulation and electrochemical oxidation, to sanitary landfill leachates treatment. Fundamentals of each technology are presented to better understand its advantages and limitations in the treatment of sanitary landfill leachates and the effect of the main process variables in leachates treatment efficiency is discussed. Updated information on the application of these technologies to sanitary landfill leachates is given.

Thereafter, the third chapter presents the characterization of the sanitary landfill leachate samples used in this work and the description of the electrodegradation experiments and of the analytical methods used to follow those experiments.

Chapters four to seven present a description of the experimental work developed and the results obtained in the different studies performed as described in the third chapter. The results are here discussed and the main conclusions are presented.

Finally, the eighth chapter summarizes the concluding remarks obtained during this research work, regarding the application and optimization of electrochemical technologies in sanitary landfill leachates treatment. Future perspectives are also discussed.

Chapter 2

Electrochemical technologies in sanitary landfill leachate treatment

Fundamentals and literature review

The electrochemical technologies are based on electron transfer. An electrochemical cell is required, where electrodes are in contact with the polluted solution and connected by an external circuit. The main advantage of these technologies is their environmental compatibility, since its main reagent, the electron, is a clean reagent. Other advantages are related to its versatility and amenability of automation [17]. The application of electrochemical technologies in wastewater treatment has shown high effectiveness in the elimination of persistent pollutants [7,11-15].

Among the electrochemical technologies, the most studied in sanitary landfill leachate treatment are electrocoagulation, electro-Fenton and electrochemical oxidation. There are several reports describing the application of these technologies in leachates, as a single treatment, or combined with other methods. Photoassisted systems, like photoelectro-Fenton and photoelectrocatalysis, have also received great attention. However, fundamentals and literature review described in this chapter will be focused on electrocoagulation and electrochemical oxidation, since they were the treatment processes applied in the work presented in this thesis.

2.1 Electrocoagulation

Electrocoagulation is a process that uses consumable electrodes to supply ions to the solution/suspension, allowing suspended, emulsified, or dissolved contaminants to form agglomerates. The coagulating ions are produced *in situ* and three different stages can be identified [56]: (i) formation of the coagulants by electrolytic oxidation of the “sacrificial electrode”, (ii) destabilization of the contaminants and particulate suspension and breaking of emulsions and (iii) aggregation of the destabilized phases to form flocs. The contaminants present in the solution are treated either by chemical reactions and precipitation or by

physical and chemical attachment to colloidal materials generated by the electrode erosion [57]. The coagulated particles can be separated from the liquid phase by sedimentation or by electroflotation, when they are attached to H₂ bubbles, evolved at the cathode and transported to the top of the solution [11,57].

EC has been successfully applied in the treatment of sanitary landfill leachates and there are several papers describing those studies [27,28,36,41-43,46,55]. The conditions used in the experiments as well as the main results obtained are summarized in Table 2.1.

There are some performance indicators used for progress and efficiency assessment of EC treatments, as well as for other electrochemical treatment processes, which allow the comparison between different cells and operational conditions. The decontamination process of sanitary landfill leachates is usually monitored from the abatement of COD, total organic carbon (TOC) and nitrogen forms, such as total nitrogen (TN), total Kjeldahl nitrogen (TKN) and AN. From these data, the removal percentages are calculated by Equation (2.1) [14]:

$$X_{\text{removal}} (\%) = \frac{\Delta X}{X_0} \times 100 \quad (2.1)$$

where X represent the parameter, ΔX is the corresponding removal in g L⁻¹, at electrolysis time t, and X₀ is its initial value before treatment, in g L⁻¹. The decolourization efficiency or percentage of colour removal during the EC treatment of leachates is also widely applied and can be determined by Equation (2.2) [14]:

$$\text{Colour removal (\%)} = \frac{\text{Abs}_0 - \text{Abs}_t}{\text{Abs}_0} \times 100 \quad (2.2)$$

where Abs₀ and Abs are the absorbances before electrolysis and after an electrolysis time t, respectively, at the wavelength of maximum absorbance (λ_{max}) of the leachate. The specific anode consumption, X_{sp}, in g L⁻¹, resulting from the oxidation of the consumable anode in the EC process, is another parameter normally used to evaluate EC efficiency and it is calculated according to Equation (2.3):

$$X_{\text{sp}} = \frac{I t M_x}{F n V} \quad (2.3)$$

where X represents the anode metal, I is the applied current, in A, t is the electrolysis time, in s, M_x is the anode metal molar mass, in g mol⁻¹, F is the Faraday constant, in C mol⁻¹, n is the number of electrons involved in the oxidation reaction of the anode and V is the volume of the sample, in L. Important specific energetic, E_{sp}, parameters such as energy consumption per volume of treated leachate, in W h m⁻³, per consumed mass of anode, in W h (g metal)⁻¹,

or per amount of COD removed, in $W\ h\ (g\ COD)^{-1}$, can be obtained through Equations (2.4) to (2.6) [14]:

$$\text{Energy consumption (W h m}^{-3}\text{)} = \frac{I U t}{3.6 V} \quad (2.4)$$

$$\text{Energy consumption (W h (g metal)}^{-1}\text{)} = \frac{I U t}{3.6 \Delta m_{\text{anode}}} \quad (2.5)$$

$$\text{Energy consumption (W h (g COD)}^{-1}\text{)} = \frac{I U t}{3.6 \Delta \text{COD} V} \quad (2.6)$$

where U is the cell voltage, in V , Δm_{anode} is the anode mass dissolved, in g , and ΔCOD is the decay in COD ($g\ m^{-3}$). The instantaneous specific energy consumption, IE_{sp} , in $W\ h\ (g\ COD)^{-1}$, can also be calculated using Equation (2.7):

$$IE_{\text{sp}} = \frac{1000}{V} \frac{\partial E}{\partial (\Delta \text{COD})} = \frac{1000}{V} \frac{\partial E / \partial t}{\partial (\Delta \text{COD}) / \partial t} \quad (2.7)$$

where E ($= I U t / 3600$) is the energy consumption, in $W\ h$. Determination of $\partial E / \partial t$ and $\partial (\Delta \text{COD}) / \partial t$ is usually performed by adjusting the polynomial equations to the variations of E and ΔCOD with time, and calculating the corresponding derivatives. Current efficiency of the EC process, φ , can be calculated based on the comparison of experimental weight loss of the anode during EC, which will correspond to the anode mass dissolved, with the specific anode consumption, as presented by Equation (2.8) [41]:

$$\varphi (\%) = \frac{\Delta m_{\text{anode}}}{X_{\text{sp}} V} \times 100 \quad (2.8)$$

Several process variables can influence the EC treatment efficiency, such as reactor design, electrode material, current density, pH, conductivity, etc. The main goal in the design of an EC cell is to achieve the maximum efficiency of the process. In its simplest form, an electrocoagulating reactor may be made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. This arrangement may not be suitable for wastewater treatment, since for a workable rate of metal dissolution, the use of electrodes with large surface area is required.

EC cells have been built in several different configurations, as a batch or a continuous system, with monopolar or bipolar electrodes, connected in parallel or in series, each one with advantages and disadvantages [14,57]. As it can be seen in Table 2.1, for most of the EC experiments performed with sanitary landfill leachates, a batch reactor with monopolar electrodes in parallel connection has been used, varying the number of electrodes between 2

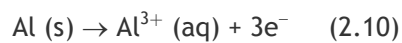
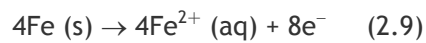
and 14. In Figure 2.1, the sketches of the EC cells used in some of the studies reported with sanitary landfill leachates are presented.

Iron and aluminium are the most widely used EC electrode materials, since they are cheap, readily available and effective [42]. When iron is the anode in the EC process, Fe^{2+} is dissolved into the solution from Fe oxidation at the anode and produce iron hydroxide, $\text{Fe}(\text{OH})_n$, where $n = 2$ or 3 . The $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ flocs formed have strong affinity for colloids, dispersed particles and ionic species and cause the flocculation, which generates bigger particles. Fe^{3+} ions may also be present and, depending on the pH, different insoluble hydroxide mononuclear complexes may be formed [58]. In the case of EC with Al, the electrolytic dissolution of the aluminium anode produces species such as Al^{3+} and $\text{Al}(\text{OH})_2^+$ that are transformed initially into $\text{Al}(\text{OH})_3$ and finally polymerized to $\text{Al}_n(\text{OH})_{3n}$ [64]. However, depending on the pH of the aqueous medium, other ionic species, such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}(\text{OH})_4^-$ may also be present in the system.

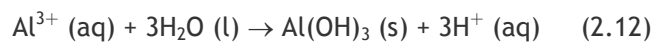
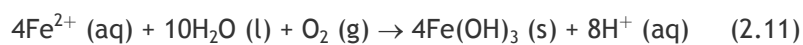
Two different mechanisms have been described for the production of the metal hydroxide, depending on the pH of the solution [27]. The reactions are given in Equations (2.9) to (2.17).

- Mechanism 1 (acidic medium)

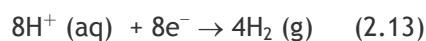
Anode:



In solution:

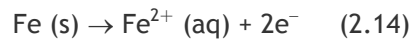


Cathode:

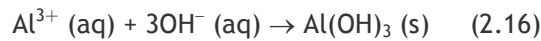
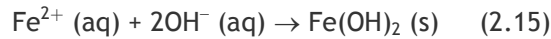


- Mechanism 2 (basic medium)

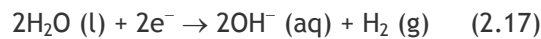
Anode:



In solution:



Cathode:



There are several studies reporting the effect of the electrode material, iron or aluminium, on the EC treatment efficiency of sanitary landfill leachates (Table 2.1). High treatment efficiencies were obtained with both electrode materials and, depending on the leachate characteristics and operating variables imposed, Al electrodes presented higher treatment efficiencies than Fe ones and vice-versa. COD removals up to 21000 mg L⁻¹ after 30 minutes of electrolysis were reported for both electrode materials [41].

It is known that, despite the high coagulation efficiency of Al³⁺, the aluminium electrodes passivation is detrimental to the reactor performance [57]. The presence of some anions in aqueous solution can slow down the electrode passivation, especially the presence of Cl⁻ that is known to largely inhibit the passivation process [57]. In fact, according to Table 2.1, the more pronounced difference between the treatment efficiencies using Al or Fe electrodes was obtained in a comparative study in which the initial Cl⁻ concentration in the leachate was 3.1 g L⁻¹, being the highest efficiencies assigned to Al electrodes [27]. Also, from data presented in Table 2.1, and focusing on the comparative studies of both electrode materials [27,28,41,42], it can be seen that Al electrodes lead to better results than Fe electrodes in experiments where high current density values are applied. This can be consistent with the possible chemical attack on the aluminium cathode by hydroxyl ions generated during water reduction, which generates an extra amount of aluminium ions [36].

High current density promotes the formation of higher concentration of hydroxyl ions because water electrolysis at the cathode depends on the quantity of electricity passed through the solution. An electrical energy consumption analysis was performed by Bouhezila *et al.* [41]

and it was found that, despite the better removal efficiencies obtained by Al electrodes, Fe electrodes were energetically more efficient than aluminium. Also, iron is less toxic and more acceptable in agriculture field and thus can be considered as the most appropriate electrode material for the treatment of leachates by electrocoagulation processes [41].

In order to investigate the effect of inter-electrodes distance on the efficiency of the EC process in sanitary landfill leachate treatment, studies were performed where the inter-electrode distance was varied (Table 2.1). Bouhezila *et al.* [41] reported that, when the inter-electrode distance was increased from 0.5 to 2.8 cm, the removal of COD increased by about 10% after 15 min of treatment time. However, for turbidity and colour removal, no discernible differences were observed. Ricordel *et al.* [55] found that the differences of COD removal efficiency were not significant between 2 and 4 cm gaps. Although the obtained results of these two studies did not converge, they are consistent since in the study performed by Bouhezila *et al.* [41] the organic load of the leachate and the applied current densities were significantly higher than those used in Ricordel *et al.* [55] experiments. Indeed, despite shorter inter-electrodes distances minimize the IR-drop between the electrodes, they also potentiate faster electrode passivation, which happens more intensely when the organic load of the solution is high. Other EC studies performed with sanitary landfill leachates, and reported in Table 2.1, used inter-electrodes distances between 0.2 and 6.5 cm. Although it is a wide range, no trend is found in the influence of the inter-electrode distance on the efficiency of the EC process in sanitary landfill leachate treatment. An adequate inter-electrode distance is function of leachate characteristics and must be determined balancing the IR-drop and the passivation effects.

The effect of mechanical stirring on the EC efficiency treatment of leachates has also been studied. Ilhan *et al.* [27] reported that mixing process negatively affected COD removal efficiency, although it increased AN treatment performance, according to the authors because ammonia is easily stripped by mixing. Different results were obtained by Bouhezila *et al.* [41], which reported an increase in COD removal and in sludge production when the magnetic stirring speed was increased from 50 rpm to 150 rpm. In fact, EC process is realized by mobilization of ions by means of applied electrical charge, and mixing operation will influence the movement of ions in the suspension. Considering this, mixing can promote a more homogeneous solution medium that will be much more efficient for the contact between the contaminant and coagulants. On the other hand, mixing can also cause a disturbance of ion mobilization and the breakup of flocs. Depending on the experimental conditions applied, moderate stirring can be considered an advantage in EC treatment of leachates, despite the disadvantages associated to extra costs that it implies.

A key factor in the EC process is the operating current density, since it exerts a significant influence on the reaction kinetics and energy consumption. Increasing the current density, the extent of anodic dissolution of consumable electrodes increases, resulting in an increase

in hydroxide flocs that promote pollutants removal. Moreover, with the increasing in current density the rate of bubble-generation increases and the bubble size decreases, resulting in a faster removal of pollutants by H₂ flotation [46].

There are several studies reporting the effect of current density on the EC treatment efficiency of leachates [27,46,55]. Despite the difference in leachate characteristics and in operational conditions applied in the different studies, all have shown that pollutant removal increased with the increase in current density, as can be seen in Table 2.1. According to the explanation given above, no other result was expected. However, when energy consumption is analysed, the results obtained with the high current densities do not seem so appealing, since the energy consumption is greatly increased with the current density increase. So, an optimum current density must invariably involve a trade-off between energy consumptions and efficient use of the introduced coagulant [57]. For instance, Orkun *et al.* [46] have found that the maximum removal efficiency occurred for the highest current density tested (300 A m⁻²) but, by considering the energy and electrode consumptions, the optimum current density was determined as 200 A m⁻².

The pH of the solution is an important operating factor influencing the performance of the EC process, and the effect of current density on the pH variation during electrolysis can be a drawback. High current densities promote the formation of hydroxyl ions due to the water reduction, which depends on the amount of electricity passed through the solution [55]. Under certain conditions, various complex and polymer compounds can be formed via hydrolysis and polymerization reaction of the electrochemically dissolved metal ions [57].

The influence of pH in the EC efficiency treatment of leachates was also subject of study by some authors [42,46]. Organic load removal at different initial pH values, ranging between 3 and 10, was assessed for landfill leachates with different characteristics. It was observed that higher COD removal efficiencies were obtained at neutral conditions, whereas in acidic or basic medium the COD removal efficiency was found to decrease [42,46]. pH variation along the EC treatment was also assessed in the studies performed [27,41-43,46,55]. An increase in the pH value was registered and was explained by the excess of hydroxyl ions produced at the cathode and by OH⁻ release due to the occurrence of a partial exchange of OH⁻ by Cl⁻ in Al(OH)₃ [43].

Along with pH, electrical conductivity plays an important role in the electrochemical processes because, when it is low, the current efficiency decreases, and higher applied potentials are needed to avoid the passivation of the electrode, thus increasing the energy consumption. One of the most common electrolytes used to increase the conductivity is NaCl. It contributes to the wastewater disinfection, due to the formation of active chlorine, and doesn't present the negative impact of adding carbonate or sulphate salts that in the

presence of calcium and magnesium ions may cause the precipitation of their salts and the consequent passivation of the electrode [57].

Sanitary landfill leachates generally present high conductivity and addition of electrolyte is not needed to ensure high current efficiencies in the EC process. Despite this, Orkun *et al.* [46] investigated the effect of the conductivity in the EC treatment efficiency of leachates at four different conductivity values, ranging between 16.40 and 40.00 mS cm⁻¹, by using NaCl as supporting electrolyte. These authors have found that, despite the decrease in energy consumption with the increase in conductivity, the COD removal efficiency decreased steadily, maybe due to a change in the ionic strength that affects the kinetics and equilibrium of the reactions occurring between charged species during electrocoagulation. Also Li *et al.* [42] studied the effect of the conductivity by adding NaCl at concentrations of 819, 1500, 2000, 2500 and 3000 mg L⁻¹. They observed that an increase in the concentration of Cl⁻ from 819 mg L⁻¹ to 2500 mg L⁻¹ yield an increase in the COD removal from 29.8 to 38.9% and in the AN removal from 23.5 to 32.6%. But after 2500 mg L⁻¹ no significantly changes were observed. As can be seen in Table 2.1, the leachates used in these two studies had very different composition and so different reactions could occur during the EC process. Also, the conductivity of the raw samples used by Li *et al.* [42] was not presented. In fact, the different results obtained in these studies cannot be completely ascertained to conductivity since the only electrolyte used to alter this parameter was a chloride salt that, frequently, presents a unique behaviour, particularly if the applied potentials are high enough to promote hypochlorite and chlorine species.

In sum, EC has demonstrated to be an effective and practical technology to treat leachates from sanitary landfills. Its application requires simple equipment, is easy to operate and, in most of the cases, no chemicals addition is required. Nevertheless, there are some drawbacks associated to the application of this process to sanitary landfill leachates, namely: the need for regular replacement of the “sacrificial electrodes”, since they are dissolved into the wastewater streams as a result of oxidation, and the consequent increase in conductivity of the remaining effluent; the eventual formation of an impermeable oxide film on the cathode, disabling the EC unit; and, not less important, the sludge that is formed during the process, that will have in its content significant amounts of iron or aluminium and other recalcitrant pollutant species that need to be treated before its disposal. Moreover, some toxic chlorinated organic compounds and trihalomethanes may be formed *in situ* if chloride and high humic and fulvic acid contents are present [56].

Table 2.1 - EC studies performed with sanitary landfill leachates: conditions used and main results obtained.

Reactor design	Electrode material	Inter-electrode gap /cm	Current density / A m ⁻²	Electrolysis time / min	Stirring speed/ rpm	pH ₀	COD ₀ / mg L ⁻¹	AN ₀ / mg L ⁻¹	COD removal / %	AN removal / %	Energy consumption	Ref.	
Batch reactor with 2 electrodes in parallel connection	Al	6.5	348	30	No	8.2	12860	2240	45	9	12.5 kW h m ⁻³ or 0.46 W h (g COD) ⁻¹	[27]	
			631		200				44	16	NS		
	Fe	6.5	348	30	No	8.2	12860	2240	59	14	39.7 kW h m ⁻³ or 1.1 W h (g COD) ⁻¹	[27]	
					631				No	35	11		NS
Batch reactor with 14 electrodes in parallel connection	Al	0.3	NS	NS	NS	7.7	4022	NS	88	NS	NS	[28]	
	Fe	0.3	NS	NS	NS	7.7	4022	NS	90	NS	NS	[28]	
Continuous reactor with 2 bipolar electrodes	Al	0.2 - 1	NS	NA	No	7.2	380	NS	45	NS	NS	[36]	
Batch reactor with 6 electrodes in parallel connection	Fe	0.9	50	120	200	6.5	11000	1247	30 ⁽¹⁾	NS	1.0 W h (g COD) ⁻¹	[46]	
			200						41				3.5 W h (g COD) ⁻¹
			300						53				6.3 W h (g COD) ^{-1 (1)}
			300						47 ⁽¹⁾				6.9 W h (g COD) ⁻¹
			300						57 ⁽¹⁾				8.7 W h (g COD) ⁻¹
Batch reactor with 2 electrodes in parallel connection	Al	0.5	250	30	150	7.6-8.9	31200 ⁽¹⁾	NS	60 ⁽¹⁾	NS	NS	[41]	
			125						56				
			250						70 ⁽¹⁾				
	Fe	2.8	125	30	150	7.6-8.9	31200 ⁽¹⁾	NS	58 ⁽¹⁾	NS	22 kW h m ⁻³	[41]	
									500				70
									500				68

(1) Value obtained indirectly from data presented in the paper or from a figure; NA - Not Applied; NS - Not Specified.

Table 2.1 - (cont.)

Reactor design	Electrode material	Inter-electrode gap /cm	Current density / A m ⁻²	Electrolysis time / min	Stirring speed/ rpm	pH ₀	COD ₀ / mg L ⁻¹	AN ₀ / mg L ⁻¹	COD removal / %	AN removal / %	Energy consumption	Ref.
Batch reactor with 10 electrodes in parallel connection	Al	1	30	30	200	6.7	2566	386	21	21	NS	[42]
	Fe		20			6.7			24	20		
			30			3.9			27	14		
						6.7			33	25		
						10			22	16		
			50		6.7	93	32					
Batch reactor with 4 electrodes in parallel connection	Al	1.6	79	30	No	6.6-	6200	110	29	NS	NS	[43]
			198			7.0			45			
Batch reactor with 2 electrodes in parallel connection	Al	2	23	210	Yes	8	260	187	33 ⁽¹⁾	NS	18 W h (kg COD) ⁻¹	[55]
			95						56 ⁽¹⁾	0	135 W h (kg COD) ⁻¹	
		4	23						33 ⁽¹⁾	NS	70 W h (kg COD) ⁻¹	
		95	56 ⁽¹⁾						NS	165 W h (kg COD) ⁻¹		

(1) Value obtained indirectly from data presented in the paper or from a figure; NS - Not Specified.

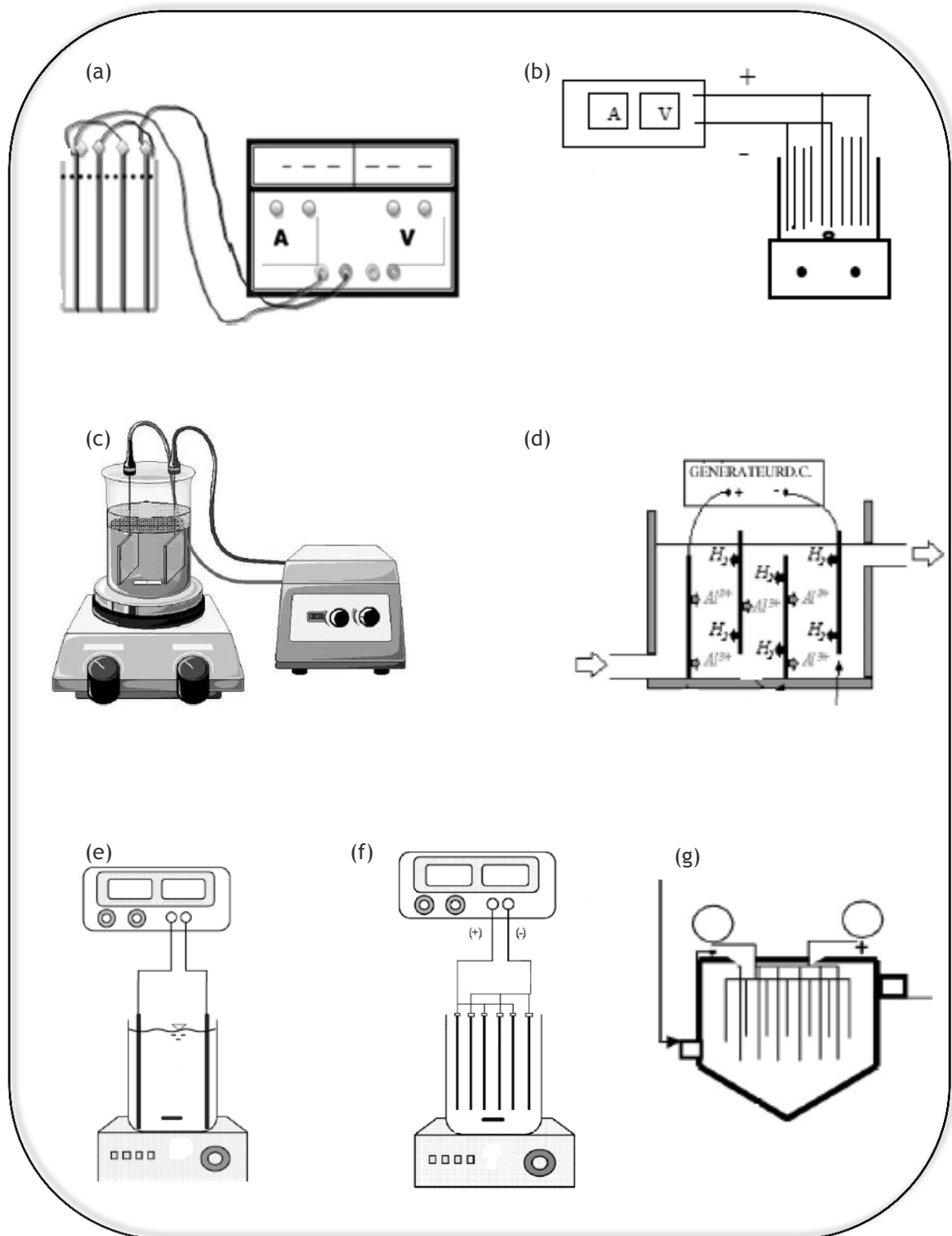
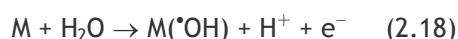


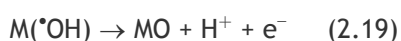
Figure 2.1 - Sketches of EC cells used for the electrocoagulation of sanitary landfill leachates: (a) Batch reactor with 4 electrodes in parallel connection [43]; (b) Batch reactor with 10 electrodes in parallel connection [42]; (c) Batch reactor with 2 electrodes in parallel connection [41]; (d) Continuous reactor with 2 bipolar electrodes [36]; (e) Batch reactor with 2 electrodes in parallel connection [27]; (f) Batch reactor with 6 electrodes in parallel connection [46]; (g) Batch reactor with 14 electrodes in parallel connection [28].

2.2 Electrochemical oxidation

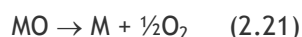
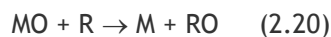
Electrochemical oxidation is the most popular electrochemical procedure for removing organic pollutants from wastewaters [14]. It is a process based on the effluent electrolysis and in its simplest form, consists in the oxidation of pollutants in an electrolytic cell, which is formed by two electrodes connected by an external circuit, so that electrochemical reactions can take place. During the electrochemical reaction, electrons transfer occurs between the electrodes' surface and the species present in solution and pollutants oxidation takes place, either through direct electron transfer to the anode (direct anodic oxidation), or by chemical reaction with electrogenerated species at the anode, such as physically adsorbed "active oxygen" (physisorbed hydroxyl radical) or chemisorbed "active oxygen" (oxygen in the lattice of a metal oxide anode) generated from water discharge [14,18]. To interpret this behaviour, Cominellis [59] has proposed a model for the organic compounds oxidation with hydroxyl radicals considering the existence of two types of anodes, the "active" and the "non-active" ones. According to the proposed model, there is an initial reaction, which is common for both types of anode (generically denoted as M), that corresponds to the oxidation of water molecules to physisorbed hydroxyl radical (Equation (2.18)).



For "active" anodes, there will be a strong interaction between anode surface and HO[•] that will lead to the formation of a superoxide (MO), according to Equation (2.19).

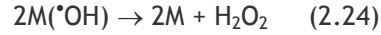
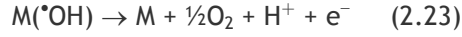
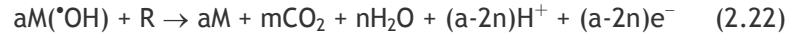


The redox couple MO/M will act as a mediator in organic compounds oxidation (Equation (2.20)), which competes with the side reaction of oxygen evolution from chemical decomposition of superoxide (Equation (2.21)).



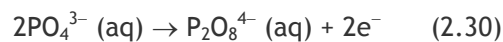
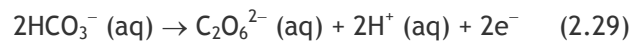
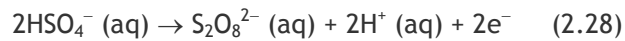
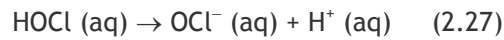
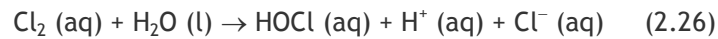
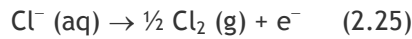
With "non-active" anodes, interactions between anode surface and HO[•] will be so weak that will allow the direct reaction of the organic compounds with M(^•OH) to give fully oxidized reaction products such as CO₂ through Equation (2.22), where R is an organic compound with m carbon atoms and without any heteroatom, which needs a = (2m + n) oxygen atoms to be totally mineralized to CO₂. The weaker is the interaction between anode surface and HO[•], the higher is the reactivity for organic compounds oxidation (fast chemical reaction). This reaction will compete with side reactions of M(^•OH) such as direct oxidation to O₂ (Equation

(2.23)) or indirect consumption through dimerization to hydrogen peroxide (Equation (2.24)) [14].



Some examples of “active” anodes are Pt, IrO₂ and RuO₂. On the other hand, PbO₂, SnO₂ and BDD are some of the “non-active” anodes that can be found. A “non-active” does not provide any catalytic active site for the adsorption of reactants and/or products from the aqueous medium. In this case, the anode serves only as an inert substrate, which can act as a sink for the removal of electrons [14].

Although the model proposed by Comninellis [59] assumes that EO is mediated by hydroxyl radicals, either adsorbed at the surface, in the case of “active” anodes, or very weakly adsorbed, in the case of the “non-active” ones, there are other oxidizing species that can also be generated by oxidation at the anode, such as ozone, generated from water discharge at the anode, H₂O₂, from Equation (2.24), Cl₂, HClO and ClO⁻, derivate from Cl⁻ oxidation at the anode (Equations (2.25) to (2.27)), and peroxodisulphate (Equation (2.28)), peroxodicarbonate (Equation (2.29)) and peroxodiphosphate (Equation (2.30)), from the anodic oxidation of bisulphate (or sulphate), bicarbonate and phosphate, respectively [14,17].



During the electrochemical oxidation of an aqueous effluent the oxidation mechanisms may follow two different routes: (i) Electrochemical conversion, in which organic compounds are partially oxidized and transformed into a variety of more biodegradable reaction by-products, being a subsequent treatment still required, generally a biological one; (ii) Electrochemical combustion, where organic compounds are completely mineralized and transformed into

water, carbon dioxide and other inorganic species, being no further purification required [12,13,17].

The nature of the anode material also strongly influences the selectivity and the efficiency of the EO process [14]. Thus, its choice must be well considered. Competition between organic compounds oxidation at the anode and the oxygen evolution side reaction must be taken into account and can be analysed by the oxygen evolution overpotential of the anodes' material. Anodes with low O_2 overvoltage will present high electrochemical activity toward oxygen evolution and low chemical reactivity toward organic compounds oxidation. Due to the production of oxygen, a significant decrease in current efficiency is expected at high current densities, which means that effective oxidation of pollutants at these anodes may occur at low current densities. On the other hand, at high O_2 overvoltage anodes, higher current densities may be applied with minimal contribution from the oxygen evolution side reaction and thus these anodes are usually the chosen ones for the EO process [14]. Among the most commonly used anodes in EO, BDD electrodes have been reported to yield the highest organic oxidation rates and the greatest current efficiencies [13]. In fact, this anode material presents extraordinary properties such as an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high O_2 evolution overvoltage [60,61].

A theoretical model to predict the COD and instantaneous current efficiency (ICE), during the electrochemical oxidation of organic pollutants on BDD electrodes in a batch recirculation system under galvanostatic conditions, was developed by Panizza *et al.* [62]. The model assumes that the rate of the electrochemical mineralization of the organic compounds, with electrogenerated OH radicals and/or direct electron transfer, is a fast reaction and it is controlled by mass transport of the organic compounds towards the anode. Under these conditions, the limiting current density, for the electrochemical incineration of organic pollutants can be given by Equation (2.31) [62]:

$$j_{lim} = 4 F k_m COD \quad (2.31)$$

where j_{lim} is the limiting current density, in $A m^{-2}$, F is Faraday constant, in $C mol^{-1}$, k_m is the mass transport coefficient in the electrochemical reactor, in $m s^{-1}$, and COD is the chemical oxygen demand, in $mol O_2 m^{-3}$. Depending on the applied current density, two different operating regimes can be identified [62]:

- $j < j_{lim}$

The electrolysis is under current control, the current efficiency is 100%, and the COD decreases linearly with time. At these conditions, the equation that describes the temporal evolution of COD can be obtained as follows:

$$\text{COD}(t) = \text{COD}_0 \left(1 - \frac{\alpha A k_m}{V} t \right) \quad (2.32)$$

where $\text{COD}(t)$ is the COD at electrolysis time t , in $\text{mol O}_2 \text{ m}^{-3}$, COD_0 is the COD before electrolysis, in $\text{mol O}_2 \text{ m}^{-3}$, $\alpha = j/j_{\text{lim}}^0$, being j the current density and j_{lim}^0 the initial limiting current density, A is the electrode area, in m^2 , V is the sample volume, in m^3 , and t is the electrolysis time, in s .

Replacing j by I/A , where I is the applied current intensity, in A , and j_{lim}^0 by $(4 F k_m \text{COD}_0)$, Equation (2.32) can be found:

$$\text{COD}(t) = \text{COD}_0 - \frac{I}{4 F V} t \quad (2.33)$$

This behavior persists until a critical time (t_{cr}), corresponding to the time at which the applied current density is equal to the limiting current density. At this time, the COD critical value can be calculated through Equation (2.34):

$$\text{COD}_{\text{cr}} = \alpha \text{COD}_0 = \frac{I}{4 A F k_m} \quad (2.34)$$

where COD_{cr} is the critical COD, in $\text{mol O}_2 \text{ m}^{-3}$.

Replacing Equation (2.34) in Equation (2.32), the critical time, in s , can be calculated by Equation (2.35):

$$t_{\text{cr}} = \frac{1 - \alpha}{\alpha} \frac{V}{A k_m} \quad (2.35)$$

- $j > j_{\text{lim}}$

The electrolysis is under mass transport control, secondary reactions (such as oxygen evolution) are involved, resulting in a decrease of current efficiency. Under these conditions, the COD removal, due to mass transport limitation, follows an exponential trend. At these conditions, the equation that describes the temporal evolution of COD can be obtained as follows:

$$\text{COD}(t) = \text{COD}_0 \exp \left[- \left(\frac{A k_m}{V} \right) t \right] \quad (2.36)$$

The ICE can be defined as:

$$ICE = \frac{j_{lim}}{j} = \frac{COD(t)}{\alpha COD_0} = 100 F V \left(\frac{COD(t) - COD_0}{8 I t} \right) \quad (2.37)$$

being the volume unit in L, COD_0 and COD units in $g L^{-1}$ and 8 the oxygen equivalent mass.

Despite this model [62] has shown excellent agreement with experimental results obtained in the electro-oxidation by BDD anodes of synthetic solutions of single organic compounds, it has also shown deviations when dealing with complex mixtures such as those found in landfill leachates, where the presence of electrogenerated secondary oxidants also contributes to the overall kinetics [13].

Application of the EO process to sanitary landfill leachates treatment has been reported by numerous authors [18,19,21,22,24,25,29,31-35,38-40,44,45,47,52,53]. A summary of the studies performed and of the main experimental conditions tested and respective results is presented in Table 2.2. As it can be seen there, several anode materials have been investigated for EO of sanitary landfill leachates, being BDD the most studied, followed by Ti/PbO₂, Ti/RuO₂-IrO₂ and graphite, among others.

Chiang *et al.* [18] applied four different anode materials to treat sanitary landfill leachates: graphite, Ti/PbO₂, binary oxide-coated titanium Ru-Ti oxide (DSA) and ternary Sn-Pd-Ru oxide coated titanium (SPR), and found that the best results for COD and ammonium removals were obtained in the following order SPR > DSA > Ti/PbO₂ > graphite. Also, authors found that chlorine/hypochlorite production efficiencies of these four anode materials followed the same order, indicating that indirect oxidation could be dominant in landfill leachates EO. The high removals obtained with SPR anode were attributed to the high current efficiency owned to its high electrocatalytic activity and high O₂ evolution overvoltage [18].

Cossu *et al.* [19] reported that no significant differences on COD and ammonium removals were found between Ti/PbO₂ and Ti/SnO₂ anodes. According to the authors, this happens because both materials have close oxygen evolution potentials. A comparison between Ti/Pt, PbO₂ and graphite anodes, applied to sanitary landfill leachates EO, showed that Ti/Pt anode allowed the highest COD, ammonium and colour removals [32]. More recently, studies comparing BDD and metallic oxides anodes were performed [52]. When BDD was compared with TiRuSnO₂ and PbO₂, results showed that whereas BDD yields complete COD, colour and ammonium removal, with PbO₂ a residual COD ($115 mg L^{-1}$) remained and, when TiRuSnO₂ was used, the organic pollutants were only partially oxidized, obtaining reductions of COD, colour and ammonium of 35%, 52% and 65%, respectively. Also, faster oxidation rate, higher current efficiency and lower specific energy consumption were achieved using the BDD anode, consequently, resulting in lower treatment costs [52].

From Table 2.2, it can be seen that BDD anodes were the most used in EO studies with sanitary landfill leachates. In a general way, the best results for the EO of the sanitary landfill leachates were attained using BDD anodes, being reached removals of 100% in COD and ammonium contents, although other anode materials presented very promising results.

EO experiments with landfill leachates have been conducted either at laboratory and pilot plant scale. Undivided cells with two-dimensional static parallel or cylindrical electrodes are generally used, operating in batch mode, with or without recirculation or with stirring. Alternatively, a three-dimensional electrode electrochemical reactor has been chosen by Zhang *et al.* [39] to provide larger electrode surface and higher mass transfer. Performances of two-dimensional and three-dimensional electrode electrochemical reactors were compared and results showed that, despite no significant differences were found in the COD removal, AN removal was higher in the three-dimensional electrochemical reactor. COD removals of 20.2 and 26.5% and AN removals of 57.7 and 81.1% were achieved for two-dimensional and three-dimensional electrochemical reactors, respectively, under the same experimental conditions [39]. Batch reactors with recirculation using parallel plate electrodes configuration are the most applied in sanitary landfill leachates treatment by EO, probably because is the simplest configuration and the one that allows an easier access to the exchange of the cell components.

Besides the anode material and the reactor design, there are other factors that influence the efficiency of the EO process. Current density plays an important role in the EO performance. In the literature revision compiled in Table 2.2, applied current densities ranged from 20 to 3000 A m⁻². Literature points to 50 A m⁻² as the minimum current density required to achieve an effective oxidation of organics, otherwise the leachate solution may become darker and brown precipitates may form at the anode surface under weak oxidative conditions [19]. Generally, an increase in current density increases COD and AN removals. Chiang *et al.* [18] reported that when current density increased from 500 to 1500 A m⁻² both COD and AN removals increased, although COD removal increased slightly while the AN removal increased sharply. According to the authors, this increase in the removals with current density was caused by the indirect oxidation effect of chlorine/hypochlorite, since their production was improved by increasing the operating current density. Additionally, Moraes and Bertazzoli [22] reported that colour removal also strongly depends on current density, being five times higher at 1160 A m⁻² than at 130 A m⁻². Similar results were described by other authors for COD and colour removals [31,32].

In a study performed by Anglada *et al.* [29], it was seen that an increase in current density from 300 to 450 A m⁻² scarcely affected the removal rate of the organic matter, but at higher current densities the oxidation levels increased with current density, which suggested a change in the oxidation mechanism of the organic matter, since at high current densities mediated electrochemical oxidation processes such as indirect oxidation by hydroxyl radicals

and by electrogenerated oxidants (from the oxidation of the electrolyte support) had a strong influence. Also, the influence of the applied current density was much more significant in the ammonium oxidation than in the case of COD removal, even if AN removal occurred at a slower rate than that of COD. Different results were achieved by Zhang *et al.* [39,45] that reported an increase in COD removal with the increasing current density, but only until a limit of current density value, from which a further increase would lead to a decrease of COD removal. This behaviour was explained by the authors taken into account that, at lower current densities, anodic organic matter oxidation with hydroxyl radicals was favoured against chlorine evolution at the anode and thus the increase in current density would lead to the increase in COD removal. Furthermore, an increase of current density would enhance chlorine generation and hence the anodic oxidation with hydroxyl radicals would be depressed. In the meantime, the AN removal would be dominant in the competition between AN and COD removal by the indirect oxidation and, consequently, COD removal efficiency would decrease with current density after the highest COD removal was achieved [39,45].

Regarding energy consumption, Anglada *et al.* [34,40] found that, despite an increase in current density led to a reduction in the electrolysis time needed to reach a set out value for ammonium and COD, an higher electrical charge is involved and thus a lower efficiency. The energy consumption required to reduce the concentration of COD from an average initial value of 860 mg L⁻¹ to 160 mg L⁻¹, increased from 50 W h (g COD)⁻¹ to 160 W h (g COD)⁻¹ when current density was increased from 300 A m⁻² to 1200 A m⁻² [34]. From the results reported above it can be inferred that an increase in current density does not necessarily results in an increase in the oxidation efficiency or oxidation rate and that, for a given anode material, the effect of the current density on the treatment efficiency depends on the characteristics of the effluent to be treated [13].

The effect of chloride ion concentration in EO efficiency of sanitary landfill leachates has also been widely studied. As can be seen on Table 2.2, adding extra Cl⁻ generally improves electrooxidation of landfill leachate, which is explained by the enhanced indirect oxidation through higher chlorine/hypochlorite production efficiency [18,19,24,25,44,47].

In order to clarify the indirect oxidation effect of chlorine/hypochlorite in EO treatment of landfill leachates, Chiang *et al.* [18] provided additional chloride ions to the leachate as the supporting electrolyte during the electrolysis. The experimental results showed that when 2500 mg L⁻¹ chloride was added, both COD and AN removals increased, being the AN removal much higher than that of COD. Identical study was performed with addition of sulphate instead of chloride and a negative effect in the EO was observed, since, according to the authors, the addition of sulphate suppresses the chlorine/hypochlorite production and consequently lowers the landfill leachate treatment efficiency. Different results were found by Cossu *et al.* [19] with no significant variation on the COD removal by the addition of 1600

and $3600 \text{ mg L}^{-1} \text{ Cl}^{-}$, maybe due to the different current density used, 50 A m^{-2} , which is much lower than the 1500 A m^{-2} used by Chiang *et al.* [18].

An exceptional increase in AN removal by addition of extra Cl^{-} was reported in different studies [24,25,47]. Pérez *et al.* [47] identified nitrogen and nitrate as the main products obtained from the oxidation of ammonium using a BDD anode and, for high chloride concentrations, nitrogen was the main product, having the percentage of ammonium transformed into nitrogen increased from 74 to 85% after 4 hours when the chloride content was increased from 5000 to 20000 mg L^{-1} , while for nitrate it was observed the opposite effect, varying from 26% when the chloride content was 5000 mg L^{-1} to 15% for 20000 mg L^{-1} of chloride. Also, the formation of chloramines, chlorate and perchlorate was hindered by the increasing concentration of chloride ions [47].

Although high chloride ion concentrations generally causes a higher pollutants removal and an improvement in the landfill leachates electro-oxidation efficiency, the typical Cl^{-} concentrations found in sanitary landfill leachates are not enough for effective indirect oxidation and the addition of an extra amount of Cl^{-} is often required, which may lead to the potential formation of chlorinated organic intermediate and hazardous organic compounds as final products [7]. Regarding energy consumptions, the use of high initial chloride concentrations reduce the energy consumed (Table 2.2), mainly due to an increase in the conductivity, which leads to lower cell potentials [44,47].

Although the EO process is not yet fully optimized for sanitary landfill leachates treatment and there are some aspects that need further investigation and clarification, there is no doubt that EO is a technically feasible alternative to eliminate the organic pollutants from leachates. Total COD, colour and ammonium removals were already reported in the EO treatment of sanitary landfill leachates.

Table 2.2 - EO studies performed with sanitary landfill leachates: conditions used and main results obtained.

Anode material	Applied intensity or current density	Volume treated / L	Flow rate / L h ⁻¹	Electrolysis time / h	COD ₀ / mg L ⁻¹	AN ₀ / mg L ⁻¹	[Cl ⁻] ₀ / mg L ⁻¹	COD removal / %	AN removal / %	Energy consumption	Ref.
Graphite	750 A m ⁻²	0.6	NA	4	4550 ⁽¹⁾	2550 ⁽¹⁾	2500	21	11	NS	[18]
Ti/PbO ₂							5000	34 ⁽¹⁾	44 ⁽¹⁾		
DSA							2500	29	36		
SPR	500 A m ⁻²						5000	27 ⁽¹⁾	38 ⁽¹⁾		
	750 A m ⁻²						2500	30	38		
							5000	35 ⁽¹⁾	57 ⁽¹⁾		
	1500 A m ⁻²							38 ⁽¹⁾	80 ⁽¹⁾		
							10000	92	100 ⁽¹⁾		
Ti/PbO ₂ and Ti/SnO ₂	20 to 400 A m ⁻²	0.3	1.1 to 5.4	NS	1200	380	1600 and 3600	NS	NS	NS	[19]
Pt/Ti	100 A	5	2400	2.5	53300	1094	3500	84 ⁽¹⁾	100	40 W h (g COD) ⁻¹ ₍₁₎	[21]
Ti/TiO ₂ -RuO ₂	480 A m ⁻²	13.5	2000	3	1790	1380	2560	33	NS	NS	[22]
	1160 A m ⁻²				1855	1060	2800	73	49		
BDD	150 A m ⁻²	1	660	8	773	487	1900	100	100	NS	[24, 25]
	300 A m ⁻²			4	1030 ⁽¹⁾	742 ⁽¹⁾	1420	88 ⁽¹⁾	35 ⁽¹⁾		
							3670	86 ⁽¹⁾	70 ⁽¹⁾		
							8570	86 ⁽¹⁾	95 ⁽¹⁾		
	900 A m ⁻²			6	3800	1710	2760	100	100		
BDD	300 A m ⁻²	230	18000	4	1000	783	1640	60 ⁽¹⁾	25 ⁽¹⁾	NS	[29]
	600 A m ⁻²							82 ⁽¹⁾	50 ⁽¹⁾		
	1200 A m ⁻²							100 ⁽¹⁾	85 ⁽¹⁾		

(1) Value obtained indirectly from data presented in the paper or from a figure; NA - Not Applied; NS - Not Specified.

Table 2.2 - (cont.)

Anode material	Applied intensity or current density	Volume treated / L	Flow rate / L h ⁻¹	Electrolysis time / h	COD ₀ / mg L ⁻¹	AN ₀ / mg L ⁻¹	[Cl ⁻] ₀ / mg L ⁻¹	COD removal / %	AN removal / %	Energy consumption	Ref.
Graphite carbon	400 A m ⁻²	0.5	NA	4	1870	NS	NS	38	NS	NS	[31]
	600 A m ⁻²							57			
	800 A m ⁻²							65			
								70			
Ti/Pt	50 A m ⁻²	0.25	NA	1	2750	408	5500	23 ⁽¹⁾	NS	NS	[32]
	150 A m ⁻²							40 ⁽¹⁾			
	400 A m ⁻²							63			
PbO ₂								30	58		
Graphite								22	45		
BDD	2143 A m ^{-2 (1)}	10	1200	6	444	NS	NS	90 ⁽¹⁾	NS	NS	[33]
	3000 A m ^{-2 (1)}							90 ⁽¹⁾			
BDD	300 A m ⁻²	1	660	NS	1370	950	2042	82 ⁽¹⁾	70	60 W h (g COD) ⁻¹	[34]
		250	18000		860	780	1630	50 W h (g COD) ⁻¹			
	1200 A m ⁻²	1	660	1370	950	2042	155 W h (g COD) ⁻¹				
		250	18000	860	780	1630	160 W h (g COD) ⁻¹				
BDD	450 A m ⁻²	1	660	8	1100	970	1717 ⁽¹⁾	90 ⁽¹⁾	93 ⁽¹⁾	NS	[35]
		250	18000					100 ⁽¹⁾	100 ⁽¹⁾	94 W h (g COD) ⁻¹	
Ti/PbO ₂	0.5 A	0.35	420	4	780	NS	1800	42 ⁽¹⁾	NS	NS	[38]
	2 A		50					65 ⁽¹⁾			
			420					68 ⁽¹⁾			
	3 A		NS					80			
	4	81 ⁽¹⁾	NS								

(1) Value obtained indirectly from data presented in the paper or from a figure; NA - Not Applied; NS - Not Specified.

Table 2.2 - (cont.)

Anode material	Applied intensity or current density	Volume treated / L	Flow rate / L h ⁻¹	Electrolysis time / h	COD ₀ / mg L ⁻¹	AN ₀ / mg L ⁻¹	[Cl ⁻] ₀ / mg L ⁻¹	COD removal / %	AN removal / %	Energy consumption	Ref.
Ti/RuO ₂ -IrO ₂	300 A m ⁻² 900 A m ⁻²	0.8	NA	NS	3782	3143	3702	20 10	35 85	NS	[39]
BDD	1200 A m ⁻² ⁽¹⁾ 1714 A m ⁻² ⁽¹⁾ 2571 A m ⁻² ⁽¹⁾	10	600	8	3385	1235	2574	30 ⁽¹⁾ 35 ⁽¹⁾ 50 ⁽¹⁾	19 ⁽¹⁾ 21 ⁽¹⁾ 30 ⁽¹⁾	98 kW h m ⁻³ 190 kW h m ⁻³ 360 kW h m ⁻³	[40]
Ti/IrO ₂ -RuO ₂	80 A m ⁻² 160 A m ⁻² 320 A m ⁻²	0.12	NA	4	2960	14	6150 9695 ⁽¹⁾	20 ⁽¹⁾ 40 ⁽¹⁾ 35 ⁽¹⁾ 75 ⁽¹⁾	NS NS	NS NS 79 W h (g COD) ⁻¹ 20 W h (g COD) ⁻¹	[44]
Ti/RuO ₂ -IrO ₂	260 A m ⁻² 680 A m ⁻²	0.2	NA	1.5	560	520	831	44 66	50 98	NS	[45]
BDD	400 A m ⁻² 600 A m ⁻²	1	600	6 4 6	2863	1000	1200 5000 10000 1200	NS NS	60 100 100 65	NS 104 kW h m ⁻³ 39 kW h m ⁻³ NS	[47]
BDD	400 A m ⁻² ⁽¹⁾	0.35	420	2.5	780	266	1800	95	100	82 kW h m ⁻³	[52]
PbO ₂				4				68 ⁽¹⁾	100	130 kW h m ⁻³ ⁽¹⁾	
TiRuSnO ₂				8				35	65	150 kW h m ⁻³ ⁽¹⁾	
BDD	900 A m ⁻²	1	660	3	2055 ⁽¹⁾	928 ⁽¹⁾	2280 ⁽¹⁾	90	NS	NS	[53]

(1) Value obtained indirectly from data presented in the paper or from a figure; NA - Not Applied; NS - Not Specified.

Chapter 3

Materials and methods

This chapter presents the characterization of the samples studied in this work and describes the type of electrochemical cells used in the experimental assays. A brief description of the analytical methods used to follow the electrochemical assays is also presented.

3.1 Leachates characterization

The landfill leachates used in this work were collected in three landfill sites, located in different regions of Portugal, and managed by the companies Resistrela, Amarsul and Tratolixo.

The intermunicipal sanitary landfill facility managed by Resistrela serves a population of 200,000 inhabitants in thirteen municipalities, with an area of 6132 km², mostly rural, located in the interior of the country. This landfill site, with a capacity of 1,755,000 m³, divided in 3 cells, has been filled since 2001, being one of the cells sealed since 2009. The produced leachates in this landfill facility fit the category of young/medium age stage. The onsite leachate treatment facility is capable of processing daily up to 47 m³ of leachate. The *in situ* treatment comprises a biological step (nitrification and denitrification process), followed by an ultrafiltration operation. The samples used in this work were collected in the stabilization lagoon, before the biological treatment, and at the entrance of the ultrafiltration operation.

Amarsul is responsible for the municipal solid wastes from the nine municipalities of Setubal peninsula, covering an area of 1421 km², and serving a population of over 800,000 inhabitants. Their infrastructures include two sanitary landfills, one located in Seixal and another in Palmela. The samples used in this work were collected at Palmela sanitary landfill. This landfill site, initiated in 1997, has an area of 1 km² divided in 7 cells, being 6 of them sealed since 2012. Approximately 250 m³ of leachate are daily produced at this landfill facility (average value), being considered as a medium age leachate. Samples were collected in the stabilization lagoon, before being submitted to any treatment.

Tratolixo manages the solid wastes produced in the urban municipalities of Sintra, Oeiras, Cascais and Mafra, located near the coast, which include more than 750,000 inhabitants in an

area of 460 km². Leachate samples used in this work were from Trajouce sanitary landfill, a sealed landfill since 2003, with an area of approximately 7 hectares. The samples were collected in the stabilization lagoon, before any kind of treatment.

After collected, the samples were kept refrigerated until their use, in order to maintain its initial characteristics. Samples characterization was performed just after the collection and just before their use in experiments and no significant difference on the parameter values was found.

Table 3.1 presents the characterization of the different leachates samples collected (mean value \pm standard deviation). The mean values are the results obtained in at least five determinations performed for each parameter. As expected, the leachates collected from the different sanitary landfill sites presented very distinct properties mainly due to the age of the landfill, the type of wastes disposed and the climatic conditions.

Comparing the different samples that came from Resistrela, big differences were found between the samples collected at the same collection point but in different dates. Such a difference was not expected, especially among samples collected in analogous seasons, like for example samples B/F and C/G. Nevertheless, there are two reasonable explanations to justify these disparities. The first one is the climatic conditions, since the summer of 2011 was very hot and lasted until mid-November, with almost no rainfall, which caused the concentration of the leachate. The other reason is related to an existing composting station operated by Resistrela. During its regular functioning, organic wastes are triaged and routed to the composting process, meaning that a big part of the organic wastes does not go to landfilling. However, there was a malfunction occurred since August 2011, and the composting station was closed until being repaired one year later, and during that year the organic wastes were deposited on the landfill and, consequently, the organic load of the produced leachate increased. Although this was an unexpected situation, it reflects the reality of hundreds of landfill sites all over the world and gave the opportunity to study the application of the electrochemical treatments to a wider range of leachate compositions.

Another fact that is obvious from the analysis of Table 3.1 is that leachate I clearly came from an old sanitary landfill site, since it presents all the characteristics of a very recalcitrant wastewater.

Table 3.1 - Characterization of the leachate samples used in this work.

	A	B	C	D	E	F	G	H	I
Landfill site	Resistrela	Resistrela	Resistrela	Resistrela	Amarsul	Resistrela	Resistrela	Resistrela	Tratolixo
Pre-treatment	Biological nitrification/denitrification	No	Biological nitrification/denitrification	No	No	No	Biological nitrification/denitrification	Biological nitrification/denitrification	No
Collecting date	March 2011	October 2011	October 2011	February 2012	June 2012	October 2012	October 2012	April 2013	December 2013
COD / g L ⁻¹	5.8 ± 0.1	12.6 ± 0.9	11.6 ± 0.2	17.6 ± 0.7	8.9 ± 0.8	21.7 ± 0.5	8.4 ± 0.7	6.2 ± 0.4	3.6 ± 0.2
BOD ₅ / g L ⁻¹	-	-	-	-	1.3 ± 0.3	6.5 ± 0.5	0.37 ± 0.08	0.80 ± 0.09	0.96 ± 0.08
BOD ₅ /COD	-	-	-	-	0.15 ± 0.05	0.30 ± 0.03	0.04 ± 0.02	0.13 ± 0.02	0.27 ± 0.01
DOC / g L ⁻¹	0.83 ± 0.08	2.88 ± 0.07	1.83 ± 0.03	7.3 ± 0.5	3.5 ± 0.4	8.5 ± 0.2	2.5 ± 0.3	2.06 ± 0.02	1.0 ± 0.1
TN / g L ⁻¹	-	-	-	2.9 ± 0.2	2.8 ± 0.2	2.1 ± 0.1	0.66 ± 0.04	0.82 ± 0.09	2.1 ± 0.3
TKN / g L ⁻¹	1.47 ± 0.02	-	-	-	2.4 ± 0.2	2.0 ± 0.1	-	0.78 ± 0.06	1.9 ± 0.1
AN / g L ⁻¹	1.21 ± 0.05	-	-	-	2.2 ± 0.3	1.2 ± 0.1	-	0.48 ± 0.08	1.68 ± 0.08
Nitrate / g L ⁻¹	-	-	-	-	-	-	-	0.08 ± 0.01	ND
Nitrite / g L ⁻¹	-	-	-	-	-	-	-	0.30 ± 0.07	ND
Chloride / g L ⁻¹	4.4 ± 0.4	-	-	-	4.5 ± 0.3	4.4 ± 0.1	-	4.7 ± 0.2	2.5 ± 0.2
Suspended Solids / g L ⁻¹	1.77 ± 0.04	0.7 ± 0.1	2.4 ± 0.3	1.15 ± 0.07	0.7 ± 0.1	-	1.7 ± 0.2	-	-
Dissolved Solids / g L ⁻¹	20.9 ± 0.2	19.6 ± 0.5	24.3 ± 0.9	22.7 ± 0.5	16.6 ± 0.1	-	24.5 ± 0.2	-	-
pH	8.4 ± 0.4	8.6 ± 0.3	7.8 ± 0.6	8.4 ± 0.2	8.3 ± 0.2	8.5 ± 0.1	8.5 ± 0.1	9.0 ± 0.1	8.12 ± 0.04
Conductivity / mS cm ⁻¹	22.1 ± 0.1	29.9 ± 0.4	24.0 ± 0.3	29.4 ± 0.8	29.1 ± 1.0	36.1 ± 0.4	25 ± 1	22.0 ± 1.2	22.0 ± 0.4

DOC - Dissolved organic carbon

ND - No detectable

3.2 Electrochemical experiments

All the electrochemical experiments performed during this work were conducted in batch mode using two electrodes placed vertically and parallel to each other. EO assays were run either at laboratory scale, using a stirred or a recirculated cell, or at semi-pilot scale with recirculation. EC experiments were conducted only at laboratory scale, with and without stirring. Figure 3.1 shows the schematic description and the images of the different electrochemical cells used.

The performed experiments were grouped in four main parts, according to the goals proposed, being these main parts divided into case studies, in agreement with the outlined strategy.

Part 1: Application of EO as a post treatment

Case study 1 - Application of EO to a biologically treated leachate: Laboratory scale stirred reactor

Case study 2 - Application of EO to a biologically treated leachate: Semi-pilot plant with recirculation

Part 2: Application of EO to treat raw leachates

Case study 3 - Application of EO to raw leachates: Stirred reactor vs. feed-recirculated reactor

Case study 4 - Application of EO to a raw leachate: Semi-pilot plant with recirculation

Part 3: Use of EC and EO integrated process in the leachate treatment

Case study 5 - Use of EC and EO integrated process in the leachate treatment: EC/EO integrated process as pre-treatment vs. polishing step

Case study 6 - Use of EC and EO integrated process in the leachate treatment: Biodegradability enhancement by EC/EO integrated process

Part 4: Application of Ti/Pt/PbO₂ anodes for the EO of leachates

Case study 7 - Ti/Pt/PbO₂ vs. BDD anode for the EO treatment of a biologically pre-treated sanitary landfill leachate and simulated samples

Case study 8 - Ti/Pt/PbO₂ vs. BDD anode for the EO of leachates and simulated samples: Influence of current density and chloride concentration

In Table 3.2 a compilation of the experimental setups characteristics and of the main operational conditions used in each case study is presented.

BDD anodes used in EO electrochemical cells I and II (Figure 3.1) were purchased from CSEM, now NeoCoat. Setup III (EO semi-pilot plant) was equipped with a single compartment electrochemical cell, BDD DiaCell 100, manufactured by Adamant. Ti/Pt/PbO₂ anodes used in Case studies 7 and 8 were previously prepared at the laboratory according to literature [63].

A GW, Lab DC, model GPS-3030D (0-30 V, 0-3 A) was used as power supply in EO and EC laboratory scale experiments, except in Case study 7 where a Multimetrix XA 3033 unit was used. In the semi-pilot scale experiments a DiaCell-PS1500 power supply, with automatic polarity reversal, was used. In these assays automatic polarity reversal occurred every minute.

Samples recirculation in the laboratory scale experiments was enabled by a centrifugal pump, Pan World Magnet, Model: NH-30PX, Pan World Co., Ltd. Tokyo, Japan. At the semi-pilot plant, for the assays run with 5 L of leachate sample, a peristaltic pump with a 280 rpm 24 V DC induction gearmotor, from Williamson Manufacturing Company Ltd, UK, was used. For the assays performed with 10 and 15 L, the recirculation was enabled by a centrifugal pump, with a maximum flow of 5 m³ h⁻¹ and a maximum height of 22 m, from Wilo, Germany.

All experiments were run at least twice. Samples were collected regularly during the assays, to perform the analytical determinations.

Between experiments, EO cells were cleaned with a NaCl solution 0.1 M, for 10 min, using an applied current density of 500 A m⁻², and rinsed well, after that, with distilled water. EC electrodes were just washed, first with tap water and then with distilled water.

All the reagents used were analytical grade and were purchased from Sigma Aldrich and used without additional purification.

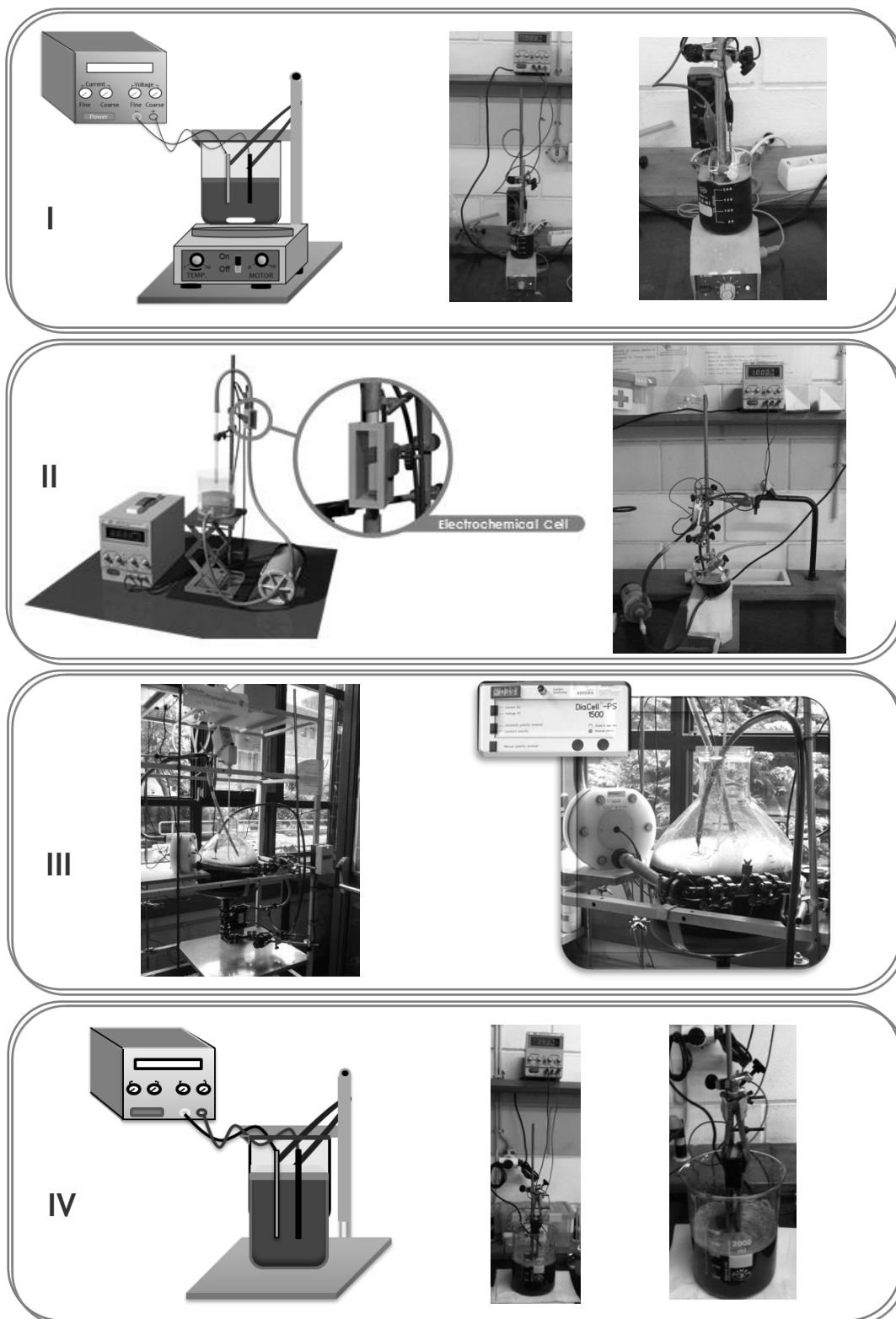


Figure 3.1 - Setups and images of the electrochemical cells used: I - Laboratory scale EO or EC with stirring; II - Laboratory scale EO with recirculation; III - Semi-pilot scale EO with recirculation; IV - Laboratory scale EC.

Table 3.2 - Reactors characteristics and operational conditions used.

Case study	1	2	3		4	5		6		7	8	
Process	EO	EO	EO		EO	EC	EO	EC	EO	EO		
Leachate sample	A	G	E		E	B, C	B, C	D	F	F	H	I
Cell configuration	I	III	I	II	III	I, IV	I	I, IV	IV	II	I	
Sample volume / L	0.2	10	0.2	0.2	5-15	0.15, 0.45	0.2	0.5	0.2	0.2		
Anode/cathode material	BDD/SS	BDD/BDD	BDD/SS		BDD/BDD	Fe/SS	BDD/SS	Fe/Fe	BDD/SS	BDD/SS Ti/Pt/PbO ₂ / SS		
Anode/cathode area / cm ²	10/10	70/70	10/10	20/20	70/70	20/16	20/20	40/40	20/20	10/10		
Inter-electrode distance / cm	2	0.5	2	1	0.5	2.3	2	1	1	2		
Flow rate or Stirring speed	100 rpm	360,500 L h ⁻¹	100 rpm	75 L h ⁻¹	100-950 L h ⁻¹	0, 600 rpm	100 rpm	0, 100 rpm	-	75 L h ⁻¹	100 rpm	
I or V	0.05-0.7 A	7-21 A	0.3-1 A	0.6-2 A	3.5-14 A	4-6 V	0.2-0.6 A	2.5 A	0.6-1.4 A	0.3 A	0.3-0.7 A	

SS - Stainless steel

3.3 Analytical methods

Several parameters were used to characterize the leachate samples and to follow the electrochemical experiments, namely COD, BOD₅, DOC, TN, TKN, AN, pH, conductivity (Cond.), suspended solids, dissolved solids (DS) and UV-visible (UV-vis) absorption spectrophotometry. Also, chloride, nitrate, nitrite and ammonium concentrations were determined by ion chromatography (HPLC) and iron, chromium and zinc concentrations by flame atomic absorption spectrometry (FAAS). In subsections below, a brief description of the analytical methods and equipments used to determine each parameter is presented.

3.3.1 Chemical oxygen demand

The COD is commonly used to indirectly measure the amount of organic matter in samples and to evaluate the performance of the oxidation treatment in these samples. It represents the measure of the oxygen equivalent to the organic matter content in the sample, susceptible of being oxidized by a strong oxidant. The COD values are expressed in terms of oxygen concentration. The basis for the COD determination methods is that nearly all carbon content of the organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions.

In this work, COD was determined by closed reflux titrimetric method, following the procedure described in Section 5220C of Standard Methods [64]. Dichromate ion is the specified oxidant used in this method, being reduced to the chromic ion. In COD determinations, digestion of the samples occurred in strongly acid solution with a known quantity of potassium dichromate that has to be in excess, and containing also a silver catalyst to oxidize resistant organic compounds and mercury sulphate to reduce interferences from the oxidation of chloride ions. The samples closed reflux digestion was performed, using a thermoreactor Merck Spectroquant TR 420, during 2 h at 150 °C. After digestion, the remaining unreduced K₂Cr₂O₇ was titrated with ferrous ammonium sulphate, using ferroine as indicator, to determine the amount of K₂Cr₂O₇ consumed. The titration was performed using an automatic titrator Metrohm 876 Dosimat Plus. The dichromate consumed by the sample is equivalent to the amount of oxygen required to oxidize the organic matter.

3.3.2 Biochemical oxygen demand

The BOD is defined as the amount of oxygen required for microbial metabolism of organic matter dissolved in samples. Its function is similar to that of COD, since both measure the amount of organic compounds present in waters and wastewaters. However, COD is less

specific, since it measures everything that can be chemically oxidized, and the BOD evaluate biologically active organic matter. Biochemical oxygen demand determination occurs over some variable period of time depending on temperature, nutrient concentrations, and the enzymes available to indigenous microbial populations. This is not a precise quantitative test, although it is widely used as an index of the biodegradable organic matter present in a wastewater, being an important parameter to evaluate the quality of wastewaters' treatment results.

BOD determination is a slow process that theoretically requires an infinite time to be completed. To overcome this drawback, it is determined the BOD₅, which corresponds to an incubation period of 5 days at which about 60-70% of reaction has occurred. It is also used the BOD₂₀, that corresponds to an incubation period of 20 days in which 95-99% of organic matter has already been degraded.

In this work, BOD₅ was determined by the respirometric method, following the procedure described in Section 5210D of Standard Methods [64], which provided the direct measurement of the oxygen consumed by microorganisms from an air enriched environment, in a closed vessel, under conditions of constant temperature (20±1 °C) and stirring. Manometric respirometers were used, which relate oxygen uptake to the change in pressure caused by oxygen consumption while maintaining a constant volume. The assays were performed in a WTW Oxitop IS 12 Inductive Stirring System, in a WTW TS 606-G/2-i Thermostat Cabinet, using lyophilized biomass PolySeed, commercially available.

3.3.3 Dissolved organic carbon

The total organic carbon is the amount of organic carbon in the samples, expressed in concentration of carbon. Unlike COD or BOD₅, TOC is independent of the oxidation state of the organic matter. It is a global parameter that allows the evaluation of the mineralization efficiency of the leachate treatment. In the present work, it was measured DOC, which is the fraction of TOC that passes through a 0.45 µm pore-diameter filter.

DOC was determined by the high-temperature combustion method, following the procedure described in Section 5310B of Standard Methods [64]. Its value is not achieved by direct measurement, the method used in this work analyses separately the dissolved fractions of total carbon (DC) and inorganic carbon (DIC), and DOC is then determined by subtracting DIC from DC.

The DOC determinations were performed in a Shimadzu TOC-VCPH analyser, which combines combustion catalytic oxidation at 680 °C and non-dispersive infrared (NDIR) detection method. The samples were filtered through a glass fiber filter, from Whatman (GF/F filter, 0.45 µm).

For the DC determinations an automated process injected the sample into the combustion furnace, where it undergoes combustion through heating at 680 °C, with a platinum catalyst in an oxygen rich atmosphere. The water is vaporized and the organic and inorganic carbons are oxidized to CO₂ and H₂O. The gas phase, containing the CO₂, is transported in the carrier gas through a moisture trap and halide scrubbers, to remove water vapour and halides from the gas stream before it reaches the detector. The CO₂ generated concentration is then measured with non-dispersive infrared detector. DIC is measured separately by injecting the sample into a reaction chamber where it is acidified, and all inorganic carbon is converted to CO₂, which is carried to the detector and measured. The obtained DIC or DC values are the average of, at least, two measurements. Regularly, calibration curves are performed with potassium hydrogenophthalate solutions.

3.3.4 Total nitrogen

The total nitrogen determination accounts for all forms of organic and inorganic nitrogen present in the leachate sample. Since before TN determinations samples are filtered through a GF/F Whatman filter, 0.45 µm, it is assumed that, in complex matrix samples as sanitary landfill leachates, TN stands for total dissolved nitrogen.

TN was measured in a Shimadzu TNM-1 unit coupled with the TOC-VCPH analyser. All nitrogen present in samples is first converted to nitrogen monoxide and nitrogen dioxide by catalytic combustion in the furnace. The nitrogen species are then reacted with ozone, to form an excited state of nitrogen dioxide. Upon returning to ground state, the emitted light energy is measured, using a chemiluminescence detector, and converted to TN.

3.3.5 Total Kjeldahl nitrogen and ammonia nitrogen

TKN measures the sum of organic nitrogen, ammonia and ammonium. It is determined using the Kjeldahl method that determines all the nitrogen in the trinegative state present in the samples. This method fails to account for nitrogen in the form of azide, azine, azo, hydrazine, nitrate, nitrite, etc.

TKN determinations followed the procedure described in Section 4500-Norg B of Standard Methods [64], and as equipment it was used a Kjeldatherm block-digestion-system and a Vapodest 20 s distillation system, both from Gerhardt, and an automatic titrator Metrohm 876 Dosimat Plus.

The method to determine TKN consists of heating the sample with sulphuric acid, which decomposes the organic substance by oxidation to liberate the reduced nitrogen as

ammonium sulphate. In this step, potassium sulphate is added to increase the boiling point of the medium and cupric sulphate is used as catalyst. After samples digestion, a small quantity of sodium hydroxide is added and the resulting ammonia solution is distilled from an alkaline medium, after adding a boric acid solution in the presence of a mixture of indicators (methyl red and methylene blue). The ammonia present in the sample, corresponding to the amount of nitrogen contained in the initial sample, reacts with the boric acid, and is determined indirectly by the titration of the borate ion formed with a H_2SO_4 standard solution.

The determination of ammonia nitrogen followed the procedure described in Section 4500- NH_3 B and Section 4500- NH_3 C of Standard Methods [64], using the same distillation and titration systems used to determine TKN. The determination of ammonia nitrogen is similar to the determination of Kjeldahl nitrogen, although in this case the sample does not undergo digestion. For AN determinations, samples were buffered at pH 9.5 using a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds. Then, they were distilled into a boric acid solution, containing the mixture of indicators used in TKN determination, and titrated with a standard H_2SO_4 0.2 N solution.

3.3.6 Suspended and dissolved solids

Suspended solids refer to small solid particles which remain in suspension in water as a colloid or due to the motion of the water. According to Standard Methods definition, suspended solids are the portion of solids retained when a solution passes through a filter of 2.0 μm pore size or smaller [64]. Suspended solids are important, since pollutants and pathogens are carried on the surface of those particles. The smaller the particle size, the greater the total surface area per unit mass of particle, and so the higher the pollutant load that is likely to be carried.

Suspended solids determination followed the procedure described in Section 2540 D of Standard Methods [64]. In this method, a well-mixed sample is filtered through a weighted standard glass-fiber filter (Whatman GF/F filter, 0.45 μm) and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the suspended solids.

Dissolved solids are a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal) suspended form. According to Standard Methods definition, solids must be small enough to be retained in a filter with 2.0 μm (nominal size, or smaller) pores [64].

Dissolved solids determination followed the procedure described in Section 2540 C of Standard Methods [64]. In this method, a well-mixed sample is filtered through a weighted

standard glass-fiber filter (Whatman GF/F filter, 0.45 μm) under vacuum. 10 mL of the filtrate are placed in a previously weighted crucible and dried in an oven, at 103 to 105 $^{\circ}\text{C}$, until constant weight. The increase in weight of the crucible represents the filtered solids.

3.3.7 Ion chromatography

Ion chromatography is a process that allows the separation of ions based on their affinity to the ion exchanger. The basic process of ion chromatography can be represented in four steps: eluent loading to equilibrate the column, sample injection, separation of sample, and elution of the analyte. Elution is the process by which the compound of interest is moved through the column. This happens because the eluent is constantly pumped through the column. Ion chromatography retains the analyte ions on the column based on coulombic interactions. The stationary phase surface displays ionic functional groups that interact with analyte ions of opposite charge. As the sample elutes through the column, the analyte ions interact differently with the stationary phase. The affinity of the ions present in the sample with the stationary phase depends primarily on the ion charge and radius.

In this work, ion chromatography was used in the determination of Cl^- , NO_3^- , NO_2^- and NH_4^+ ions. It was performed using a Shimadzu 10Avp HPLC apparatus coupled with a Shimadzu CDD 10Avp conductivity detector. Anions were separated using an IC I-524A Shodex (4.6 mm ID \times 100 mm) column at 40 $^{\circ}\text{C}$. The elution was performed in isocratic mode using an aqueous solution of 2.5 mM of phthalic acid and 2.3 mM of tris(hydroxymethyl)aminomethane as a mobile phase at a flow rate of 1.5 mL min^{-1} . For the determination of the NH_4^+ , an IC YK-A Shodex (4.6 mm ID \times 100 mm) column at 40 $^{\circ}\text{C}$ was used. The isocratic elution mode was used and the mobile phase was a 5.0 mM tartaric acid, 1.0 mM dipicolinic acid and 24 mM boric acid aqueous solution at a flow rate of 1.0 mL min^{-1} . For both analyses, the sample volume injected was 20 μL . The retention time of the ions determined were the following: Cl^- - 2.32 min; NO_3^- - 3.89 min, NO_2^- - 2.78 min and NH_4^+ - 5.13 min. The concentrations of the different ions were determined using calibration curves, prepared with standard solutions.

3.3.8 Flame atomic absorption spectrometry

Flame atomic absorption spectrometry is a very common technique for detecting metals and metalloids in environmental samples. It is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Flame atomic absorption requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases, such as acetylene and air or acetylene and nitrous oxide. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800 $^{\circ}\text{C}$. The

characteristic wavelengths are element specific and accurate to 0.01-0.1 nm. To provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. A device such as photomultiplier can detect the amount of reduction of the light intensity due to absorption by the analyte, and this can be directly related to the amount of the element in the sample. During combustion, atoms of the element of interest in the sample are reduced to free, unexcited ground state atoms, which absorb light at characteristic wavelengths.

The determination of the total content of metals in leachate samples by FAAS involves the solubilisation of the elements to be analyzed. Thus, the analytical procedure for the determination of metals in the samples includes two distinct stages: (i) dissolution or digestion of the sample and (ii) instrumental analysis by FAAS.

Before performing flame atomic absorption analyses, the samples were subjected to an attack/treatment consisting in the acid digestion of the sample, using a mixture of HNO₃-HCl, based on the procedure 3030F described in Standard Methods [64].

In this work, the absorbance of the leachate samples, that previously underwent acid digestion, were measured, to monitor Cr, Fe and Zn. Operating conditions for the analysis of these elements are shown in Table 3.3.

Table 3.3 - Operational conditions for FAAS analyses.

Element	Wavelength / nm	Slit	Flame	Burner height
Chromium	357.9	0.5	Air / Acetylene *	3
Iron	248.3	0.5	Air / Acetylene	6
Zinc	213.9	0.5	Air / Acetylene	6

* Oxygen-rich flame

Iron, chromium and zinc determinations by flame atomic absorption followed the procedure described in Section 3111 B of Standard Methods [64], using a Perkin Elmer apparatus and Perkin Elmer hollow cathode lamps. To determine the total content of metals, the method of external standards was used to plot the calibration curve. The standards were prepared by dilution of 1000 ppm commercial solutions, with addition of 0.01 M nitric acid.

3.3.9 Other parameters

- pH

In this work, the pH of the samples, thermostatised at 20 °C, was measured using a pH meter HANNA (HI 931400).

- Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, on their total concentration and mobility, and on the temperature. In this work, samples conductivity was measured using a conductivity meter Mettler Toledo (SevenEasy S30K). Before measurement samples were kept at 20 °C.

- UV-vis absorption spectrophotometry

UV-vis absorption spectrophotometry uses light in the visible and adjacent (near-UV and near-infrared) ranges. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. According to Beer-Lambert law, the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV-vis absorption spectrophotometry can be used to determine the concentration of the absorber in a solution.

In this work, UV-vis absorbance was measured from 200 to 800 nm using a Shimatzu UV-1800 spectrophotometer. The method was used to determine the variation of the content in aromatic compounds during the electrodegradation assays.

Chapter 4

Application of EO as a post treatment

With the aim of evaluate the feasibility of an electrochemical oxidation treatment applied as a polishing step, assays at bench and semi-pilot scales were performed. These assays were divided into two case studies, Case study 1 and Case study 2, as defined in Chapter 3. A description of the experimental conditions used and the results obtained in these studies is presented in this chapter.

4.1 Case study 1

Application of EO to a biologically treated leachate: Laboratory scale stirred reactor

In this study, the effect of initial pollutants concentration on the EO efficiency was investigated. With that purpose, EO assays were performed using samples of the biologically pre-treated leachate (1:1) and several dilutions of this wastewater, between 1:2 and 1:16, being the dilution expressed as volumes of the raw leachate:total volume of the sample. Also, different current densities were tested, between 50 and 700 A m⁻². In Table 4.1 the different experimental conditions tested in this study are summarized.

Table 4.1 - Experimental conditions tested in Case study 1 assays.

Leachate dilution	1:1	1:2	1:4	1:8	1:16
	50				
	150				200
Applied current density / A m ⁻²	300	300	300	300	300
	400				400
	500				700

All the assays were performed in a double-wall cell that enabled the recirculation of water from a thermostatic bath, set to 25 °C. The biologically pre-treated leachate used in this

study, Sample A, is characterized in Table 3.1. In those experiments in which leachate samples were further diluted (1:8 and 1:16), the conductivity of the mixture was not enough to allow the regular progress of the electrochemical degradation, since for the same applied current density a huge increase in potential difference was observed. This way, a supporting electrolyte, 0.03 M sodium sulphate, was added in those experiments. The electrolysis duration was 6 hours.

Figure 4.1 presents the results of the COD variation with time for these electrodegradation assays. For 1:1, 1:2 and 1:4 dilutions, it can be observed a regular linear decay, typical of an electrochemical reaction controlled by current. For higher dilutions a different behaviour is observed, since at least part of the assay is controlled by the diffusion of the species undergoing degradation towards the electrode surface.

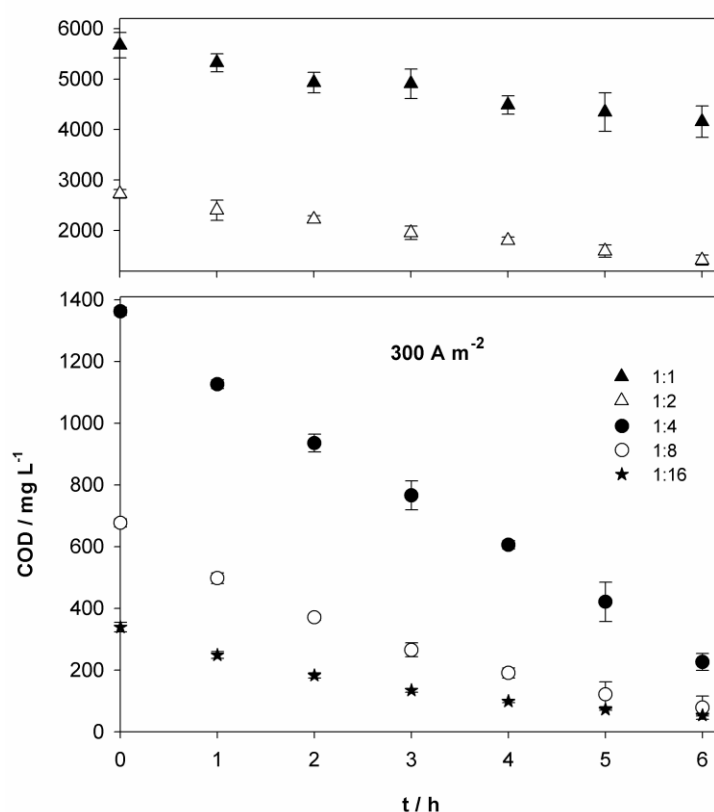


Figure 4.1 - Variation of COD with time for the electrodegradation assays performed without dilution and with different initial dilutions of the biologically pre-treated leachate, at a current density of 300 A m^{-2} . Error bars refer to the standard deviation of the COD mean values.

Figure 4.2 shows the DOC results for the assays, which COD are presented in Figure 4.1. During the first 2 h, a slight increase of the DOC values can be observed for almost all solutions. Only the most diluted solution presents an expected behaviour, i.e., a regular decrease with time. Two possible explanations for the initial increase in DOC were found: (a) some of the inorganic carbon can be converted into organic carbon, via the attack of

carbonate radical to the organic molecules, as it is already described in literature [65]; (b) the initial solution contains aggregates of organic and inorganic matter that, during the pre-filtration of samples to perform DOC analysis, are retained in the filter. However, they may disaggregate during the assay and contribute to the dissolved organic carbon posterior determinations. This last explanation is corroborated by the results obtained with the most diluted solution, as the extent of aggregation may be lower as a result of dilution, and consequently in these assays a regular decrease in DOC is shown.

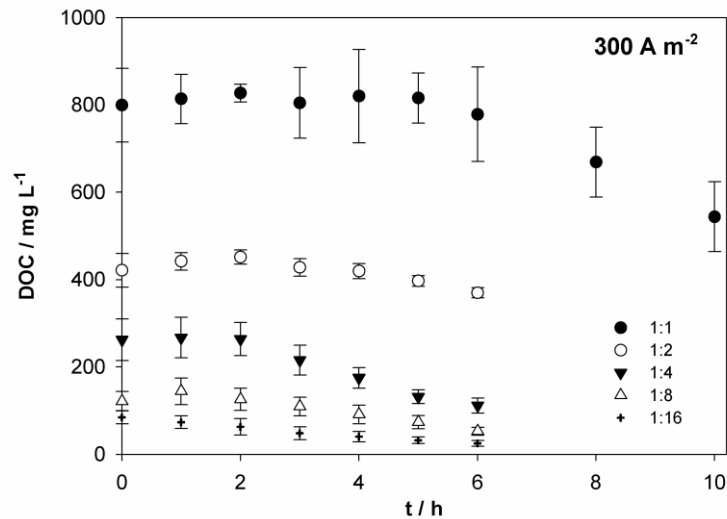


Figure 4.2 - Variation of DOC with time for the electrodegradation assays performed without dilution and with different initial dilutions of the biologically pre-treated leachate, at a current density of 300 A m⁻². Error bars refer to the standard deviation of the DOC mean values.

In Table 4.2 the COD, DOC, TKN, AN and absorbance (275 nm) removals, calculated through Equation (2.1), and the specific energy consumptions, E_{sp} , calculated by means of Equation (2.6), are shown after 6 hours of EO treatment. As can be seen, the sample without dilution (1:1) had the highest COD removal (absolute value), although it represents only 27% of the initial value. For dilutions from 1:1 up to 1:4, there are significant differences in efficiency removals due to samples dilution. These differences are not so evident if we look at the absolute COD removals. In fact, if the electrodegradation had an ideal behaviour, the absolute removals for these samples should be constant, since for pure kinetic control the oxidation rate is independent of the concentration.

For higher dilutions, 1:8 and 1:16 (see Table 4.2), COD percentage removals above 85% were achieved and lead to final COD values below the Portuguese legal discharge limit (150 mg L⁻¹) [66]. For these dilutions, the increase in COD removal with concentration observed presents the typical behaviour of a diffusion controlled process [62]. In all cases, after 6 hours assay DOC removal was smaller than that of COD, probably due to the formation of low molecular mass organic compounds with high degree of oxidation that resist to further oxidation.

Table 4.2 - Initial values of COD, DOC, TKN and AN for the samples used in the assays performed at 300 A m⁻², their respective removals, absorbance removal and specific energy consumption after 6 h of electrolysis.

Dilution		1:1	1:2	1:4	1:8	1:16
COD	initial* / g L ⁻¹	5.8±0.1	2.73±0.06	1.36±0.01	0.68±0.01	0.33±0.01
	removal / g L ⁻¹	1.52	1.31	1.14	0.60	0.30
	removal / %	27	48	83	88	86
DOC	initial* / g L ⁻¹	0.83±0.09	0.42±0.03	0.204±0.009	0.109±0.005	0.056±0.002
	removal / g L ⁻¹	0.02	0.05	0.151	0.069	0.040
	removal / %	3	12	57	56	71
TKN	initial* / g L ⁻¹	1.47±0.02	0.75±0.02	0.38±0.01	0.185±0.009	0.091±0.003
	removal / g L ⁻¹	0.17	0.22	0.26	0.080	0.033
	removal / %	11	29	66	41	35
AN	initial* / g L ⁻¹	1.21±0.05	0.60±0.01	0.290±0.006	0.150±0.005	0.075±0.003
	removal / g L ⁻¹	0.16	0.18	0.158	0.036	0.013
	removal / %	14	30	55	24	18
Abs (275 nm)	removal / %	43	64	83	87	88
E _{sp} / W h (g COD) ⁻¹		52	68	115	166	307

* Values determined in the initial samples characterization, not necessarily equal to the medium values of the different electrolyzed samples.

Regarding the absolute TKN and AN removals, they follow a similar trend to that of COD for the dilutions up to 1:4, mainly by the same reason. However, for the cases with higher dilution, 1:8 and 1:16, where electrolyte was added, the absolute TKN and AN removals decrease with the increase in dilution. This fact may be a consequence of the decrease in chloride concentration, as well as due to the presence of extra quantities of sulphate, used as electrolyte [8,11]. For all dilutions, the UV-vis spectra showed a well-defined shoulder in the UV region at about 275 nm, which is related to the presence of aromatic compounds. According to results reported in Table 4.2, samples with higher dilutions (1:8 and 1:16) presented higher absorbance decays (around 88%), showing good removal of aromatic compounds after 6 hours of electrolysis. Energy consumptions increased with leachate dilution, but their discussion will be made later in the text.

The influence of current density on the electrodegradation rate of biologically pre-treated leachate, without dilution, was studied for current densities between 50 and 500 A m⁻² and is presented in Figure 4.3 and Table 4.3. Data reported, showed that COD removal rate increased with current density, achieving 44% after 6 hours of electrolysis with an applied current density of 500 A m⁻². The regular linear decay, observed in Figure 4.3 for all the applied current densities, indicates that electrolysis is mainly under current control.

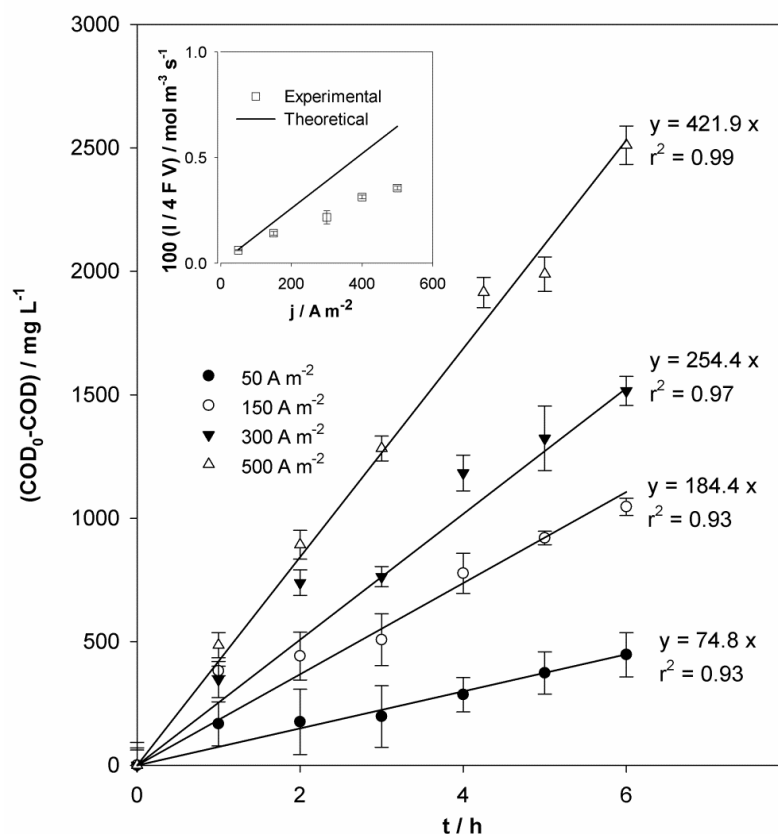


Figure 4.3 - COD removal with time for the electrodegradation assays performed with biologically pre-treated leachate, without dilution, at different current densities and fittings of Equation (2.33). Error bars refer to the standard deviation of the COD mean values. Inset: experimental (from the main figure) and theoretical (from Equation (2.33)) values of $1/4FV$ vs. current density.

According to the model previously proposed in the literature for electrolysis under current limited control [62], the trend of COD during electrochemical oxidation can be predicted by Equation (2.33). Thus, theoretical slopes, $1/4FV$, were calculated, using Equation (2.33), for each of the assayed current intensities. The comparison between these theoretical values and the slopes obtained with the fitting of linear equations to experimental values (inset of Figure 4.3) shows that the discrepancy between experimental and predicted values increases with current density. This was expected, since when current density decreases, the number of species present in the leachate complex mixture, which are under kinetic control, increases. Other reasons may also contribute to the difference between theoretical and experimental values, namely the fact that the theoretical model applied was deduced for the EO of organic species and, in the case of a leachate, there are also several inorganic species that may undergo oxidation. Also, at the end of the assay, due to the reduction in COD, the control of the oxidation process can be mainly diffusive.

If data from Figure 4.1 for dilutions 1:2 and 1:4 are adjusted to Equation (2.33), zero order kinetic constants can be calculated for those assays run also in current control, at the current

density of 300 A m^{-2} , and their values are: dilution 1:2 - $213 \text{ mg L}^{-1} \text{ h}^{-1}$; dilution 1:4 - $184 \text{ mg L}^{-1} \text{ h}^{-1}$. In fact, these values are further away from the theoretical value $448 \text{ mg L}^{-1} \text{ h}^{-1}$ than the one obtained for the raw leachate in similar experimental conditions ($254.4 \text{ mg L}^{-1} \text{ h}^{-1}$, see Figure 4.3), showing that, there is also a decrease in COD removal rate with dilution.

As showed in Table 4.3, DOC removal rate increased with applied current density. However, as reported for the study performed at higher dilutions, and for the same reasons, DOC percentage removal was smaller than that of COD.

Table 4.3 - COD and DOC removals and specific energy consumption for the samples used in the assays performed at different current densities, without dilution and with the highest dilution (1:16), after 6 h of electrolysis.

Current density / A m^{-2}		50	150	200	300	400	500	700
Without Dilution (1:1)								
COD removal	g L^{-1}	0.45	1.05	-	1.52	2.21	2.51	-
	%	8	18	-	27	28	44	-
DOC removal	mg L^{-1}	-	-	-	20	251	303	-
	%	-	-	-	3	30	37	-
$E_{\text{sp}} / \text{W h (g COD)}^{-1}$		15	24	-	52	-	56	-
Dilution 1:16								
COD removal	g L^{-1}	-	-	0.30	0.30	0.32	-	0.32
	%	-	-	91	86	97	-	97
DOC removal	mg L^{-1}	-	-	29	40	48	-	50
	%	-	-	52	71	86	-	89
$E_{\text{sp}} / \text{W h (g COD)}^{-1}$		-	-	217	307	341	-	4513

Apparently, the results presented in Figure 4.1 indicate that for higher dilutions the electrolysis is under mass transport control. To verify this assumption, several assays at dilution 1:16 and different current densities were performed, and critical COD was determined. According to electrochemistry basic principles, if the limiting step in the electrolysis is the organic pollutant transfer from the bulk to the anode surface, changing the current density would not affect the COD removal rate. Thus, current densities between 200 and 700 A m^{-2} were applied and results are shown in Figure 4.4 and Table 4.3.

As it can be seen in Figure 4.4, COD decay becomes constant for current densities higher than 400 A m^{-2} , which means that the assays occurred under mass transport control. The application of the model proposed in the literature for mass transport limitations [62], given by Equation (2.36), and using data obtained at 400 and 700 A m^{-2} , allowed the determination of the medium mass transport coefficient, $k_m = 2.74 \times 10^{-5} \text{ m s}^{-1}$. This value is higher than

that presented in the literature ($1.75 \times 10^{-5} \text{ m s}^{-1}$) [40], determined using the limiting current technique with a ferricyanide/ferricyanide/ Na_2CO_3 electrolyte solution. The medium mass transport coefficient obtained can be used in Equation (2.34) to calculate the critical COD, that depends on the current intensity and has the value of 908 mg L^{-1} for $I = 0.3 \text{ A}$. This COD_{cr} value indicates that, for $I = 0.3 \text{ A}$, which corresponds to $j = 300 \text{ A m}^{-2}$ (Figure 4.1), only assays performed at dilutions 1:8 and 1:16 are mainly under mass transport control. In fact, if the initial limiting current density is calculated by means of Equation (2.31) the values obtained for j_{lim} , with the initial COD of the experiments 1:8 and 1:16, are 225 and 109 A m^{-2} , respectively, i.e., much lower than the applied current density.

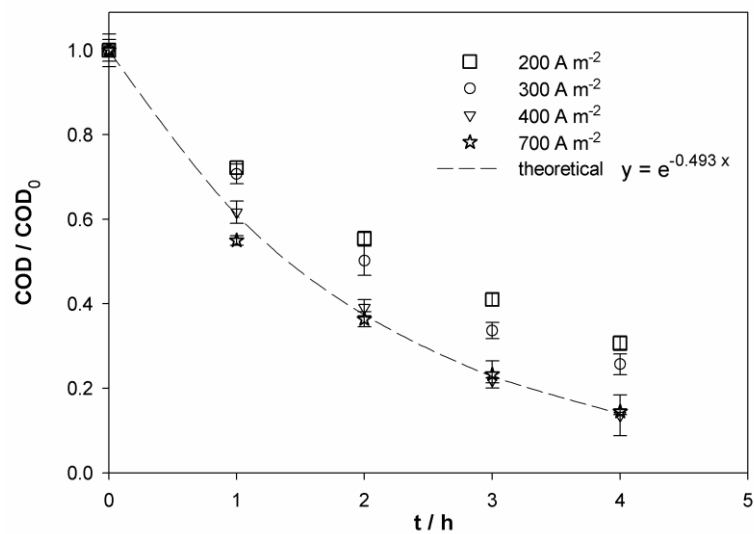


Figure 4.4 - Normalized COD variation with time for the electrodegradation assays performed with biologically pre-treated leachate diluted at 1:16, at different current densities. Error bars refer to the standard deviation of the normalised COD mean values.

Table 4.3 shows that for current densities higher than 400 A m^{-2} , 97% of COD removal and 86% of DOC removal were achieved after 6 hours. After 2 hours, COD values were below the legal discharge limit. The agreement between the theoretical models, Equations (2.33) and (2.36), and experimental data can be visualized in a COD parity plot (Figure 4.5) for the different assays performed. The best correspondences are attained at lower applied current density (50 A m^{-2}) for sample 1:1 and at higher applied current density (700 A m^{-2}) for sample 1:16. These results, that may seem unexpected for the degradation of model solutions containing organic molecules, can be explained since the leachate samples used have a very complex composition. This way, it is very difficult to achieve a situation that guarantees that all species present are either in kinetic or in diffusion control. Thus, the situation that best approaches the kinetic control for all the species present in the sample is at very low current intensity, being the opposite true for the process controlled by mass transport.

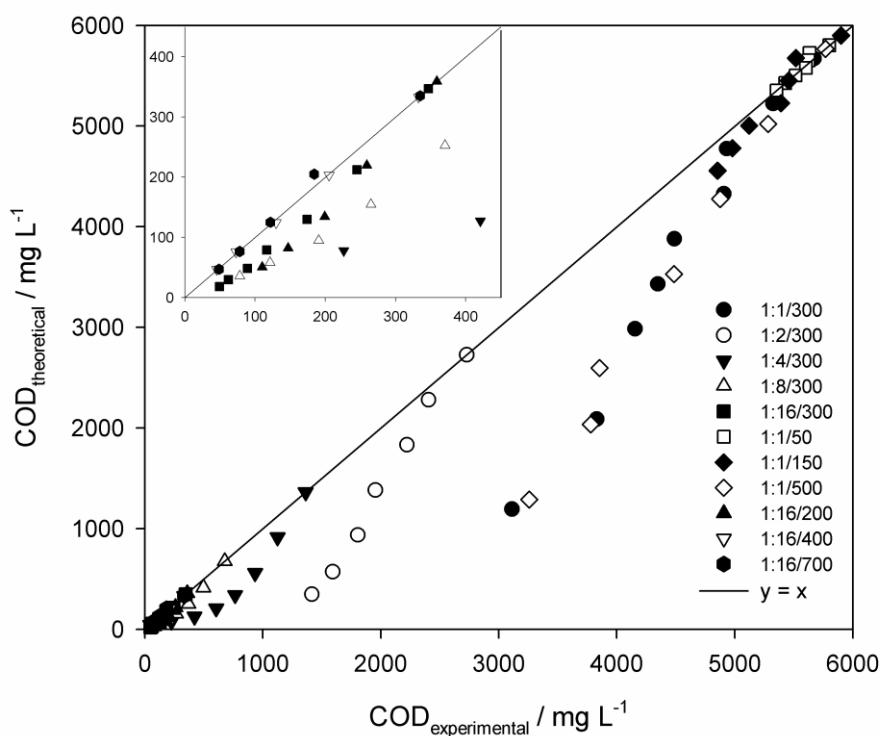


Figure 4.5 - COD parity plot for the assays performed with the biologically pre-treated leachate and with its different dilutions at several current intensities [dilution/(current intensity/mA)].

Another aspect that may be interesting to analyse is the influence of leachate dilution on the ratio of DOC/COD (Figure 4.6). If a linear regression is made with data collected at 300 A m^{-2} for 1:8 and 1:16 dilutions, a $\text{DOC/COD} = 0.3$ was obtained. However, this ratio decreases substantially if the linear regression is made with data collected at 300 A m^{-2} for 1:1 sample, using only the points obtained after the initial period, i.e., when DOC starts to decrease with time (this way it is expected to eliminate the influence of the aggregates present at the beginning of the assay). Apparently, the mineralization of the organic matter improves with the dilution of the leachate.

In order to analyse the influence of dilution and current density on the energetic costs, the obtained E_{sp} values for the different assays performed, divided by the highest value found, are represented in Figure 4.7. It can be seen that an increase in the dilution or in the current intensity greatly increases the energy consumption. In fact, the ratio of specific energy consumption between the assays (1:16 at 700 A m^{-2}) and (1:1 at 50 A m^{-2}) is 300. This was expected, since as the process approaches kinetic control, the energetic costs become smaller.

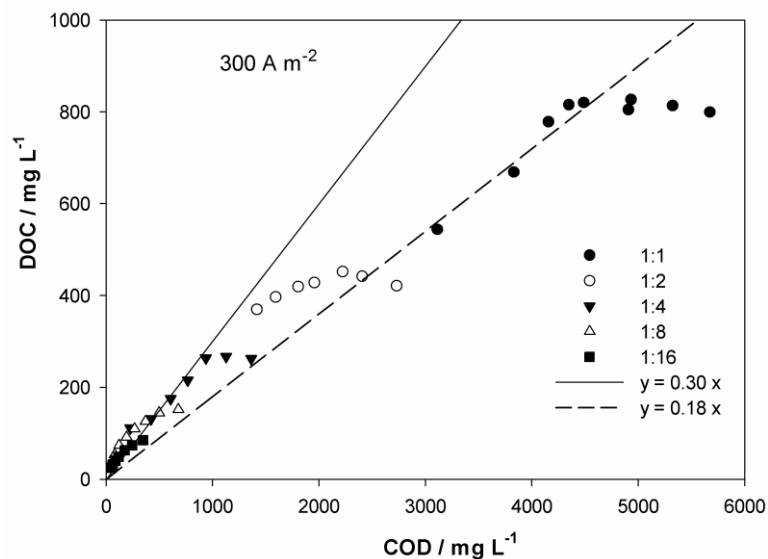


Figure 4.6 - DOC/COD experimental ratio (points) for the electrodegradation assays performed with different initial dilutions at a current density of 300 A m^{-2} and DOC/COD curve fittings for the assays performed without dilution (1:1) and with dilution 1:16 (lines).

Although after 6 hours assay, samples with dilutions 1:8 and 1:16 were the only ones that presented values below the Portuguese legal discharge COD limit, a different approach could be done, i.e., dilute the sample obtained in the 6 hours treatment of the raw leachate in order to meet those limits. However, to obtain the same final COD as the sample 1:16 treated, it had to be diluted by 1:142, since for the sample 1:1 the final COD is $(5.8-1.52) = 4.28 \text{ g L}^{-1}$ and for the sample treated with an initial dilution of 1:16 is $(0.33-0.3) = 0.03 \text{ g L}^{-1}$. This procedure, although less expensive, would also increase the net amount of COD discharged in the environment.

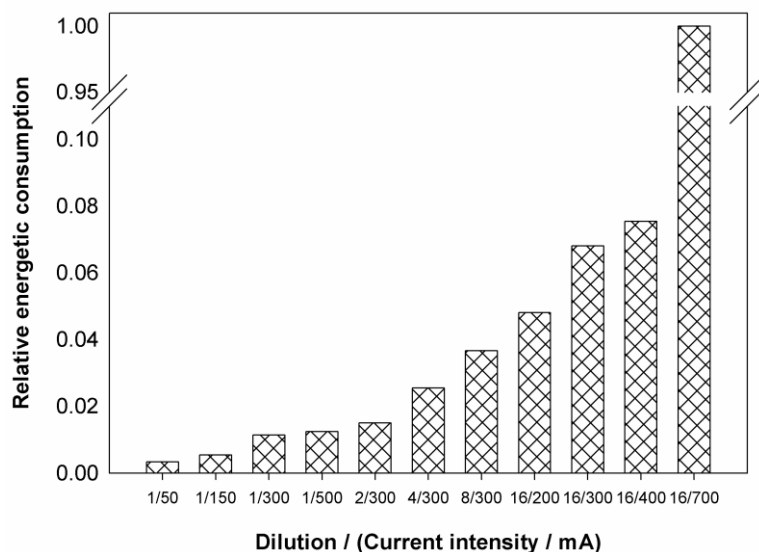


Figure 4.7 - Relative energetic consumption for the different assays performed.

Attending to the aim of this case study, which was to evaluate the feasibility of an electrochemical oxidation treatment applied to sanitary landfill leachates as a polishing step, after a biological process, and to determine the optimal conditions for its application, the following conclusions can be drawn:

- ✓ EO with BDD anodes can successfully be employed to treat biologically pre-treated sanitary landfill leachates, eliminating the remaining organic load.
- ✓ Because of the complexity of the leachate composition, the applicability of the theoretical models for the electrochemical degradation is limited, since it is very difficult to find a situation where the electrodegradation of all the compounds present in the mixture are simultaneously in identical control process, kinetic or diffusional.
- ✓ The operational conditions that best fit the kinetic control or the mass transfer control models are, respectively, the assays run with the sample without dilution, at very low current intensity, and with the most diluted sample, at high current intensity.
- ✓ An increase in the dilution (lower pollutants concentration) or in the current intensity greatly increases the energy consumption.
- ✓ Mineralization of the organic matter is higher for low pollutants concentration.
- ✓ To increase the current efficiency and to decrease energy costs, it is preferable to work with low current intensities, although this leads to an increase in the treatment period.

The work described in this case study led to the publication of an article in an international scientific journal with scientific arbitration [67] and also to an oral scientific communication [68].

4.2 Case study 2

Application of EO to a biologically treated leachate: Semi-pilot plant with recirculation

To evaluate the feasibility of an EO treatment applied as a polishing step, semi-pilot scale assays were performed using a biologically treated leachate. The effects of the recirculation flow rate and of the applied current density on the oxidation rate were studied. Table 4.4 summarizes the experimental conditions evaluated. All assays were conducted at room temperature (22-25 °C) and natural pH, without adding background electrolyte. The volume of biologically treated leachate used in each experiment was 10 L and the duration of the assay was 12 hours. The characterization of the samples used in these assays is presented in Table 3.1, Sample G.

AN and TKN values were not determined because of the samples characteristics that lead to the formation of foams during the analyses, with the consequent sample loss. Thus, nitrogen decay along the assays was followed only by TN.

Table 4.4 - Experimental conditions tested in Case study 2 assays.

Flow rate / L h ⁻¹	Applied current density / A m ⁻²
360	1000, 2000, 3000
500	

Figure 4.8 presents the results of the variations with time of COD removed and of normalized DOC and TN for those EO assays. It can be seen that COD, DOC and TN removal rates increased with current density for both flow rates studied, showing the importance of the indirect oxidation process during electrolysis.

Theoretical slopes of $COD_0 - COD_t$ vs. time, $I/4FV$, calculated according to the Equation (2.33), are also depicted in Figure 4.8 a and b, for each of the assayed flow rates and current densities. The comparison between experimental data and predicted slopes shows that, for both flow rates studied, at the applied current density of 1000 A m⁻² the COD decay in time is higher than that theoretically predicted. At 2000 A m⁻² the discrepancy between experimental and predicted slopes is minimal and at 3000 A m⁻² it increases, being the COD removal rate lower than the theoretically predicted. This can be explained if it is assumed that the degradation process happens also by indirect oxidation in the bulk of the solution. In fact, depending on the electrolyte composition, the organics can be oxidized by hydroxyl radicals as well as by other inorganic oxidant species, electrogenerated on BDD surface [69]. The co-existence of an indirect oxidation process promoted by these oxidizing species will increase

the COD removal rate, leading to current efficiencies higher than 100%. However, as the applied current is being increased, the current efficiency decreases, due to mass transport limitation and side reactions, such as oxygen evolution [69]. Another factor that contributes to high current efficiency is the use of two BDD electrodes, as anode and as cathode, and the polarity reversal system that avoided the anode's polarization. This polarization that would be more important at lower current densities is thus avoided.

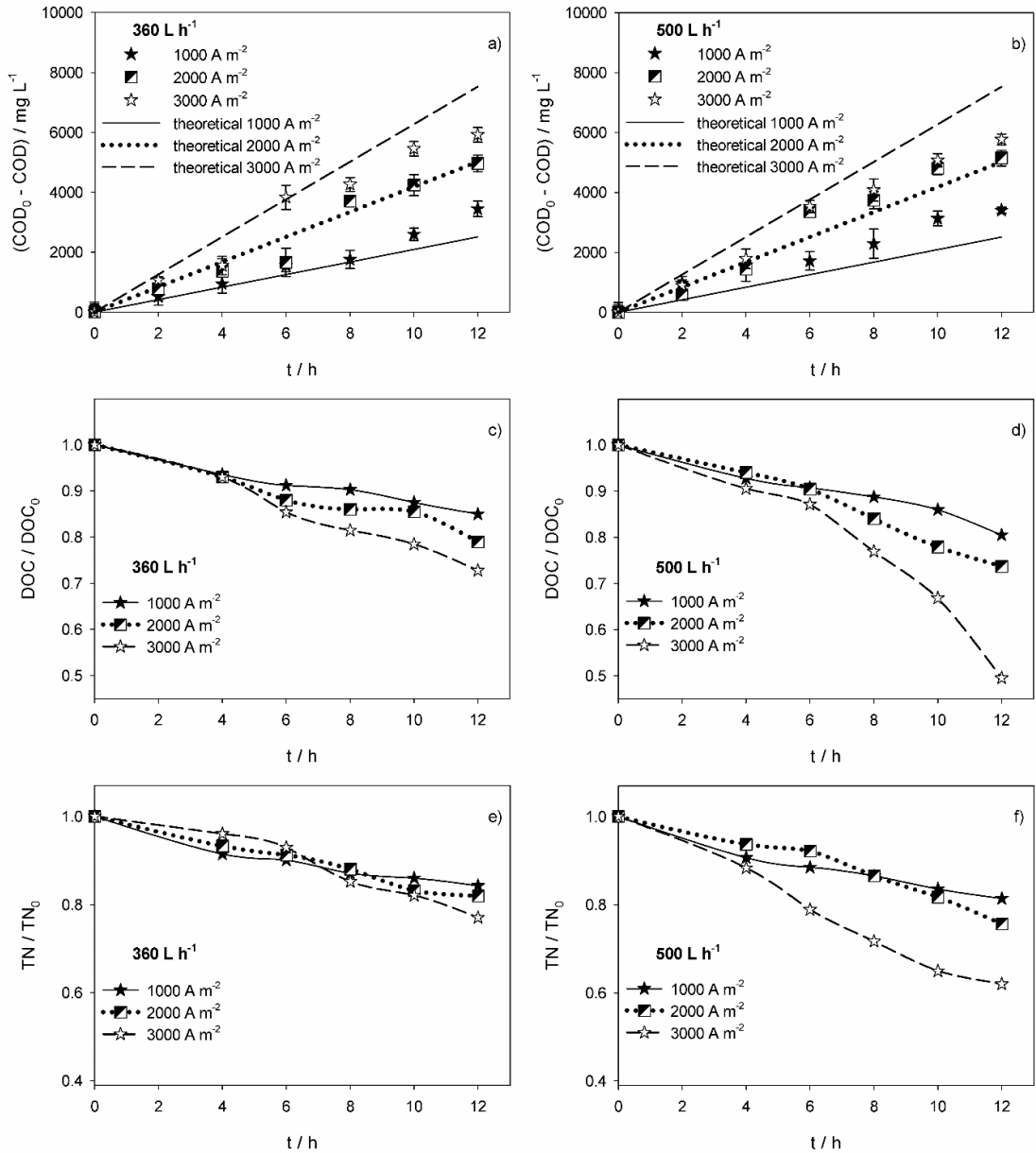


Figure 4.8 - Variation with time of COD removed (a,b) and normalized decays of DOC (c,d) and TN (e,f) at the flow rates of 360 and 500 L h⁻¹, respectively, for the electrodegradation assays performed at different current densities. Error bars refer to the standard deviation of the COD mean values.

Still focusing in Figure 4.8 a and b, it can be seen that, up to 4 h assay there is almost no influence of the applied current density, for both flow rates tested. This behaviour is in agreement with the existence of oxidation of the organic matter through an indirect oxidation mechanism promoted by strongly oxidant species, such as, for instance, those resulting from the direct oxidation at the anode of chloride ions (Equations (2.25) to (2.27)) since this ion content is constant for all the assays performed at different experimental conditions. After that initial period, the oxidation of the organic matter mediated by hydroxyl radical becomes more important, and since its concentration increases with current density, consequently, the quantity of organic matter oxidized by hydroxyl radicals increases, leading to higher COD removal rates [29].

Regarding the effect of the recirculating flow rate, it has almost no influence on the absolute COD removal, as can be observed from data presented in Table 4.5, being the observed differences within the experimental error of the assays. This behaviour can be explained by the importance of the indirect oxidation, that partially overcomes the mass transport limitations, and, for the higher applied current densities, of the oxygen evolution that increases turbulence near the electrode's surface. The polarity reversal system may also play here an important role, since organic molecules that, at a particular instant, were far from the anode, rapidly stay very close to the "new" anode surface, due to the reversal of the polarity, without the needing of being transferred to the reaction place.

Table 4.5 - Experimental results for the EO assays performed at the semi-pilot plant using leachate G, after 12 h, at different flow rates and applied current densities.

Flow rate / L h ⁻¹	360			500		
Current density / A m ⁻²	1000	2000	3000	1000	2000	3000
COD removal g L ⁻¹	3.4	5.0	5.9	3.4	5.1	5.8
DOC removal g L ⁻¹	0.42	0.46	0.72	0.55	0.69	1.07
ΔDOC/ΔCOD	0.12	0.09	0.12	0.16	0.14	0.18
TN removal g L ⁻¹	0.10	0.12	0.15	0.13	0.16	0.24
Conductivity* / mS cm ⁻¹	26.0	25.8	25.1	25.3	25.3	25.6
pH*	8.1	8.0	8.1	8.0	7.9	8.3
E _{sp} / W h (g COD) ⁻¹	24	37	52	21	36	52

*Final values

DOC removal rate (Figure 4.8, c and d; Table 4.5) increases with applied current density and recirculation flow rate, most likely due to the increase in the indirect oxidation and in the improvement of the mass transfer process of some oxidizing species from the electrode surface to the bulk of the suspension.

The global ratio $\Delta\text{DOC}/\Delta\text{COD}$ (Table 4.5), an expression of the mineralization index, increased with flow rate and presented an irregular variation with current density, although the highest values were observed for the highest current density applied at each flow rate. The increase in that ratio is related mainly with the indirect oxidation process that is less specific in the attack of the organic molecules, leading to combustion rather than conversion processes. This behaviour may also be due to the formation of more stable compounds when turbulence is lower, due to lower oxygen evolution at lower current density or to lower flow rate.

The nitrogen removal increases with current density and recirculating flow rate (Figure 4.8, e and f; Table 4.5). The TN removal rate is low at the beginning of the assays and increases with time, particularly for the highest flow rate and current density. Similar results were reported by Cossu *et al.* [19], using a Ti/Pt electrode. These authors found that the removal rate of ammonium was lower than that of COD at the initial stage of electro-oxidation, when direct oxidation was dominant, and then AN was substantially removed in the subsequent electrochemical oxidation stage when indirect oxidation became prevalent.

The observed removals of organic load during the assays are very well expressed by the aspect of the samples collected during the experiments (Figure 4.9). In fact, after 12 h assay at a flow rate of 500 L h^{-1} and a current density of 3000 A m^{-2} , the samples are incolor.

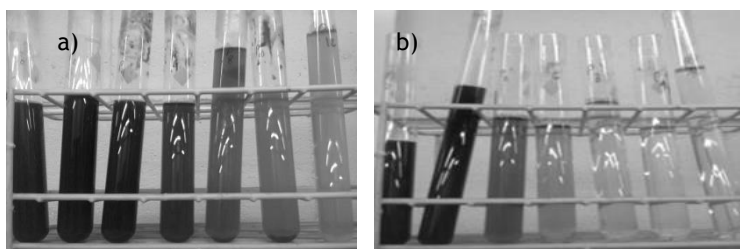


Figure 4.9- Images of the samples collected at 0, 2, 4, 6, 8, 10 and 12 h for the assays performed with a flow rate of 500 L h^{-1} at (a) 2000 and (b) 3000 A m^{-2} current density.

The conductivity and the pH of the final samples, as well as the specific energy consumption, calculated by means of Equation (2.6), after 12 hours of EO treatment, are also presented in Table 4.5. Conductivity and pH presented very small variations at the end of the assays (Table 3.1: Initial conductivity $25 \pm 1 \text{ mS cm}^{-1}$ and initial pH 8.4 ± 0.7). Regarding the energy consumptions, and as expected, the energy consumption increased with applied current density, being the lowest value achieved at 1000 A m^{-2} and 500 L h^{-1} . The influence of the flow rate was almost inexistent.

According to the purpose of this case study, which was to evaluate the feasibility of an EO treatment applied as a polishing step on a semi-pilot scale, some conclusions can be drawn:

- ✓ EO process using a BDD anode can be successfully applied as a polishing step in sanitary landfill leachates treatment. At a semi-pilot plant scale, COD removals of 71% were achieved after 12 h of treatment.
- ✓ Organic load removal rate increases with applied current density, but also do the energetic costs. The lower energy consumption measured, $21 \text{ W h (g COD)}^{-1}$ was attained for a COD removal of 45%.
- ✓ High flow rates conjugated with high current density enhance DOC and TN removals.
- ✓ Relative DOC removals are always lower than that of COD and these differences decrease with flow rate. Thus, an increase in flow rate seems to increase the mineralization index.

Part of the work described in this case study was presented in a scientific meeting [70].

Chapter 5

Application of EO to treat raw leachates

In order to study the application of an electrochemical oxidation treatment to raw sanitary landfill leachates and determine the operational conditions that may lead to higher treatment efficiencies, case studies 3 and 4 were performed, as defined in Chapter 3. Following, there is a description of the experimental conditions used and of the results and conclusions obtained in both case studies.

5.1 Case study 3

Application of EO to raw leachates: Stirred reactor vs. feed-recirculated reactor

This study was performed using two different laboratory scale electrochemical cells, both operating in batch mode, one with recirculation and the other with stirring. Different current densities were tested. In the studies performed with recirculation, current density was either kept constant or decreased by steps, in order to study this effect on the efficiency of the process. Table 5.1 presents the experimental conditions tested in each electrochemical cell. All assays were conducted at room temperature (22-25 °C) and natural pH, without adding background electrolyte. The physical-chemical characteristics of the leachate sample used in this study are described in Table 3.1, sample E.

Table 5.1 - Experimental conditions tested in Case study 3 assays.

Cell configuration	Leachate volume / L	Electrolysis time / h	Stirring / Flow rate	Applied current density
I	0.2	6	100 rpm	300, 700, 1000 A m ⁻²
II	0.2	4	75 L h ⁻¹	1 h at 500 A m ⁻² + 3 h at 300 A m ⁻² 1 h at 500 A m ⁻² + 3 h at 400 A m ⁻² 4 h at 500 A m ⁻²
		6		300, 700, 1000 A m ⁻² 3 h at 500 A m ⁻² + 3 h at 300 A m ⁻² 3 h at 500 A m ⁻² + 3 h at 400 A m ⁻² 6 h at 500 A m ⁻²

5.1.1 Stirred reactor

In Figure 5.1, the results for the normalized COD variation in time for the assays run at different current densities are presented, showing an increase in COD removal rate with current density. The figure also includes the theoretical normalized COD, calculated according to Equation (2.33), and it can be observed that there is an increase in the bias between the theoretical and the experimental COD values, with a consequent decrease in the current efficiency. An increase in COD removal can be an indication of a process controlled by charge transfer. However, if this was the case, current efficiency should be closer to its maximum value, 100%, which is not the case. If the limiting current density is determined by means of Equation (2.31), using a literature value of $1.75 \times 10^{-5} \text{ m s}^{-1}$ for k_m [40], a value of 1878 A m^{-2} can be obtained, pointing to a current controlled process at least during the first part of the assays. This apparent contradictory behaviour was already observed and explained in Case study 1, which used the same configuration cell. In the case of leachate samples with so much suspended and dissolved solids, there is another justification for the strange behaviour that is related with the fact that the organic matter associated to the suspended solids do contribute for the leachate COD determination results but, since they are not dissolved they will not be degraded by the electrochemical process.

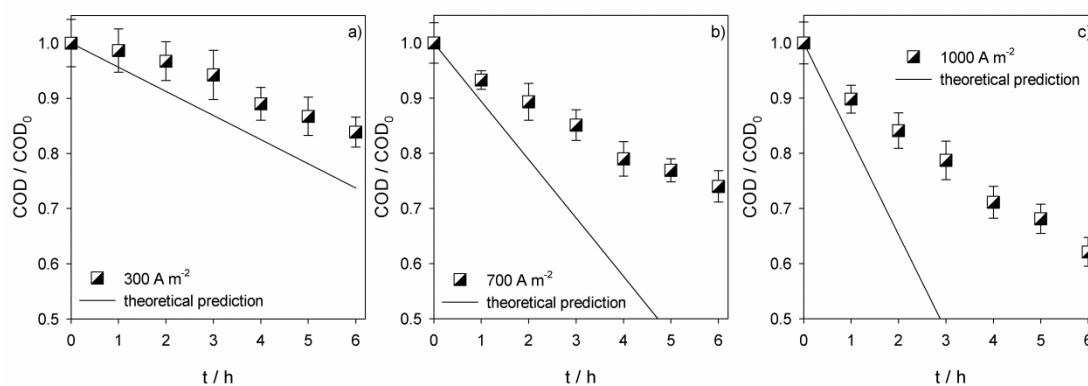


Figure 5.1 - Normalized COD variation with time for the EO assays performed in the stirred reactor at different current densities: (a) 300 A m^{-2} , (b) 700 A m^{-2} and (c) 1000 A m^{-2} . Error bars refer to the standard deviation of the normalized COD mean values.

Table 5.2 presents the results obtained in the several parameters used to follow the assays, after 6 hours of EO treatment, for all the current densities studied. Current efficiencies (CE) were calculated using Equation (2.37) and specific energy consumptions by means of Equation (2.6). From Table 5.2, it can be seen that, despite the decrease in current efficiency with applied current density, there is an increase in the removal of all the parameters. For the assays run at 700 and 1000 A m^{-2} , the data presented show that DOC removal was lower than COD removal. This behaviour was reported previously, in Case study 1, and was explained by

the formation of low molecular mass organic compounds with high degrees of oxidation that resist to further oxidation. Nitrogen removal was also assessed and results showed that there is a marked dependence of this parameter, in its different forms, with the applied current density.

Regarding the energy consumption, an increase in the applied current density leads to an increase in the energy consumption, which is a consequence of the increase in potential when the current density is increased.

Table 5.2 - Experimental results for the EO assays performed in the stirred reactor at different current densities after 6 h assay.

Current density / A m ⁻²	300	700	1000	
COD removal	/ g L ⁻¹	1.65	2.42	3.26
	/ %	16	28	38
DOC removal	/ g L ⁻¹	-	0.86	0.97
	/ %	-	26	29
TN removal	/ g L ⁻¹	-	0.68	0.86
	/ %	-	24	31
TKN removal	/ g L ⁻¹	-	0.86	0.95
	/ %	-	36	39
AN removal	/ g L ⁻¹	-	0.87	1.08
	/ %	-	39	50
CE / %	61	39	36	
E _{sp} / W h (g COD) ⁻¹	42	92	119	

5.1.2 Recirculated reactor

In order to evaluate the influence of the electrochemical cell hydrodynamics in the EO performance, this study was performed using a laboratory scale batch recirculated reactor. The influence of the applied current density was first investigated with similar current densities to those used in the stirred cell, in order to compare reactors efficiency. In a posterior stage, the current density was decreased by steps along the assays, in an attempt to increase the efficiency of the process. A recirculation flow rate of 75 L h⁻¹ was used for all the

assays. The results obtained at constant current density conditions are presented in Figure 5.2 and Table 5.3.

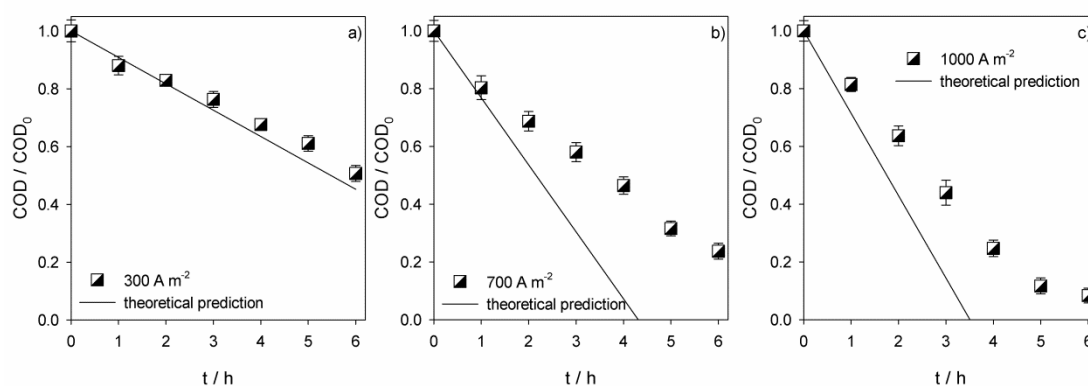


Figure 5.2 - Normalized COD variation with time for the electrodegradation assays performed in the recirculated reactor, at different current densities kept constant along the assays: (a) 300 A m⁻², (b) 700 A m⁻² and (c) 1000 A m⁻². Error bars refer to the standard deviation of the normalized COD mean values.

Figure 5.2 shows an increase in COD removal rate with applied current density, as expected. However, comparing these results with those obtained at the stirred reactor (Figure 5.1), it can be seen that COD removals obtained with the recirculated reactor are much higher than those obtained with the stirred reactor. Although similar current densities were applied to both systems, stirred and recirculated, the areas of the BDD electrodes used in those systems were different: 10 cm² for the stirred set-up and 20 cm² for the recirculated one. Thus, equal applied current densities correspond to different electrical charges, being the electrical charge applied to the batch with recirculation system twice of that applied to the batch with stirring cell. Furthermore, in the batch with recirculation system, the contact between the oxidant species and the pollutant molecules is enhanced, since the pollutant molecules are forced to pass near the electrodes surface and the negative effect of diffusion is highly decreased, thus improving the oxidation process.

The comparison between the experimental COD values and the theoretical ones, calculated through the Equation (2.33), highlights the similarity between both values in the assay performed at the lowest current density in the recirculated reactor. In fact, CE results (Table 5.3), calculated by means of Equation (2.37), show a current efficiency of 82% for the applied current density of 300 A m⁻².

From Table 5.3, it can be seen that an increase in the current density leads to an increase in the removal of all the parameters measured. DOC removals, in percentage, are very close to that of COD, suggesting that the recirculated reactor promotes the combustion of the organic matter with a very good yield.

Regarding the removal of nitrogen in its different forms, it can be observed that an increase in current density leads to an increase in nitrogen removal, being TKN the nitrogen parameter with the highest removal. This could mean that the organic nitrogen is preferably removed in detriment of ammonium nitrogen or that the organic nitrogen is eliminated in the form of AN. This last behaviour was already observed in the electrodegradation of anilines and other organic compounds [71,72].

Table 5.3 - Experimental results for the EO assays after 6 h, performed in the recirculated reactor at different current densities kept constant along the assays.

Current density/ A m ⁻²		300	700	1000
COD removal	/ g L ⁻¹	4.84	6.87	7.67
	/ %	49	76	92
DOC removal	/ g L ⁻¹	1.68	2.36	2.67
	/ %	47	72	82
TN removal	/ g L ⁻¹	-	0.77	1.07
	/ %	-	29	40
TKN removal	/ g L ⁻¹	-	1.06	1.67
	/ %	-	43	68
AN removal	/ g L ⁻¹	-	0.84	1.21
	/ %	-	39	56
CE / %		82	55	54
E _{sp} / W h (g COD) ⁻¹		26	53	78

Specific energy consumptions, calculated from Equation (2.6), were also assessed (Table 5.3). Similarly to what was noticed for the stirred reactor experiments, an increase in the current density leads to an increase in the energy consumptions. However, energy consumptions obtained for the recirculated assays are much lower than that obtained in the stirred assays.

In an attempt to reduce the operation costs, and considering that as COD decreases less current is needed to oxidize the organic matter, experiments were performed with decreases in the applied current density, by steps, along the assay, being the other operational conditions kept equal to the previous assays (200 mL of leachate at a recirculation flow rate of 75 L h⁻¹). The results obtained in these experiments are reported in Figure 5.3 and Table 5.4. Since the aim of these assays was just to evaluate the costs, by means of the energy consumption, only COD and AN were monitored along the assays because these are among the

most problematic parameters regarding the disposal of leachates in municipal wastewaters treatment plants.

The presented results indicate that COD and AN removals increased with applied current density. However, except for the assay performed at 1 h (500 A m⁻²) + 3 h (300 A m⁻²), which presented the lowest energetic consumption, all the other assays showed similar specific energy consumptions.

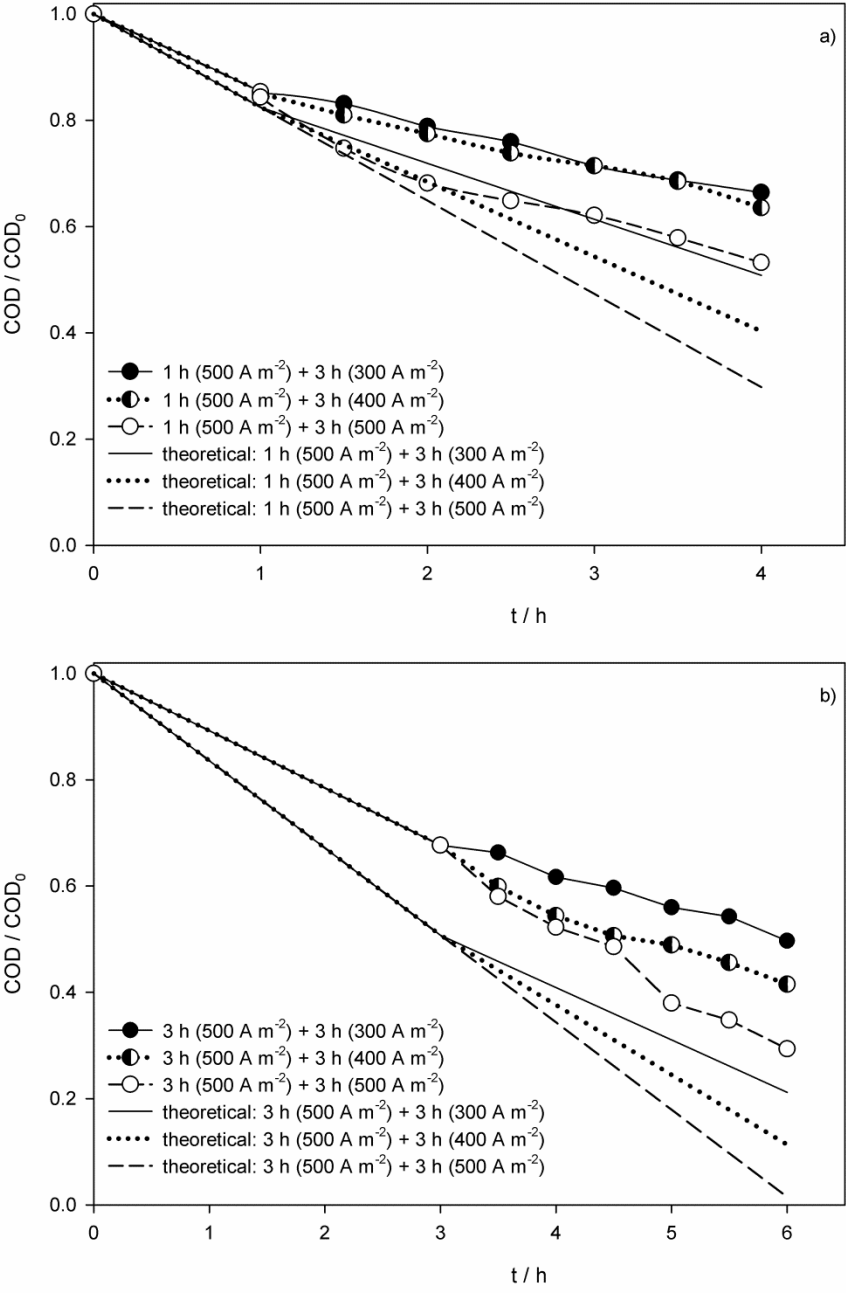


Figure 5.3 - COD variation with time for the EO assays performed in the recirculated reactor with current densities decreased by steps: (a) 1 h (500 A m⁻²) + 3 h (300, 400 or 500 A m⁻²) and (b) 3 h (500 A m⁻²) + 3 h (300, 400 or 500 A m⁻²).

Table 5.4 - Experimental results for the EO assays performed in the recirculated reactor with current densities decreased by steps.

Current density / A m ⁻²	COD removal /		AN removal /		E _{sp} / W h (g COD) ⁻¹
	g L ⁻¹	%	g L ⁻¹	%	
1 h (500 A m ⁻²) + 3 h (300 A m ⁻²)	3.45	34	0.26	11	39
1 h (500 A m ⁻²) + 3 h (400 A m ⁻²)	3.81	36	0.49	26	45
4 h (500 A m ⁻²)	4.64	50	0.52	27	45
3 h (500 A m ⁻²) + 3 h (300 A m ⁻²)	4.62	51	0.82	36	46
3 h (500 A m ⁻²) + 3 h (400 A m ⁻²)	5.11	59	0.83	36	47
6 h (500 A m ⁻²)	6.11	74	0.95	41	45

From this case study, whose purpose was to evaluate the feasibility of the application of the EO process as a first/single treatment of a sanitary landfill leachate with low biodegradability index and to study the influence of the operational conditions on the electrodegradation rate, the following outcomes can be highlighted:

- ✓ EO with BDD anodes can be an alternative to treat non-biodegradable sanitary landfill leachates, although the costs involved can significantly increase when higher pollutants removals are required.
- ✓ For the experimental conditions tested, EO process is more effective using a feed-recirculated reactor than a stirred one.
- ✓ An increase in the applied current density generally leads to an increase in the organic load removal rate, but decreases the current efficiency.
- ✓ The removal of the nitrogen compounds increases with applied current density and their removal is more effective when COD becomes low.
- ✓ For the tested conditions, the decrease of applied current density by steps along the EO process did not lead to a decrease in specific energy consumption.

The work described in this case study was presented as an oral communication in a scientific meeting [73] with the publication of a full length paper in the book of proceedings [74].

5.2 Case study 4

Application of EO to a raw leachate: Semi-pilot plant with recirculation

In order to evaluate the process efficiency of the EO treatment of a raw leachate with low biodegradability using a semi-pilot scale plant, assays were performed where the effect of the recirculation flow rate and of the applied current density on the rate of electrochemical oxidation was studied, using different leachate volumes. Similarly to what was done at laboratory scale experiments, described in Case study 3, current density was either kept constant or decreased by steps. Table 5.5 summarizes the experimental conditions evaluated. All assays were conducted at room temperature (22-25 °C) and natural pH, without adding background electrolyte. Leachate Sample E was used to perform this study, being its characteristics presented in Table 3.1.

Table 5.5 - Experimental conditions tested in Case study 4 assays.

Leachate volume / L	Electrolysis time / h	Flow rate / L h ⁻¹	Applied current density
5	48	360	1000 A m ⁻²
	16	360	2000 A m ⁻²
	20	160, 360	5 h at 2000 A m ⁻² + 5 h at 1000 A m ⁻² + 10 h at 570 A m ⁻²
10	16	100, 950	4 h at 2000 A m ⁻² + 4 h at 1500 A m ⁻² + 4 h at 1000 A m ⁻² + 4 h at 570 A m ⁻²
15	40	360	570 A m ⁻²

Figure 5.4 presents the results of the normalized COD variation with time and with specific charge passed for the electrodegradation assays performed. Specific charge was calculated as It/V , in C L⁻¹, where I is the current intensity, in A, t is the time, in s, and V is the sample volume, in L. It can be observed (Figure 5.4a) that, for the assays performed with equal leachate volume, COD removal rate increases with current density, which points to electrolysis operating under charge transfer control. In fact, for a single-compartment electrolytic reactor similar to the one used in this case study, operating at flow rates of 200 and 600 L h⁻¹, mass transport coefficients, k_m , of 1.39×10^{-5} and 1.5×10^{-5} m s⁻¹, for 200 L h⁻¹, and 2.2×10^{-5} m s⁻¹, for 600 L h⁻¹, are presented in literature [75-77]. With these k_m values from literature, limiting currents between 1485 and 2360 A m⁻² were obtained, showing that at least two of the assays presented in Figure 5.4 started at current limited control conditions.

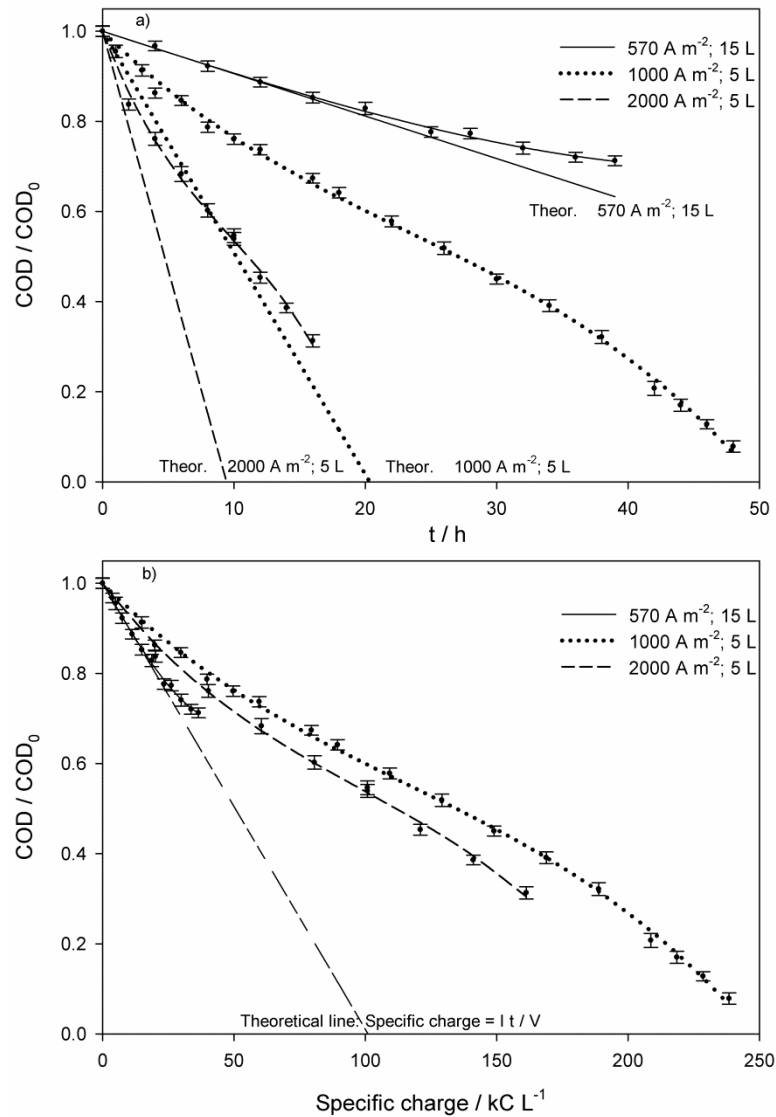


Figure 5.4 - (a) Normalized COD variation with time for the electrodegradation assays performed at different current densities, at a flow rate of 360 L h^{-1} . (b) Normalized COD variation with specific charge for the electrodegradation assays performed at different current densities, at a flow rate of 360 L h^{-1} . Error bars refer to the standard deviation of the normalized COD mean values.

According to the model previously proposed in the literature for electrolysis under current limited control [62], i.e., at maximum current efficiency, the trend of COD during electrochemical oxidation can be predicted by Equation (2.33). Thus, theoretical slopes of COD vs. time, $I/4FV$, were calculated for each of the assayed current intensities. The comparison between these theoretical slopes and the experimental curves (Figure 5.4a), for equal recirculation volume, shows that the discrepancy between experimental data and predicted slopes slightly decreases with current density. This can be explained if one assumes that the degradation process happens also by indirect oxidation. The increase in the leachate recirculation volume also seems to contribute to an increase in the efficiency of the process, due to the lower ratio electrode area/treated volume. In fact, when the volume is increased,

keeping the same anodic area, the quantity of the compounds that are more easily degraded and that behave ideally augments. Thus, their concentration is kept higher for longer times when the recirculation volume is increased.

The effect of applied current on the trend of the COD with the specific charge consumed during the treatment (Figure 5.4b) is less pronounced than the effect on the variation of COD vs. time. For equal leachate volume, an increase in current density leads to a more efficient use of the electric charge, since the experimental curve for 2000 A m^{-2} is closer to the theoretical prediction. However, since higher current densities imply higher potentials, although the electric charge is more efficient the energetic consumption can be higher. Figure 5.4b also shows that an increase in the leachate recirculation volume approaches the experimental results to the theoretical prediction.

To try to improve the current efficiency, assays were performed with successive decreases in current density, by steps, during the oxidation process, at different recirculation flow rates. In Figure 5.5 it can be observed the variation of normalized COD with specific charge for the assays run at constant (2000 A m^{-2}) and variable current density (5 h at 2000 A m^{-2} + 5 h at 1000 A m^{-2} + 10 h at 570 A m^{-2}), at a flow rate of 360 L h^{-1} . COD removal seems to depend only on the charge passed. Variation of normalized COD with time (Figure 5.5, inset) shows that during the first five hours, where the applied current density was equal, no difference can be seen in the COD removal rate. But, when the applied current density decreases, in the assays with steps, a decrease in the COD removal rate can be observed.

The influence of the recirculation flow rate in the electrochemical oxidation performance of the assays that were run with current density decreased by steps during the experiment was also studied. Figure 5.6 shows the normalized COD variation with the specific charge consumed for the assays performed with three or four current density steps at different recirculation flow rates: three steps, 5 h at 2000 A m^{-2} + 5 h at 1000 A m^{-2} + 10 h at 570 A m^{-2} , flow rates of 160 and 360 L h^{-1} , leachate volume 5 L; four steps, 4 h at 2000 A m^{-2} + 4 h at 1500 A m^{-2} + 4 h at 1000 A m^{-2} + 4 h at 570 A m^{-2} , flow rates of 100 and 950 L h^{-1} , leachate volume 10 L. The theoretical curves at these conditions are also presented. A slight variation in the trend of the COD depletion was observed, pointing to better removals at higher recirculation flow rates. The same behaviour is observed when normalized COD variation with electrolysis time is plotted (Figure 5.6, insets). The discrepancy between experimental values and theoretical curves, after the first step of the assays, indicates a high loss in current efficiency that increases when current density is further decreased during the steps process. Comparing the discrepancy between experimental values and theoretical curves for three and four steps, it can be concluded that charge efficiency is higher when four steps are applied, although this fact must be also related with the higher recirculation volume of leachate used in the four steps experiments.

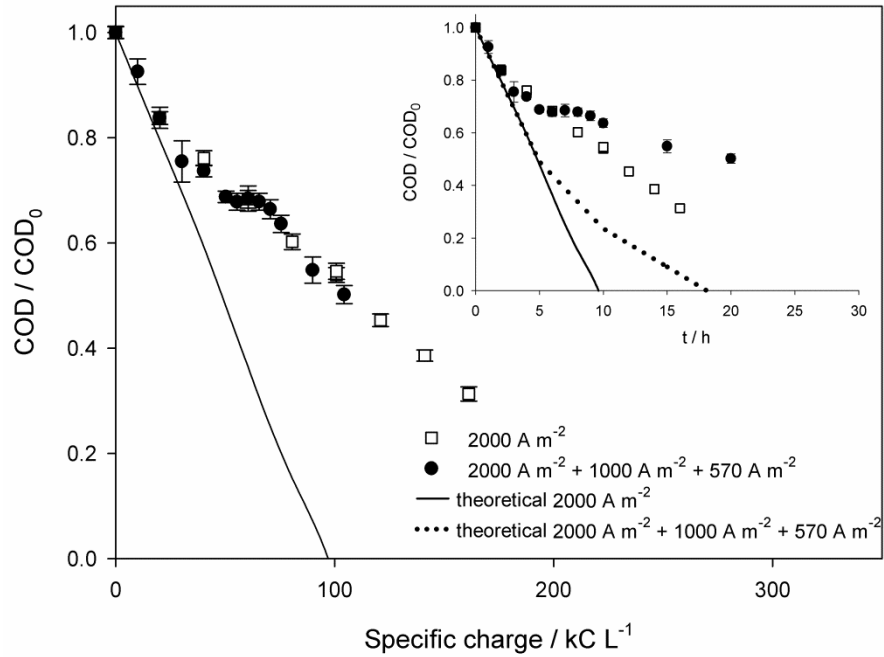


Figure 5.5 - Normalized COD variation with specific charge passed and with time (inset) for the electrodegradation assays performed at constant and variable current density, at a flow rate of 360 L h^{-1} , with a leachate volume of 5 L. Error bars refer to the standard deviation of the normalized COD mean values.

Nitrogen removal was also assessed. In Figure 5.7 are plotted the normalized variation with time of ammonia nitrogen and of total nitrogen. Both parameters present similar behaviour of that described for COD in these assays, i.e., a decrease in the applied current density, in the steps assays, leads to a decrease in the nitrogen removal rates. It can be seen that, for the experiments performed at 2000 A m^{-2} , an increase in the removal rate is observed after eight hours assay. This fact is consistent with previous reports from other authors [78], which indicate that while BDD anodes promotes the generation of hydroxyl radicals, the high content of chloride induces the simultaneous formation of free chlorine, causing indirect oxidation of ammonium. In fact, this leachate presents high chloride concentration (4.5 g L^{-1}), thus enhancing the chlorine evolution at lower COD concentrations, justifying the increase in the nitrogen removal rate when COD levels are lower. In contrast to what was observed with COD removal, nitrogen removal is higher when the recirculation flow rate is lower. In fact, at higher flow rates COD oxidation is favoured, chlorine evolution, that is a competitive reaction, is delayed as a consequence and thus it influences and slows down the rate of ammonium removal.

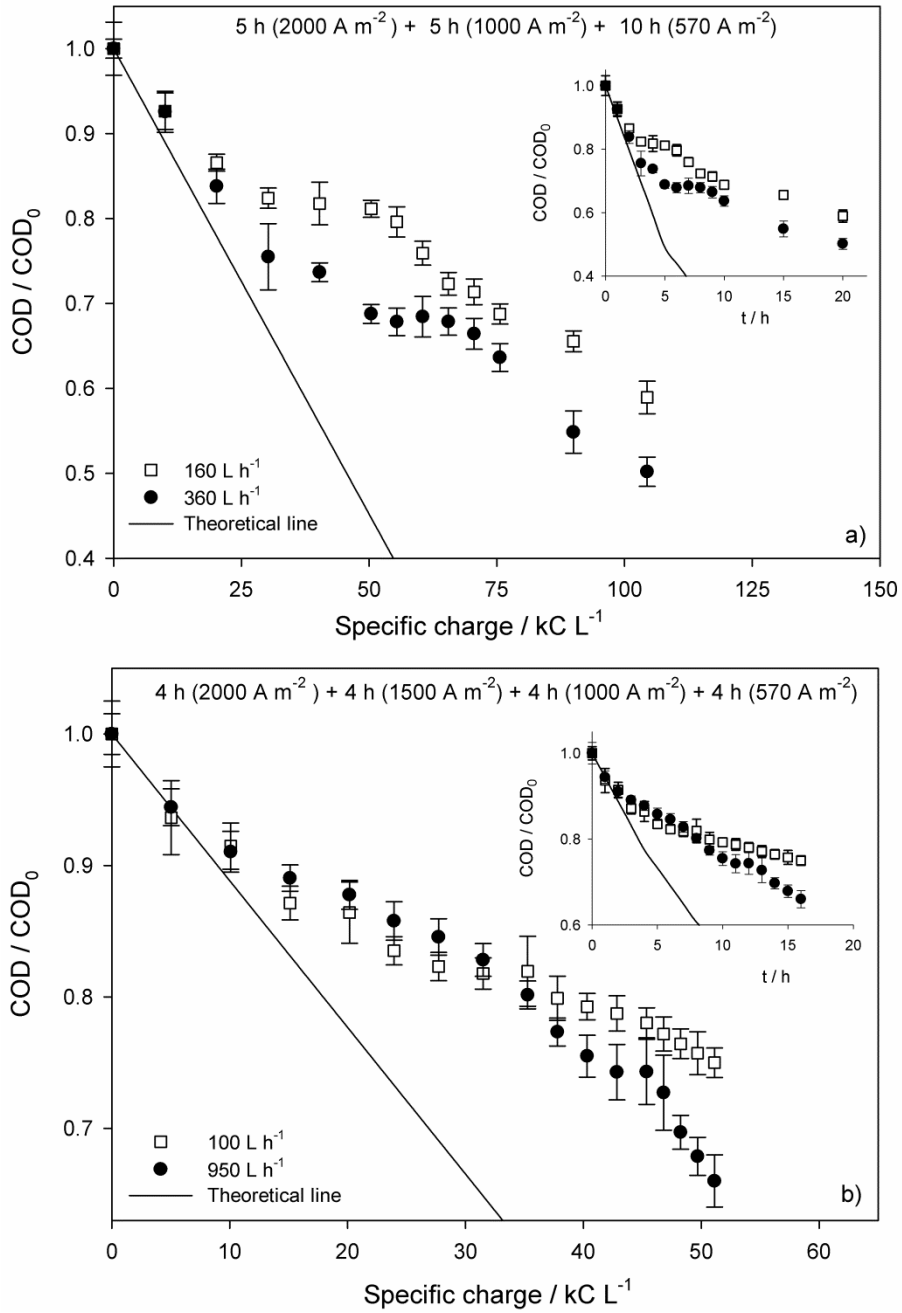


Figure 5.6 - Normalized COD variation with specific charge and with time (inset) for electrodegradation assays performed with (a) three current density steps, with a leachate volume of 5 L and with (b) four current density steps, with a leachate volume of 10 L. Error bars refer to the standard deviation of normalized COD mean values.

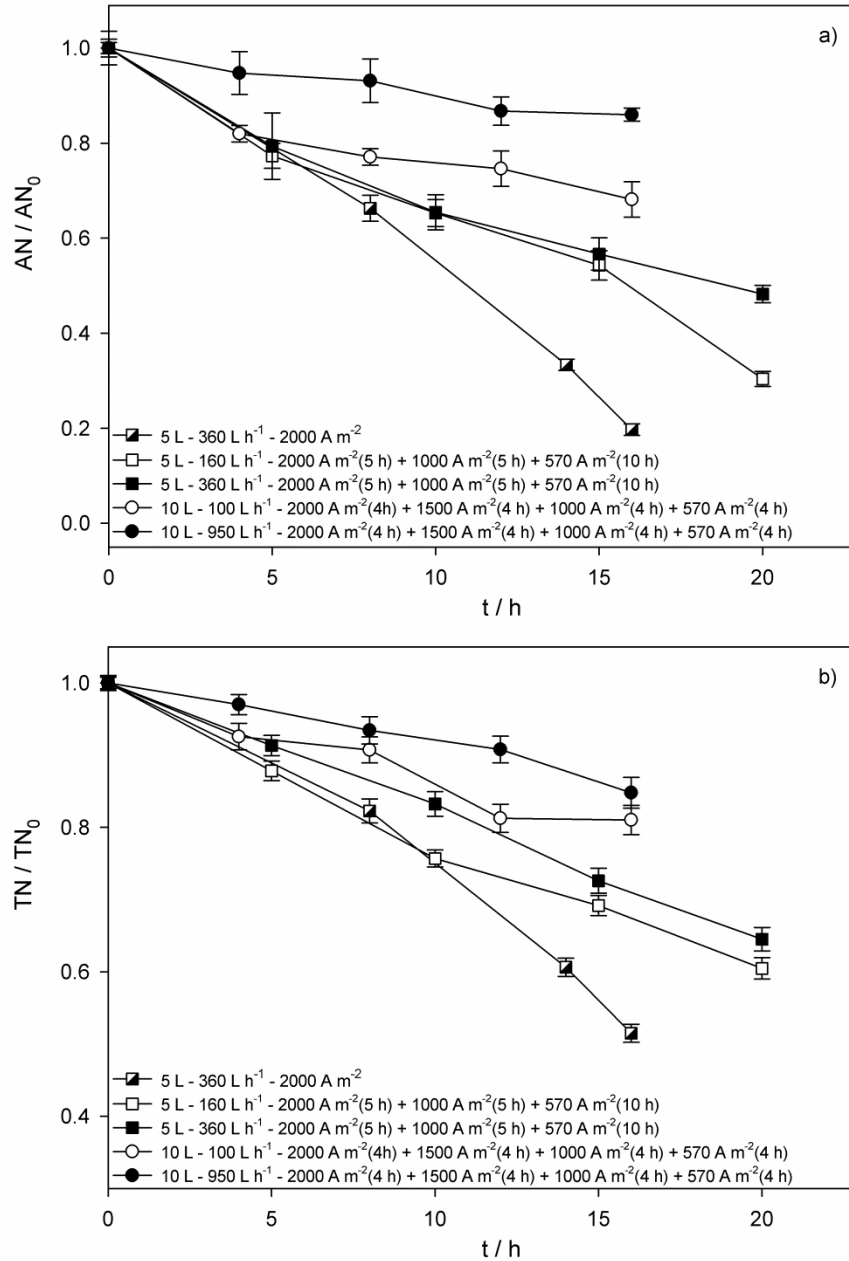


Figure 5.7 - (a) Normalized ammonia nitrogen variation with time for the electrodegradation assays performed at constant current density and at three and four current density steps. (b) Normalized total nitrogen variation with time for the electrodegradation assays performed at constant current density and at three and four current density steps. Error bars refer to the standard deviation of the AN and TN normalized mean values, respectively.

In order to analyse the energy consumption, the specific energy consumptions in W h (g COD)⁻¹ removed were calculated, by means of Equation (2.6). Figure 5.8 reports the specific energy consumption as a function of the time for the different assays performed. The specific energy consumption seems to increase with current density (Figure 5.8a), which is a consequence of the increase in potential when the current density is increased. When constant current density was imposed (Figure 5.8a), there is an increase in the energy consumption during the

first part of the assay, followed by a decrease. This behaviour must be due to the different types of compounds that are present and that are not degraded simultaneously, being first degraded those that are present in higher concentration and, among them, those who have higher diffusion coefficients. The introduction of steps, although leads to an overall decrease in the energetic consumption, did not present the expected results in terms of instantaneous specific energy consumption, since it leads to more irregular consumptions rather than lower consumptions (Figure 5.8b). For these assays, an increase in the recirculation flow rate seems to slightly decrease the IE_{sp} (Figure 5.8c and 5.8d). On the other hand, the increase in the leachate volume being recirculated really decreases the instantaneous specific energy consumption, since the values in the y' axis are much lower in Figure 5.8d (10 L) than in Figure 5.8c (5 L).

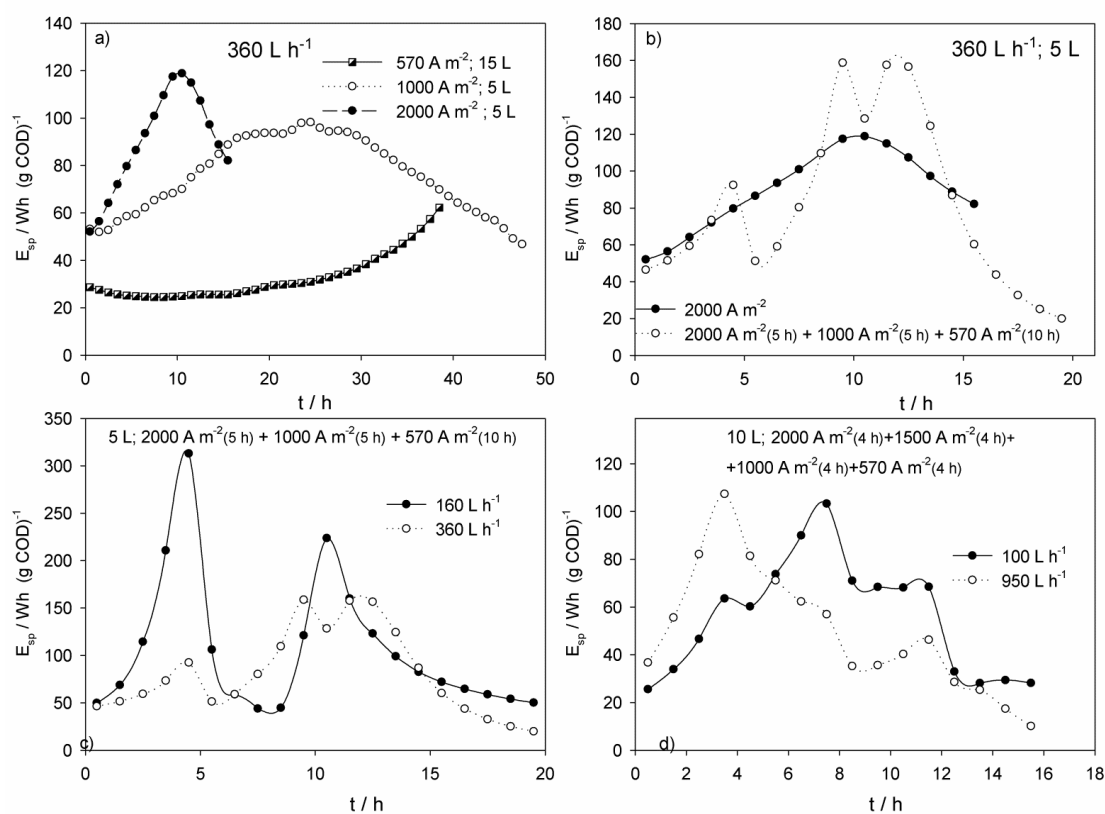


Figure 5.8 - Evolution of specific energy consumption with time for (a) electrodegradation assays performed at different current densities, at a flow rate of 360 L h^{-1} (b) electrodegradation assays performed at constant and variable current density, at a flow rate of 360 L h^{-1} (c) electrodegradation assays performed with three current density steps at different recirculation flow rates, with a leachate volume of 5 L (d) electrodegradation assays performed with four current density steps at different recirculation flow rates, with a leachate volume of 10 L.

The removals in COD, DOC, TN, TKN and AN for all assays performed with current density decreased by steps, as well as the specific energy consumption, are presented in Table 5.6. This table includes also the results obtained in the assay performed at constant current intensity of 2000 A m^{-2} and 360 L h^{-1} recirculation flow rate, in order to allow comparison

between assays performed with and without reduction in the current intensity during the assay. The apparent discrepancy between absolute and percentage values presented in Table 5.6 is due to the variation of the experimental determinations of those parameters for the different assays, due to the complexity and heterogeneity of the leachate suspension. Data reported confirm the previous analysis, showing that for both multiple step designs, with 3 or 4 current density steps, and for a wide range of recirculation flow rate, from 100 to 950 L h⁻¹, an increase in the recirculation flow rate increases COD removal rate and decreases nitrogen removal rate (TN, TKN and AN). Also, it can be seen that DOC removals are always lower than COD removals and these differences increase with flow rate, indicating that a decrease in the flow rate increases the mineralization index. Regarding the energy consumption, an increase in the recirculation flow rate leads to a decrease in the medium energy consumption, mainly because COD removal rate increases with recirculation flow rate.

Table 5.6 - COD, DOC, TN, TKN and AN removals and specific energy consumption for assays performed with one, three and four current density steps at different recirculation flow rates.

Parameter		Experimental conditions				
		16 h (2000 A m ⁻²) V = 5 L t = 16 h	5 h (2000 A m ⁻²) + 5 h (1000 A m ⁻²) + 10 h (570 A m ⁻²) V = 5 L t = 20 h	4 h (2000 A m ⁻²) + 4 h (1500 A m ⁻²) + 4 h (1000 A m ⁻²) + 4 h (570 A m ⁻²) V = 10 L t = 16 h		
		360 L h ⁻¹	160 L h ⁻¹	360 L h ⁻¹	100 L h ⁻¹	950 L h ⁻¹
COD removal	g L ⁻¹	5.42	3.11	4.09	2.56	2.57
	%	69	41	50	25	34
DOC removal	g L ⁻¹	1.35	0.50	0.94	0.61	0.18
	%	44	19	30	15	6
TN removal	g L ⁻¹	1.23	1.04	0.93	0.59	0.36
	%	48	39	35	19	15
TKN removal	g L ⁻¹	1.72	1.11	1.06	0.83	0.33
	%	72	53	45	35	15
AN removal	g L ⁻¹	1.66	0.99	0.95	0.78	0.24
	%	80	60	45	32	14
E _{sp} / W h (g COD) ⁻¹		90	106	81	56	50

According to the aim of this case study, which was to evaluate the application of an EO process at a semi-pilot plant to treat a raw sanitary landfill leachate with low biodegradability index, the following conclusions can be drawn:

- ✓ Organic load removal rate increases with applied current density. This happens mainly because, due to the high organic load content, the electrochemical processes are apparently under current control most of the assay period.
- ✓ An increase in the recirculation flow rate leads to an increase in the organic load removal rate. However, it decreases the nitrogen removal.
- ✓ In the assays performed at semi-pilot scale, by reducing the current density along the electrochemical oxidation process it is possible to reduce energetic costs. Similar results can be obtained by increasing the recirculation flow rate.
- ✓ DOC removals are always lower than COD removals and these differences increase with flow rate. Thus, a decrease in flow rate seems to increase the mineralization index.

The work described in this case study led to the publication of an article in an international scientific journal with scientific arbitration [79] and also to a poster presentation [80].

Chapter 6

Use of EC and EO integrated process in the leachate treatment

The aim of this study was to evaluate the introduction of an EC process before the EO treatment. Experiments performed were divided in case studies 5 and 6 and were conducted according to the conditions described in Chapter 3.

In this chapter the experimental conditions used are described and the results obtained in Case studies 5 and 6 are presented and discussed.

6.1 Case study 5

Use of EC and EO integrated process in the leachate treatment: EC/EO integrated process as pre-treatment vs. polishing step

This study was performed using two different leachates originating from the same landfill site and collected at the same date, one in the stabilization lagoon, Sample B, before the biological treatment, and other after the biological treatment, Sample C. Physicochemical characteristics of the samples are presented in Table 3.1.

To determine the best experimental conditions to treat leachate samples by EC, preliminary studies were performed at constant applied potential. Several different initial pH conditions were studied with applied potentials between 4 and 6 V. To study the effect of stirring in the process efficiency, all the experimental conditions mentioned above were tested with and without stirring.

In Table 6.1 the different experimental conditions tested in these EC experiments are presented. After various elapsed times, the electrocoagulated samples started to precipitate. When massive precipitation was no longer observed, current was turned off and the treated effluent was allowed to settle for 30 minutes and then the supernatant liquid was collected for the analytical determinations.

Table 6.1 - Experimental conditions tested in EC experiments of Case study 5.

Leachate	Leachate volume / L	Stirring / rpm	EC initial pH	EC applied potential / V
B	0.15	0 600	4, 6, 8.6 (natural), 10	4, 5, 6
C	0.15	0 600	4, 6, 7.8 (natural), 10	4, 5, 6

For the combined assays, EC followed by EO, the best EC operational conditions found were applied. After the EC treatment, the formed flocs were allowed to settle, and the suspension was decanted and subjected to filtration, in order to eliminate most of the suspended matter from the liquid mixture. The filtrate was then subjected to the EO treatment. EO assays were conducted for 8 hours using 200 mL of the electrocoagulated effluent. Different applied current densities were evaluated. Table 6.2 shows the EC conditions and the EO variables in the EC/EO integrated treatment.

Table 6.2 - Experimental conditions used in EC/EO experiments of Case study 5.

Leachate	Leachate volume / L	Stirring / rpm	EC initial pH	EC applied potential / V	EO applied current density / A m ⁻²
B	0.45	0	6 natural (8.6)	5	300 100, 200, 300
C	0.45	0	6 natural (7.8)	5 4	300 100, 200, 300

All experiments were run at least twice, at room temperature (22-25 °C) and with no addition of background electrolyte. pH adjustments were made by the addition of concentrated NaOH or H₂SO₄ solutions. When COD (or DOC) removals of both assays differ from more than 10%, assays were repeated, thus guaranteeing that standard deviations of the results presented for these parameters are less than or equal to 10%.

6.1.1 EC/EO integrated process as pre-treatment

The applied potential is an important parameter in EC, since it determines the coagulant dosage and the size of the bubbles produced, and, consequently, the size and growth rate of the flocs [57]. Thus, the influence of the applied potential on the time needed to electroprecipitate the suspensions, and on the COD and DOC removal efficiency, was evaluated and the assays were performed with and without stirring. Table 6.3 presents the results obtained for the electrocoagulation assays performed at natural initial pH with applied

potentials of 4, 5 and 6 V, with and without stirring, and using 0.15 L of raw leachate. The specific iron consumption, Fe_{sp} , in $g L^{-1}$, resulting from the oxidation of the anode, and the specific energy consumption, E_{sp} , in $W h (g COD)^{-1}$, also presented in Table 6.3, were calculated according to Equations (2.3) and (2.6), respectively.

For the assays run at initial pH 8.6, the most significant COD removal was obtained without stirring, at an applied potential of 5 V. In this case, it seems that the stirring makes the aggregates formation more difficult, delaying the precipitation of the suspended and dissolved matter. Regarding the influence of the applied potential, the highest iron consumption was obtained for the unstirred assays at 5 V, which probably explains the highest COD removal obtained at that potential. In almost all assays, removals in DOC were slightly lower than COD removals. In the case of dissolved solids, their values did not suffer significant changes. Regarding conductivity, a reduction was observed for all the assays performed, meaning that the suspension's constituents that most contribute to the conductivity of the solution had precipitated and also that the iron ions formed from the oxidation of the anode are mainly being used in the precipitation of the organic matter. The lowest decrease in conductivity was observed for the assay with the highest specific iron consumption, meaning that this high conductivity must be due to the iron ions that were not used in the precipitation process.

Table 6.3 - Experimental results of EC assays using leachate B, at initial natural pH (8.6), performed with and without stirring and with different applied potentials.

Stirring	stirred			unstirred			
	U / V	4	5	6	4	5	6
EC time / min		30	20	15	20	30	10
$Fe_{sp} / g L^{-1}$		1.1	1.0	1.0	0.8	1.7	0.8
$E_{sp} / W h (g COD)^{-1}$		1.8	2.0	47.6	1.3	1.9	2.1
COD/COD ₀		0.8	0.8	1.0	0.8	0.7	0.8
DOC/DOC ₀		0.9	0.8	1.0	0.9	0.8	0.8
DS/DS ₀		1.0	1.0	1.0	1.0	0.9	1.0
Cond. / Cond. ₀		0.8	0.8	0.9	0.7	1.0	0.9
pH final*		9.8	9.8	9.9	9.8	9.8	9.8

*measured in the filtrate

It has also been established that solution or suspension's initial pH is an important factor which influences the performance of EC process [57]. Thus, samples were subjected to EC performed with different initial pH, besides the initial natural pH of 8.6. The results obtained for the variation of the several parameters used to follow the assays are presented in Table 6.3 (initial pH of 8.6) and Table 6.4 (initial pH of 4, 6 and 10).

Table 6.4 - Experimental results for the EC assays performed using leachate B, in different experimental conditions: with and without stirring, at several initial pH and at various applied potentials.

Stirring	pH 4						pH 6					
	stirred			unstirred			stirred			unstirred		
U / V	4	5	6	4	5	6	4	5	6	4	5	6
EC time / min	55	50	30	40	40	30	50	50	30	55	40	30
Fe _{sp} / g L ⁻¹	3.1	2.5	3.0	1.9	2.5	1.4	2.0	2.8	2.4	2.3	2.9	2.2
E _{sp} / W h (g COD) ⁻¹	2.1	2.3	2.6	1.0	1.7	1.3	1.9	3.1	2.5	2.0	3.6	2.9
COD/COD ₀	0.5	0.5	0.4	0.4	0.4	0.4	0.6	0.6	0.5	0.6	0.6	0.6
DOC/DOC ₀	0.6	0.5	0.5	0.5	0.5	0.5	0.7	0.7	0.7	0.8	0.8	0.9
DS/DS ₀	1.5	1.7	1.5	1.7	1.5	1.6	1.2	1.3	1.2	1.3	1.2	1.0
Cond. / Cond. ₀	1.5	1.5	1.5	1.3	1.6	1.7	1.2	1.2	1.2	1.1	1.3	1.4
pH final*	5.4	4.8	4.4	4.6	4.6	4.4	6.3	6.1	6.0	6.4	6.1	6.1

*measured in the filtrate

Stirring	pH10					
	stirred			unstirred		
U / V	4	5	6	4	5	6
EC time / min	50	30	50	20	20	10
Fe _{sp} / g L ⁻¹	1.4	2.1	2.0	0.9	1.0	0.8
E _{sp} / W h (g COD) ⁻¹	4.2	4.9	-	4.8	6.3	11.9
COD/COD ₀	0.9	0.9	1.0	0.9	0.9	1.0
DOC/DOC ₀	0.9	0.9	0.9	0.9	0.9	0.9
DS/DS ₀	1.3	1.5	1.4	1.3	1.3	1.4
Cond. / Cond. ₀	1.3	1.2	1.1	1.2	1.1	1.0
pH final*	11.9	11.9	11.8	11.9	11.9	11.9

*measured in the filtrate

As it can be seen, stirring has no marked influence on the COD and DOC removal efficiency and the best COD and DOC removals were obtained for the assays run at initial pH of 4. In general, during EC, it was observed an increase on dissolved solid values, being the highest increase obtained for initial pH of 4. This observation may be related with the introduction of sulphuric acid, used to correct the initial pH. Also, with this initial pH the final conductivity was the highest, due to the same reason. A significant increase in pH was observed in the final suspension of all the assays performed. However, this increase was significantly lower in the filtrate of the electrocoagulation effluent (Tables 6.3 and 6.4). So, for the assays run at initial pH of 4, although the best COD and DOC removals were attained, the final result was a suspension that was not easily settled, with a very low pH and a very high conductivity. For the assays run at initial pH of 6, the lowest final COD and DOC observed were obtained in the assays run with stirring, which also promotes a slight tendency to increase final dissolved solids and to decrease final conductivity, when compared with the assay run without stirring, showing almost no effect on the final pH. The assays run with basic suspensions, pH of 8.6 and 10 are those that present results with the same trend, with low COD and DOC removals and a small increase in the final pH. As mentioned previously, the influence of stirring is not

very pronounced for these runs and the main difference is observed at pH of 8.6, where the absence of stirring promotes a quicker settling. The assay run at pH of 8.6, without stirring and with an applied potential of 5 V has shown particular very good settling properties, being, however, the assay with the highest iron consumption among those performed at initial pH of 8.6.

When the results of all the assays are compared, the following conclusions can be drawn: although initial pH of 4 gives the highest load removals, the final solutions present very low pH and very high conductivity; for initial pH of 10, the load removal is poor and final pH and conductivity are high; only assays run at pH of 8.6 present a reduction in the conductivity; regarding the influence of the applied potential, in most of the cases, an increase in the applied potential leads to a decrease in the time needed to form flocs with critical size (EC time), i.e., with enough mass to precipitate.

In Figure 6.1 the specific removals in COD, i.e., COD removed per iron consumed and COD removed per energy consumption, for all the assays performed, are plotted. The most economical treatments, either in iron or in energy consumptions, were obtained for the unstirred assays. The specific removals in COD are very dependent on the time necessary to observe the flocculation, and, in general, this time increased with stirring. Regarding the influence of initial pH, the most economical solutions, in terms of iron and energy consumptions, are obtained in the unstirred assays, at pH 4 and 8.6, by this order. However, according to literature, at pH lower than 5 the amount of iron dissolved from the anode is higher than the one expected from Faraday's law due to chemical attack of the anode by protons [14]. This way, the results obtained at this pH may be due to an extra quantity of dissolved iron that can be used in the precipitation of the organic matter.

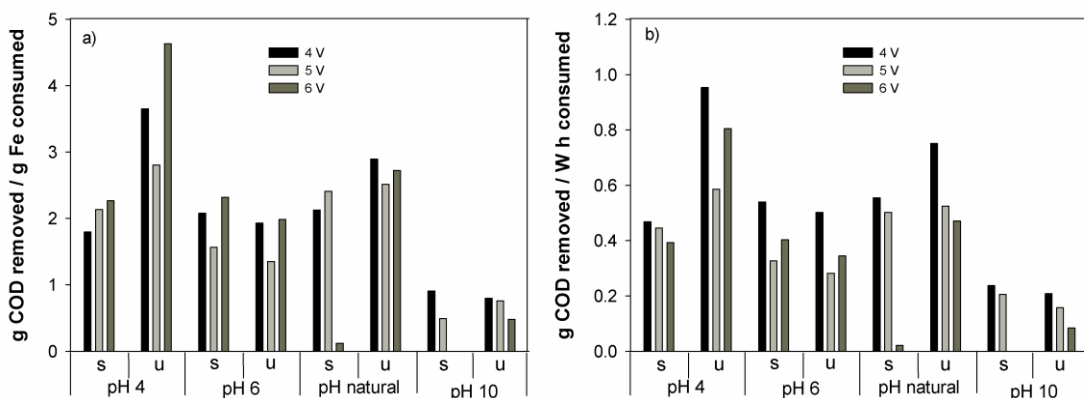


Figure 6.1 - Ratios of COD removed by iron (a) and energy (b) consumption for the electrocoagulation assays performed using leachate B, at different initial pH, stirring conditions and applied potentials.

For this case study, it was proposed the application of a combined process, an EC pre-treatment followed by EO using a BDD anode, either as pre-treatment or polishing step for sanitary landfill leachates. The results of the EC assays described above, performed using a raw leachate, allowed the determination of the experimental conditions that led to high EC efficiencies. Thus, the EC's pre-treatment conditions chosen for the combined treatment were: no stirring, because it leads to quicker settling; applied potential of 5 V, since it is the applied potential that led to a higher removal of COD and DOC; initial pH of 8.6, because it does not require addition of chemicals. Assays were also performed with EC samples of initial pH of 6, in order to evaluate the influence of the initial EC pH in the combined treatment.

The EO was performed at current densities of 100, 200 and 300 A m⁻² for the samples with EC pre-treatment performed at initial pH of 8.6 and at 300 A m⁻² for the sample with EC performed at initial pH of 6. The decays with time of COD, DOC and absorbance, measured at 250 nm, for those assays are presented in Figure 6.2. COD removals increase with applied current density and, for equal applied current density, the COD decay with time is much higher for the assay with the EC pre-treatment performed at pH of 6. However, DOC removal was not influenced by the EC pre-treatment. This means that the pre-treatment influences the way how the mixture undergoes oxidation, without changing the tendency for the mineralization of the compounds present in the solution. Apparently, a pre-treatment at acidic effluent predisposes the mixture to an easier oxidation.

Another conclusion that can be drawn from data presented in Figure 6.2b is that COD and DOC decays for the EO assay carried out at 300 A m⁻², with an EC pre-treatment performed at pH of 8.6, are very similar, pointing to a high degree of mineralization of the organic matter. This tendency was not observed for the EO assay of the sample that had been submitted to an EC pre-treatment performed at pH of 6, where removals of COD and DOC were completely different.

Regarding the absorbance variation with time, it presents the highest decay of all the evaluated parameters, being higher for the EO with the EC pre-treatment performed at pH of 6 (Figure 6.2b). Considering these applied current densities, and since the initial COD content of the samples was high, the degradation process must be controlled by the current. To elucidate this, typical mean mass transfer coefficients, k_m , for this type of samples were obtained from literature ($k_m = 1.75 \times 10^{-5} \text{ m s}^{-1}$ [40]) and from Case study 1 ($2.74 \times 10^{-5} \text{ m s}^{-1}$) and used to calculate the critical COD, i.e., the lowest COD value that, at the applied current density of 300 A m⁻², guarantees the current control, using Equation (2.34). The values of COD_{cr} thus obtained are 910 and 1420 mg L⁻¹, showing that, in fact, the EO assays performed were mainly controlled by current. This way, an increase of COD removal with current density was expected, according to Equation (2.33).

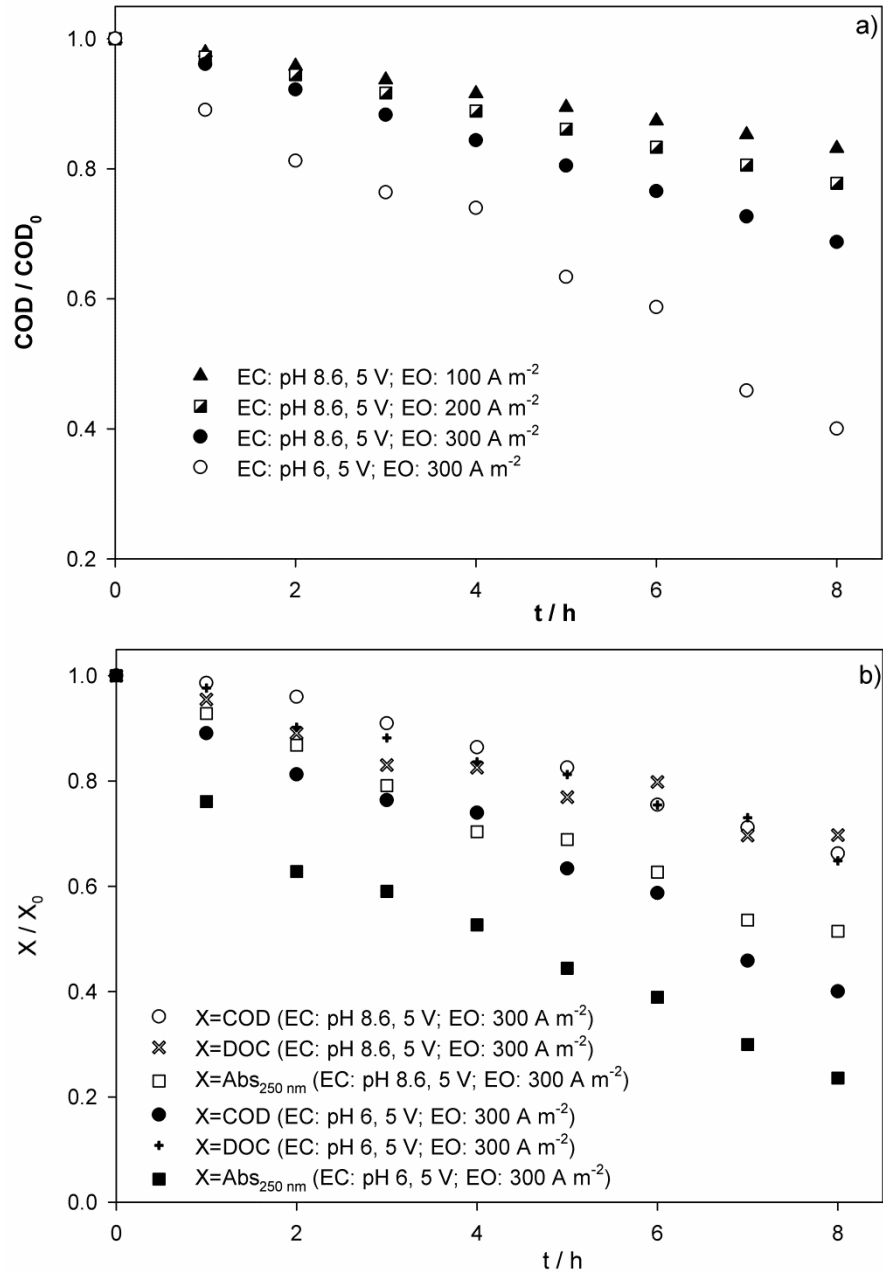


Figure 6.2 - (a) Variation of relative COD with time and (b) decays of relative COD, DOC and Abs in time, measured at 250 nm, for the EO assays run at different current densities, performed with leachate B samples submitted to different EC pre-treatments (initial pH of 6 and 8.6).

For the studied samples obtained from the EC treatment at initial pH of 8.6, as already referred, removals of COD and DOC and absorbance decay increase with current density. However, the observed increase in COD removal with current density was much lower than the expected/theoretical, predicted by Equation (2.33), as can be seen in Figure 6.3, where the theoretical slope is represented, as well as the experimental values for $COD_0 - COD_t$ vs. time and the correspondent fits of linear equations to the experimental values. There are two main reasons for this discrepancy between theoretical and observed values: a not so good

adjustment of Equation (2.33) to experimental data, since it was deduced for model organic compounds and not for such a complex mixture as leachates; and the high formation of humic and fulvic substances [81] that may promote the fouling of the electrode's surface. Regarding this last hindrance, it can be overcome with an increase in current density that increases the applied potential and reduces fouling. However, this increase in current density may lead to a decrease in CE (Table 6.5) calculated using Equation (2.37). In Figure 6.3, it can also be observed that the assay run at the lowest current density fits quite well the theoretical line, which explains the CE of 100%. Regarding the assays run at the highest current density, the one that best approaches the ideal behaviour is that with the EC pre-treatment performed at pH of 6, with a higher CE.

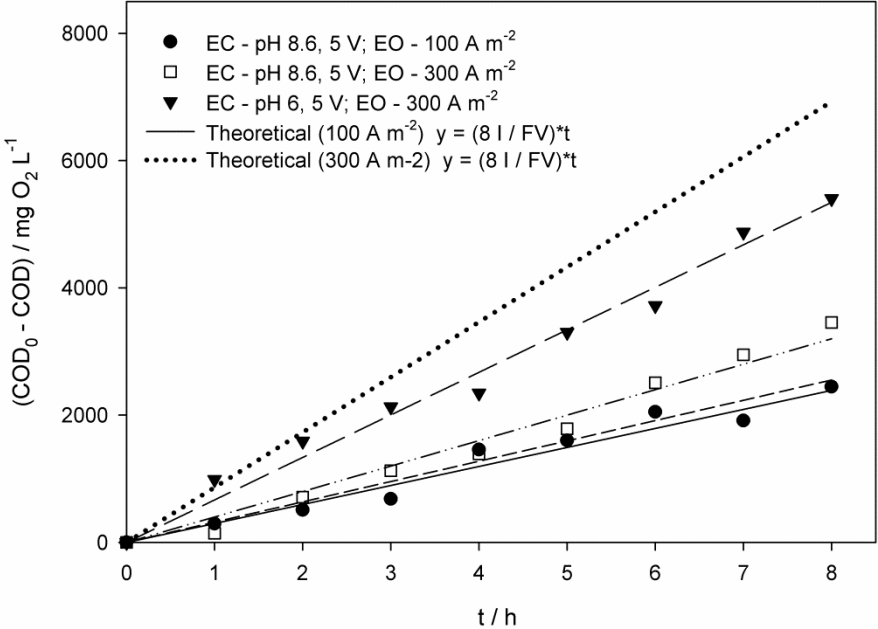


Figure 6.3 - Experimental and theoretical COD absolute removals as a function of time for the EO assays performed at 100 and 300 A m⁻² with leachate B samples submitted to different EC pre-treatments (initial pH of 6 and 8.6).

Comparing the results obtained for the EO assays performed with samples from EC pre-treatment with initial natural pH and initial pH of 6, also presented in Table 6.5 and Figures 6.2 and 6.3, it can be seen that EO assays performed with the sample obtained in EC pre-treatment with initial pH of 6 gave better overall removals of COD and higher current efficiency than those with EC performed at pH of 8.6.

Table 6.5 - Overall results for the samples subjected to EC using leachate B, at 5 V and different initial pH, followed by EO with BDD.

EC pre-treatment conditions		pH 8.6 (natural)	pH 6	
EO experimental conditions		200 mL; 8 h		
j= 100 A m ⁻²	CE (EO) / %	100		
	Total removal (EC+EO) / %	COD	33	--
		DOC	40	--
j= 200 A m ⁻²	CE (EO) / %	62		
	Total removal (EC+EO) / %	COD	47	--
		DOC	42	--
j= 300 A m ⁻²	CE (EO) / %	45	75	
	Total removal (EC+EO) / %	COD	47	72
		DOC	43	43

6.1.2 EC/EO integrated process as polishing step

In order to evaluate the application of an EC/EO integrated process as a polishing step in the treatment of sanitary landfill leachates, a similar study to that described in the previously subsection was performed using a biologically pre-treated leachate, Sample C. The best EC operational conditions, applied to this leachate, were also determined by studying the effect of applied potential, stirring and initial pH.

Table 6.6 presents the results obtained in the EC assays at natural initial pH, with applied potentials of 4, 5 and 6 V, with and without stirring.

Table 6.6 - Experimental results of EC assays using leachate C, at initial natural pH (7.8), performed with and without stirring and with different applied potentials.

Stirring	stirred			unstirred		
	4	5	6	4	5	6
U / V	4	5	6	4	5	6
EC time / min	20	20	20	30	20	20
Fe _{sp} / g L ⁻¹	1.6	1.5	1.7	1.5	1.4	1.8
E _{sp} / W h (g COD) ⁻¹	1.7	2.3	2.8	1.5	2.0	2.5
COD/COD ₀	0.7	0.8	0.7	0.7	0.7	0.7
DOC/DOC ₀	0.7	0.7	0.7	0.7	0.7	0.7
DS/DS ₀	0.9	0.9	0.9	0.9	0.9	0.9
Cond. / Cond. ₀	1.2	1.2	1.1	1.2	1.1	1.1
pH final*	9.6	9.5	9.4	9.5	9.6	9.5

*measured in the filtrate

Results show that stirring did not have a marked influence on COD removal, although the results obtained in the unstirred assays were slightly better. Furthermore, in the assays performed without stirring lower iron and energy consumptions were found. The higher COD removal was obtained without stirring, at an applied potential of 6 V. The higher COD removal was obtained without stirring, at an applied potential of 6 V. Regarding the influence of the applied potential, the highest iron consumption was also obtained for the unstirred assays at 6 V, which probably explains the highest COD removal found at that potential. Taking into account the specific energy consumption, EC performed without stirring at 4 V is the best choice for assays at natural initial pH.

The results achieved in the EC treatment performed at different initial pH of the natural (Table 6.7) also indicate that stirring has little effect in COD, in accordance with what was observed at natural pH.

Table 6.7 - Experimental results for the EC assays performed using leachate C, in different experimental conditions: with and without stirring, at several initial pH and at various applied potentials.

Stirring	pH 4						pH 6					
	stirred			unstirred			stirred			unstirred		
	U / V	4	5	6	4	5	6	4	5	6	4	5
EC time / min	30	30	20	20	20	10	30	40	25	30	20	20
Fe _{sp} / g L ⁻¹	1.8	2.2	1.6	1.3	1.2	1.1	1.5	2.1	2.2	1.7	1.3	1.6
E _{sp} / W h (g COD) ⁻¹	0.9	1.4	1.0	0.6	0.7	0.9	1.1	2.0	2.7	1.5	1.4	2.0
COD/COD ₀	0.3	0.3	0.2	0.2	0.3	0.4	0.5	0.5	0.6	0.6	0.6	0.6
DOC/DOC ₀	0.6	0.8	0.6	0.4	0.4	0.3	0.6	0.6	0.6	0.6	0.6	0.7
DS/DS ₀	0.8	1.3	0.9	1.2	1.1	1.0	0.9	1.0	1.0	0.9	1.2	1.0
Cond. / Cond. ₀	1.1	1.1	1.1	1.2	1.5	1.4	1.0	1.2	1.1	1.1	1.1	1.1
pH final*	4.5	4.7	4.5	4.3	4.3	4.2	7.2	7.1	7.4	6.9	6.8	7.0

*measured in the filtrate

Stirring	pH10					
	stirred			unstirred		
	U / V	4	5	6	4	5
EC time / min	30	20	10	30	20	20
Fe _{sp} / g L ⁻¹	1.2	1.3	0.9	1.3	1.2	1.9
E _{sp} / W h (g COD) ⁻¹	1.1	1.1	1.0	1.0	1.1	1.6
COD/COD ₀	0.6	0.5	0.6	0.6	0.6	0.4
DOC/DOC ₀	0.9	1.0	0.9	0.8	0.8	0.8
DS/DS ₀	1.0	1.0	0.9	1.0	1.0	1.0
Cond. / Cond. ₀	1.3	1.2	1.2	1.2	1.1	1.2
pH final*	12.9	13.4	12.7	12.7	12.5	12.7

*measured in the filtrate

The highest COD and DOC removals were attained at initial pH of 4 with final solutions presenting a pH around 4 in the filtrate and with an increase in conductivity, especially in the unstirred assays. These results are similar to the ones obtained with the raw leachate. Regarding iron consumption, if assay performed at pH of 10 with 6 V is excluded, the lower consumes at identical stirring and applied potential conditions were obtained for the initial pH of 10. However, those assays led to lower organic load removals with very high final pH in the filtrates.

For all the conditions tested, there was found an increase in conductivity during the treatment, probably due to two different reasons: the correction of the initial pH and the high energy consumptions, which may allow simultaneously degradation of the organic matter, originating low molecular mass compounds, besides the electrocoagulation/flocculation effect.

In Figure 6.4, the specific removals in COD, i.e., COD removed per iron and per energy consumption, are plotted. For almost all the initial pH and applied potential tested, the most economical treatments, either in iron or in energy consumptions, were obtained for the unstirred assays. The specific removals in COD are very dependent on the time necessary to perform the electrocoagulation, i.e., to observe the flocculation, and, in general, the electrocoagulation times increased with stirring. The most economical solution is obtained at pH of 4, in the unstirred solution, followed by the assays performed at initial pH of 10 with stirring. Higher energy and iron consuming were obtained at natural pH.

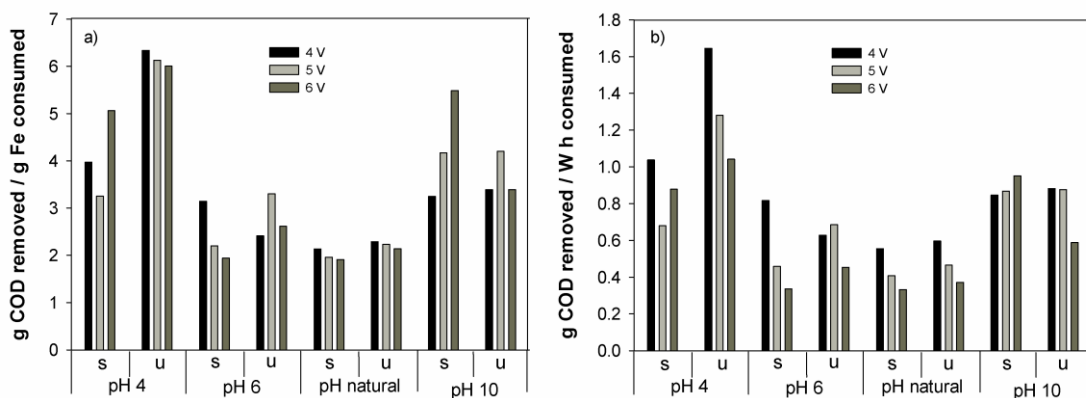


Figure 6.4 - Ratios of COD removed by iron (a) and energy (b) consumption for the electrocoagulation assays performed using leachate C, at different initial pH, stirring conditions and applied potentials.

For the combined process, EC followed by EO using a BDD anode, and according to the results obtained in the EC experiments, the following EC pre-treatment conditions were chosen: no stirring, because it leads to quicker settling; natural pH (7.8), because it does not require addition of chemicals; applied potential of 4 V, since it is the applied potential that led to lower specific energy consumptions. Assays were also performed with EC samples of initial pH

of 6 treated at 5 V, in order to evaluate the influence of the initial EC pH in the combined treatment. Although initial pH of 4 gives higher load removals than initial pH of 6, it involves the addition of high amounts of acid, due to the buffer effect of leachates, and final solutions present very low pH. Among the EC assays run at initial pH of 6, the one performed at 5 V presented the lowest specific iron and energy consumptions.

EO experiments were performed at current densities of 100, 200 and 300 A m⁻² for the samples with EC pre-treatment performed at initial natural pH and at 300 A m⁻² for the sample with EC performed at initial pH of 6. Table 6.8 presents a summary of the results obtained after EO assays, performed at different current densities, using the samples with different EC pre-treatments: without stirring, at two different initial pH values, natural and 6. This table also includes the average current efficiency for the EO experiments.

Similarly to what was observed in the combined experiments with the raw leachate, during the EO assays obtained with the EC treatment at natural pH, COD removal increases with applied current density, indicating that the process is running at current control. This was the expected behaviour attending to the analysis presented above with the raw leachate results.

Table 6.8 - Overall results for the samples subjected to EC using leachate C, at different potential and initial pH, followed by EO with BDD.

EC pre-treatment experimental conditions		Initial pH	7.8	6
		Potential / V	4	5
EO experimental conditions		200 mL; 8 h		
j= 100 A m ⁻²	Removal (EO) / %	COD	46	--
		DOC	6	--
		Abs (250 nm)	51	--
	CE (EO) / %		100	
	Total removal (EC+EO) / %	COD	58	--
		DOC	25	--
j= 200 A m ⁻²	Removal (EO) / %	COD	68	--
		DOC	10	--
		Abs (250 nm)	20	--
	CE (EO) / %		100	
	Total removal (EC+EO) / %	COD	75	--
		DOC	28	--
j= 300 A m ⁻²	Removal (EO) / %	COD	75	68
		DOC	38	33
		Abs (250 nm)	73	83
	CE (EO) / %		93	85
	Total removal (EC+EO) / %	COD	81	75
		DOC	50	52

Regarding DOC removal, although it also increases with current density, it presents much lower values than those of COD removal, maybe due to low mineralization of the organic matter.

The influence of the EC pre-treatment pH conditions in the EO treatment was also studied for the applied current density of 300 A m^{-2} . The results for these assays, also presented in Table 6.6, show that better COD and DOC removals were obtained in the EO performed with the pre-treated EC sample at natural initial pH. These results are just the opposite from those obtained with raw leachate.

The decays in time of relative COD, DOC and absorbance, measured at 250 nm, for the assays run at 300 A m^{-2} are depicted in Figure 6.5. The assay run at higher pH (7.8) shows a more regular decay of all the parameters used to follow the experiment, being the COD decay almost linear with time, typical from a current controlled process. DOC decay presents an initial resistance, indicating that the oxidation process is not leading to higher mineralization degree. On the other hand, in Figure 6.5b, it can be observed COD and Abs very irregular decays, by steps, probably due to the presence of different species that were formed during the EC pre-treatment at initial pH of 6. These assays also show an increase in relative DOC, only possible by the dissolution during the assay of suspended organic solids. Apparently, after the EC pre-treatment at pH of 6 it was left in suspension organic matter with characteristics that present more resistance to the EO and, thus, lower CE.

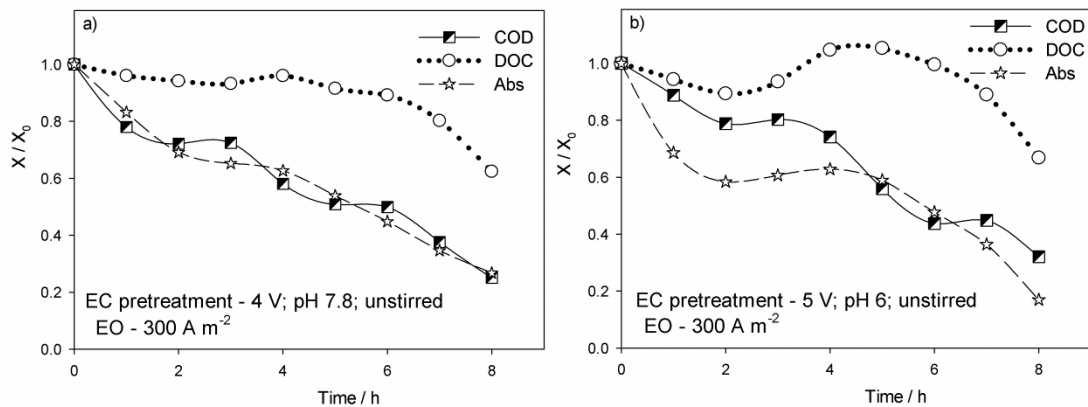


Figure 6.5 - Decays with time of relative COD, TOC and Abs, measured at 250 nm, for EO assays run at 300 A m^{-2} , performed with leachate sample C subjected to different unstirred EC pre-treatments: (a) 4 V, pH 7.8 and (b) 5 V, pH 6.

For current efficiency, the best results were attained for the samples with EC pre-treatment at natural initial pH. These results for the applied current density of 300 A m^{-2} are depicted in Figure 6.6, where the theoretical slope of Equation (2.33) is represented, as well as the experimental values for $\text{COD}_0\text{-COD}$ vs. time and the correspondent fits of linear equations to the experimental values, for all the assays performed at that current density. In fact, the

assays follow a similar behaviour to the theoretical one, especially for the assay with the EC treatment at initial natural pH.

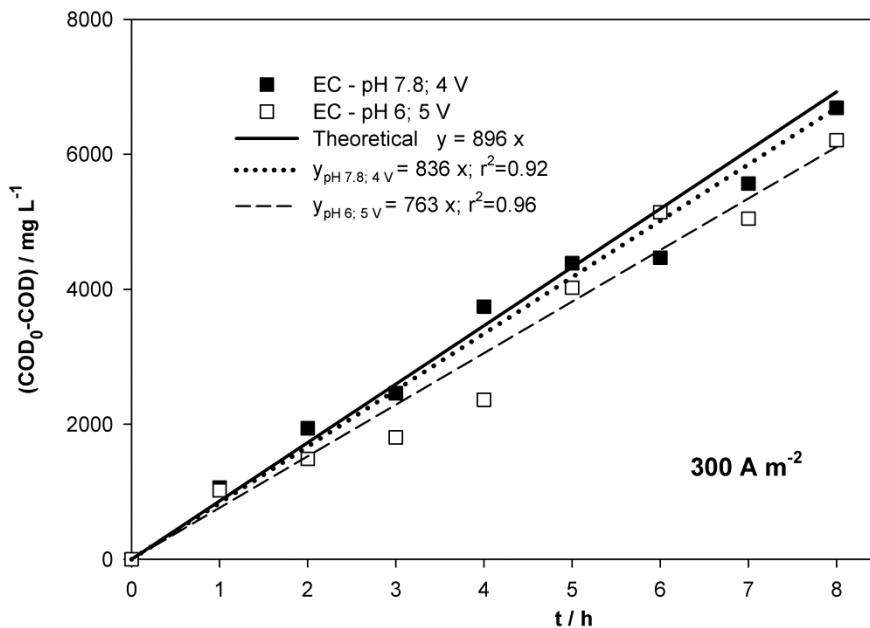


Figure 6.6 - Experimental and theoretical COD absolute removals as a function of time for the EO assays performed at 300 A m^{-2} with leachate C samples submitted to different EC pre-treatments (natural pH, 4 V and pH 6, 5 V).

According to the aim of this case study, which was to evaluate the introduction of an EC process before the EO treatment and their application as a pre-treatment or as a polishing step in sanitary landfill leachates treatment, the resulting main conclusions are:

- ✓ The introduction of an EC process before the EO treatment can be a suitable solution to reduce the electrochemical treatment costs, since it allows organic load removals of about 50% with specific energy consumptions of $2 \text{ W h (g COD)}^{-1}$.
- ✓ The EC/EO integrated process is a feasible solution for sanitary landfill leachate treatment, either as a pre-treatment or as a polishing step. For the best experimental conditions tested it was observed that, when applied to raw leachates, it successfully reduced the organic load, being achieved COD removals of 72%; when applied as polishing step, COD removals of 81% were attained.
- ✓ EC/EO integrated process efficiency is highly dependent on EC pre-treatment conditions.
- ✓ The use of stirring in EC generally increases the time needed to start, with a visible rate, the precipitation of the flocs formed in the electrocoagulation.

- ✓ In EC, an increase in the applied potential enhances the rate of iron oxidation and consequently reduces the precipitation time.
- ✓ Higher COD removals in EC/EO integrated process can be achieved applying higher current densities in EO process.

The work described in this case study led to the publication of two papers in an international scientific journal with scientific arbitration [82,83] and also to an oral scientific communication [84].

6.2 Case study 6

Use of EC and EO integrated process in the leachate treatment: Biodegradability enhancement by EC/EO integrated process

In Case study 5, the feasibility of the application of the EC/EO integrated process as a pre-treatment for sanitary landfill leachates was confirmed. In the present study, the effect of this integrated treatment on the biodegradability of the leachate was assessed, since an increase in the biodegradability would allow the posterior application of a biological step. With that purpose, EC/EO experiments were performed and the biodegradability of the treated samples was assessed. As during EC treatment large quantities of iron are introduced in the suspension, the iron concentration was also monitored during the combined treatment, as well as the concentrations of chromium and zinc already present in the leachate samples.

Since during Case study 5 it was noticed low reproducibility in the experiments run at constant applied potential, it was decided to run some EC tests before the EC/EO biodegradability study, with the aim of improving the EC conditions. Thus, preliminary EC tests were run at a constant applied current intensity of 2.5 A, during a fixed electrolysis time of 3 hours. The effect of initial pH, mild stirring conditions and initial pollutants concentration in the EC process efficiency was assessed.

This study was performed using a raw leachate from Resistrela, collected in the stabilization lagoon, before the biological treatment, at two different dates, February (D) and October (F) 2012. Collected samples characterization is presented in Table 3.1. EC optimization studies were performed with February sample and for the biodegradability study the October sample was used.

Table 6.9 presents the operational conditions of the EC assays performed. After the EC treatment, the formed flocs were allowed to settle for 30 min and then the supernatant liquid was collected for the analytical determinations.

Table 6.9 - Experimental conditions used in EC experiments of Case study 6.

Leachate	Leachate dilution*	Stirring / rpm	EC initial pH
D	1:1	0	4, 6, natural (8.4)
		100	natural (8.4)
	1:2	0	natural (8.4)

* (volumes of raw leachate:volume of total sample)

For the biodegradability study with an EC/EO combined process, EC assays were performed with raw leachate, without dilution, without stirring, and using two initial pH conditions,

natural pH (8.4) and pH of 6. The influence of the EC assay duration was also evaluated, using timed assays of 2 and 3 hours. After the EC treatment, the samples were allowed to settle, and the supernatant phase was submitted to the EO treatment.

In EO experiments three current intensities were evaluated, being the electrolysis time of 8 hours. A scheme of the experimental conditions used is shown in Table 6.10.

Adjustments to the pH were made by the addition of concentrated H₂SO₄ or NaOH solutions. All experiments were conducted at room temperature (22-25 °C) and without addition of a background electrolyte.

Table 6.10 - Experimental conditions used in EC/EO experiments of Case study 6.

Leachate	EC initial pH	EC duration / h	EO applied current density / A m ⁻²
F	6	2	300
		3	300
	8.5	2	300
		3	300, 500, 700

Figure 6.7 shows the results for the variation with time of the normalized COD and DOC for the EC assays performed with leachate D at natural initial pH, where the stirring conditions and the leachate dilution was varied.

Despite results obtained in Case study 5 showed lower pollutants removal for EC stirred assays, in this preliminary EC tests the introduction of stirring at mild conditions (100 rpm) was evaluated with the aim of minimize the electrode passivation, observed during EC assays, increasing the EC efficiency.

Also, in order to evaluate the pollutants concentration effect on EC efficiency, assays were performed where the leachate was diluted with water at 1:2 (volume of raw leachate:volume of total sample). From Figure 6.7 it can be seen that for all conditions tested, near the end of the EC time, for both COD and DOC, a plateau started to be formed, which means that the process is achieving its maximum removals. For the stirred assays, this plateau was noticed earlier on EC time and consequently COD and DOC removals were lower than for unstirred assays. So, even at mild conditions, stirring had a negative impact in EC process, most likely due to the destruction of the formed flocs.

Regarding the assays where diluted leachate was used, despite the COD and DOC removal rates were higher than on the undiluted ones, the absolute removals were much lower (Table 6.11).

The effect of initial pH was studied at three different initial pH values, 4, 6 and 8.4 (natural). Figure 6.8 shows the results for the variation with time of the normalized COD, DOC and TN and also of pH and conductivity evolution for the EC assays performed at different initial pH conditions, without stirring and using leachate D without dilution. No significant differences were found in COD removals for the three pH values studied, although pH of 6 presented a COD removal rate slightly higher than the other ones.

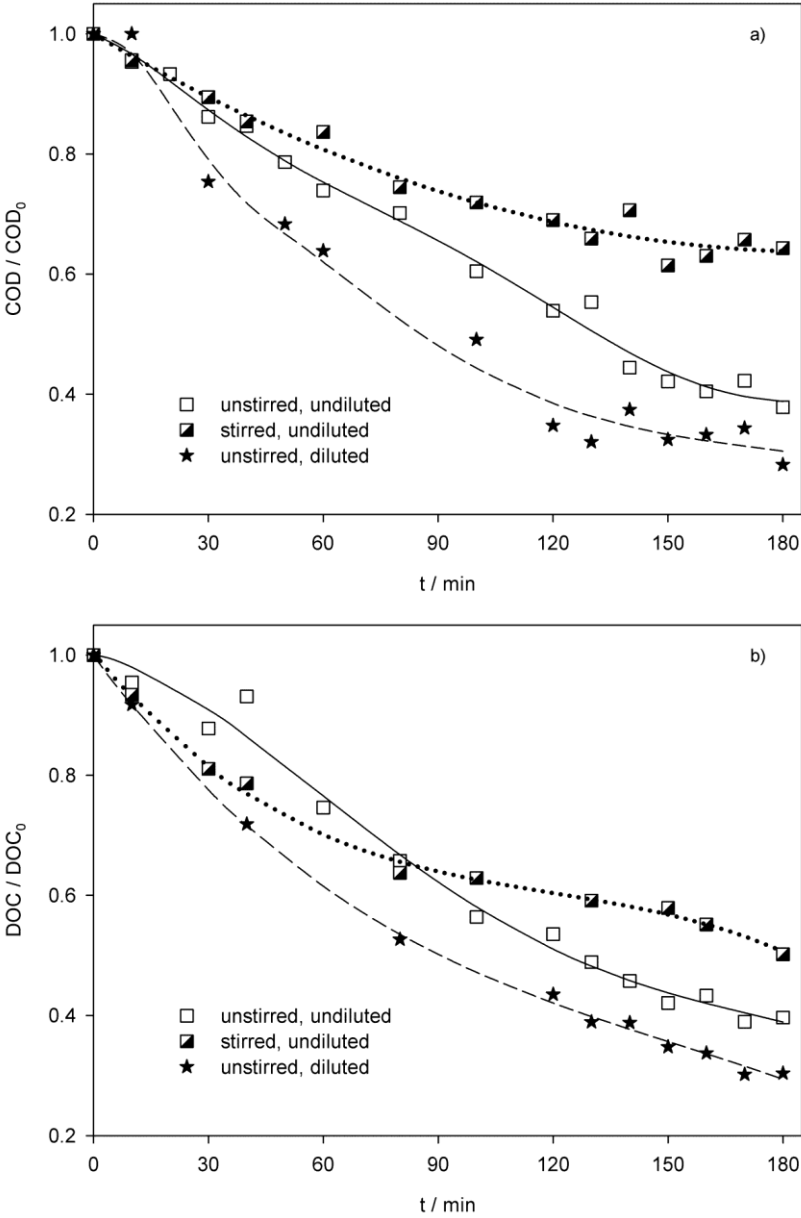


Figure 6.7 - Variation with time of the normalized (a) COD and (b) DOC for the EC experiments with leachate D at natural initial pH, with and without stirring, with and without dilution, 3 h duration and 2.5 A current intensity.

Regarding DOC removals (Figure 6.8b), a more pronounced difference was found between the assays, being the assays at pH of 6 those with higher DOC removals. For assays at pH of 4, for

both COD and DOC, an increase in the parameters values was observed at the beginning of the assay, which seems to be related with the fact that, at a pH of 4, the suspended matter is dissolved and leads to the formation of very fine particles that will later result in aggregates that will sediment. These fine particles take longer time to sediment and will influence the COD determinations, leading to higher values. This behaviour was also noticed in nitrogen decay of the assay performed at pH of 4 (Figure 6.8c), probably due to the reason already presented.

For all the initial pH values studied, nitrogen removals were significantly lower than COD and DOC removals, showing that only some nitrogen forms are prone to be removed by the EC process. Regardless the initial pH value, an increase in pH is observed during the EC assays (Figure 6.8d), being the final pH value of approximately 13, which is related with the formation of hydroxides, responsible for the organic load removal.

Different behaviours were found for conductivity in the different assays, with successive increases and decreases, most likely due to the formation of hydroxides, with high conductivity, and flocs formation and precipitation.

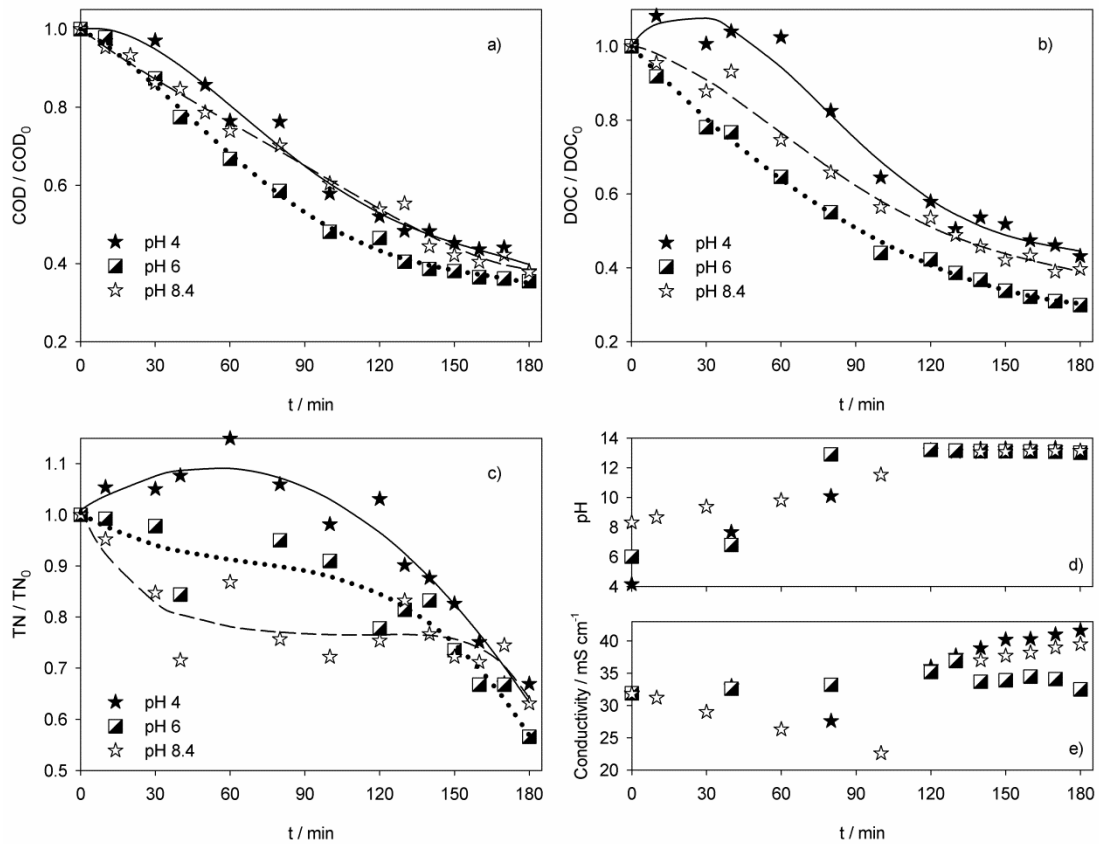


Figure 6.8 - Variation with time of (a) normalized COD, (b) DOC and (c) TN, (d) pH and (e) conductivity, for the EC experiments performed without stirring, using leachate D without dilution, 3 h duration and 2.5 A current intensity.

Table 6.11 presents the final results obtained and the specific energy consumption for the electrocoagulation assays. For the assays performed at different initial pH values, it can be seen that although initial pH of 6 promotes slightly higher removals, the energy consumption is also higher than that obtained for EC assays performed at natural initial pH. Regarding the effect of stirring and dilution on EC efficiency, both showed a negative impact, with a significant increase in the energy consumption.

Table 6.11 - Experimental results for the EC assays performed using leachate D, at 2.5 A, during 3 h, in different experimental conditions: with and without stirring, with and without dilution and at several initial pH.

pH		Natural (8.4)		6	4	
Dilution		Diluted	Undiluted	Undiluted	Undiluted	
Stirring		Unstirred	Stirred	Unstirred	Unstirred	
COD removal	g L ⁻¹	6.0	6.3	11.2	11.8	7.6
	%	72	36	62	64	53
DOC removal	g L ⁻¹	2.3	3.4	4.3	4.5	2.8
	%	70	50	62	67	57
TN removal	g L ⁻¹	0.7	0.8	1.1	1.2	1.0
	%	48	28	41	42	36
Cond. / mS cm ⁻¹		-	-	39.5	32.5	41.6
pH		-	-	13.13	13.02	13.13
E _{sp} / W h (g COD) ⁻¹		31.0	26.2	13.5	15.2	16.2

The results obtained from the EC preliminary tests performed were used to establish the EC experimental conditions of the EC/EO integrated treatment. Thus, in this combined treatment, EC assays were run at 2.5 A, without stirring and without dilution of the leachate sample. Two different initial pH values were assayed, natural pH, since it led to the better results and pH of 6, since results from Case study 5 pointed to an increase in EC/EO integrated treatment efficiency when electrocoagulated samples with an initial pH of 6 were used. Also, two different EC times were applied, 2 and 3 hours, since in the EC preliminary tests it was found that after the second hour of EC, COD and DOC removal rates decreased, meaning a loss of efficiency of the EC process during the third hour. EO assays were performed using a BDD anode and three different applied current densities were evaluated, 300, 500 and 700 A m⁻².

Figure 6.9 shows the results for the variation with time of the normalized COD, DOC and BOD₅ and of the BOD₅/COD ratio for the experiments performed with leachate under the following experimental conditions: EC at initial pH of 6 or the natural pH (8.5), duration of 2 or 3 hours, at an applied current intensity of 2.5 A, followed by EO, for an 8 h duration at 300 A m⁻². It can be seen that an initial pH of 6 enhances the COD and DOC removal rates during the first 2

hours of the electrocoagulation process. For the assays performed during 3 hours of electrocoagulation, the results show a decrease in the COD and DOC removal rates during the third hour, indicating a loss of efficiency of the process during this extra hour of electrocoagulation, as was already reported in the EC preliminary tests.

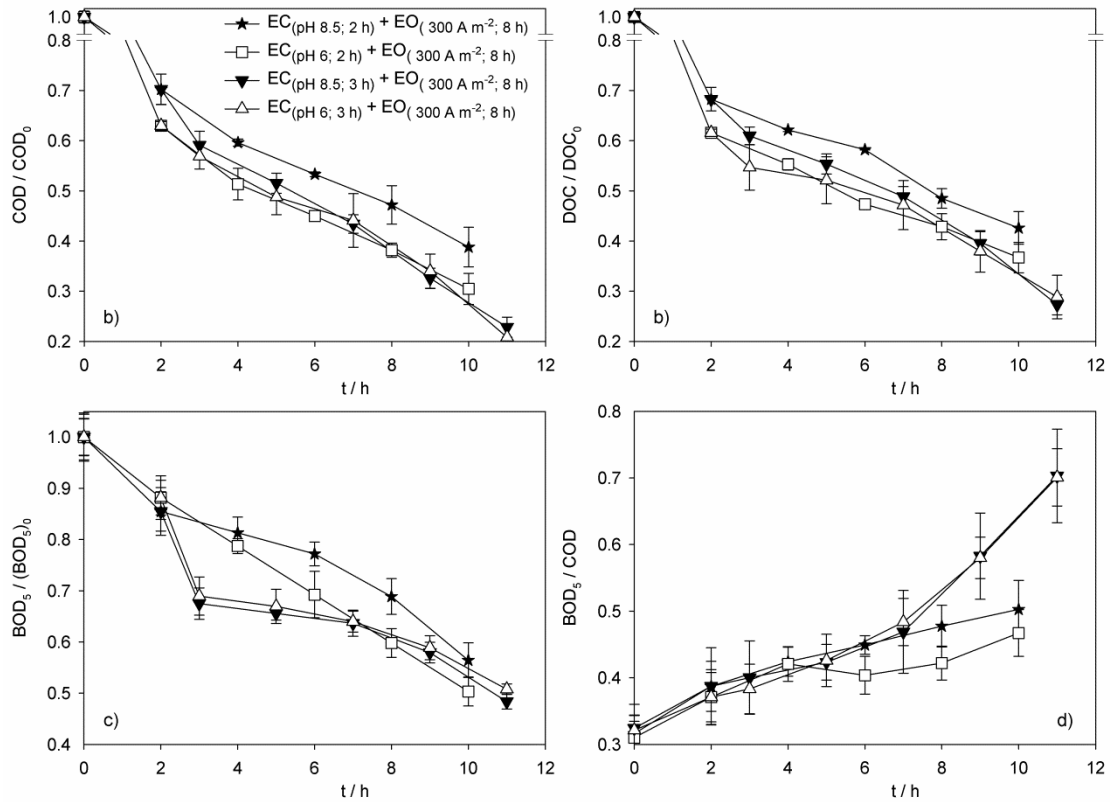


Figure 6.9 - Variation with time of the normalized (a) COD, (b) DOC and (c) BOD₅ and (d) BOD₅/COD ratio for the EC + EO experiments. EC conditions: initial pH of 6 or natural pH (8.5), 2 or 3 h duration, 2.5 A current intensity; EO conditions: 300 A m⁻² current density, 8 h duration. Error bars refer to the standard deviation of the normalized mean values.

Despite the efficiency loss of COD and DOC removal, when electrocoagulation is extended one more hour, the amount of organic load removed at the end of the combined process is higher, indicating that an extra hour of electrocoagulation benefits the combined process. According to these results, and concerning COD and DOC removal, an initial pH of 6 is favourable for the combined process performance when 2 hours of electrocoagulation are performed. However, for the experiments with 3 hours of electrocoagulation, the effect of the pH is not significant, since the amount of COD that was removed after these 3 hours remains essentially unchanged for both of the initial pH values studied.

Analysis of the BOD₅ results (Figure 6.9c) shows that the third hour of EC greatly increases the BOD₅ removal. As a consequence, the BOD₅ removal rate during the EO process is much lower than the one presented by the assays performed with 2 hours of electrocoagulation and at the

end of the combined process, no significant differences can be found in the BOD₅ removals in the assays performed. An initial pH of 6 is favourable in the assays with 2 hours of electrocoagulation, but no influence is found when 3 hours of electrocoagulation are performed.

Regarding the BOD₅/COD ratio (Fig. 6.9d), even though there is no significant difference during the electrocoagulation process, at the end of the combined processes the assays performed with 3 hours of electrocoagulation show higher BOD₅/COD ratios, indicating an important enhancement on the biodegradability index.

For the assays performed with 3 hours EC duration, no significant influence of the initial pH is found. For the combined processes with 2 hours EC duration, adjusting the initial pH to 6 slightly reduces the final BOD₅/COD ratio. In spite of lower BOD₅ and COD removals in the combined process using the initial natural pH, the biodegradability index becomes favourable.

Figure 6.10 shows the results obtained for the nitrogen removal. In the assays performed with 2 hours of electrocoagulation, the initial pH of 6 does not promote enhancement of the removal of any nitrogen forms compared with assays using an initial natural pH. When the initial pH is adjusted to 6, ammonia nitrogen is formed during the first 2 hours of the electrocoagulation process, leading to an increase in AN levels and a low removal of TKN.

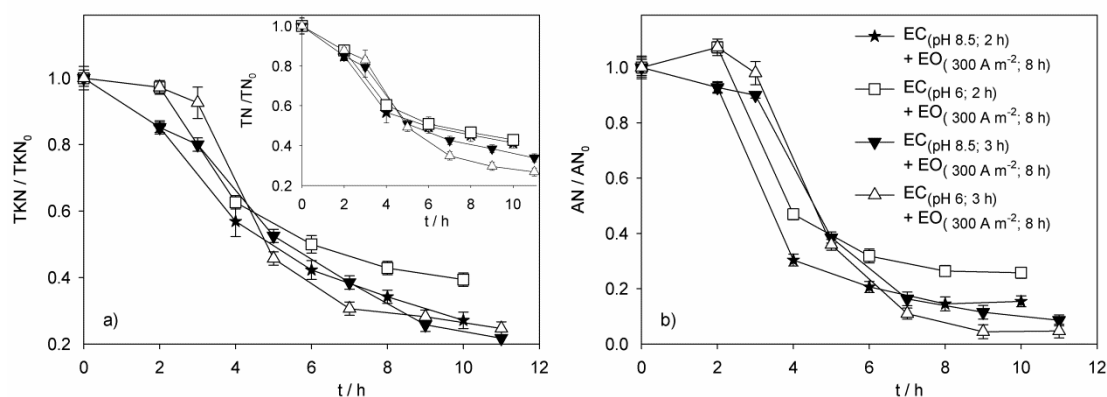


Figure 6.10 - Variation with time of the normalized (a) TKN, TN (inset) and (b) AN for the EC + EO experiments. EC conditions: initial pH of 6 or natural pH (8.5), 2 or 3 h duration, 2.5 A current intensity; EO conditions: 300 A m⁻² current intensity, 8 h duration. Error bars refer to the standard deviation of the normalized mean values.

Although electrocoagulation is here the primary mechanism, simultaneous anodic oxidation and cathodic reduction of the species present in the leachate cannot be excluded and, in fact, similar formation of ammonia nitrogen from organic nitrogen was already reported during electrochemical oxidation in previous works [71,72], being responsible for the low removal of TKN, since TKN comprises organic and ammonia nitrogen forms. Regarding the higher AN levels attained during EC performed at pH of 6 when compared to natural pH, it

must be due to the higher $\text{NH}_4^+/\text{NH}_3$ ratio, observed in acidic conditions, that reduces the elimination of nitrogen as NH_3 by stripping.

During the EC process with an initial pH of 6, the level of TN decreases due to the elimination of the inorganic and organic forms of nitrogen. Extending the electrocoagulation for one more hour improves the nitrogen removals, especially that of ammonium nitrogen, at the end of the combined process. The improvement in nitrogen removal is related to the COD removal, which is also higher in these assays.

For the chloride concentration present in the leachate samples used in this study, the ammonium removal usually occurs at a slower rate than the COD removal. The use of BDD anodes promotes the generation of hydroxyl radicals, while the high content of chloride induces the simultaneous formation of free chlorine, which is responsible for the indirect oxidation of ammonium [78]. Chlorine evolution is enhanced at lower COD concentrations, thus causing indirect oxidation of ammonium.

The pre-treatment, consisting of 3 hours of electrocoagulation at the natural initial pH, was performed to obtain samples to study the effect of the EO applied current intensity on the combined treatment. The three different current densities evaluated were 300, 500 and 700 A m^{-2} .

Figure 6.11a and b shows the normalized COD and DOC variations with time and with applied charge for these assays. Both COD and DOC removal rates increase with applied current density during the EO process, indicating that the process is operating under kinetic control, since COD values are higher than critical COD during most part of the assays duration, according to medium mass transfer coefficients presented in literature [40] and in Case study 1 for leachate samples.

In terms of applied charge, for the applied current density of 300 A m^{-2} , the COD and DOC removal rates are higher, and the removal rates for the other two current densities assayed were identical. This result is due to a higher current efficiency for the lowest current density.

The BOD_5 and BOD_5/COD ratio behaviour during the assays are also shown in Figure 6.11. For the variations in time, it can be observed that the BOD_5 removal rate and the BOD_5/COD ratio are higher for the highest current intensity. However, if these parameters are plotted against the electric charge passed, then the observed differences are small, showing that the efficiency of the different assays is similar due to the high organic load of the samples under study. The best result for the BOD_5/COD ratio, 0.88, was achieved with an applied current density of 700 A m^{-2} after 8 hours of electrochemical oxidation.

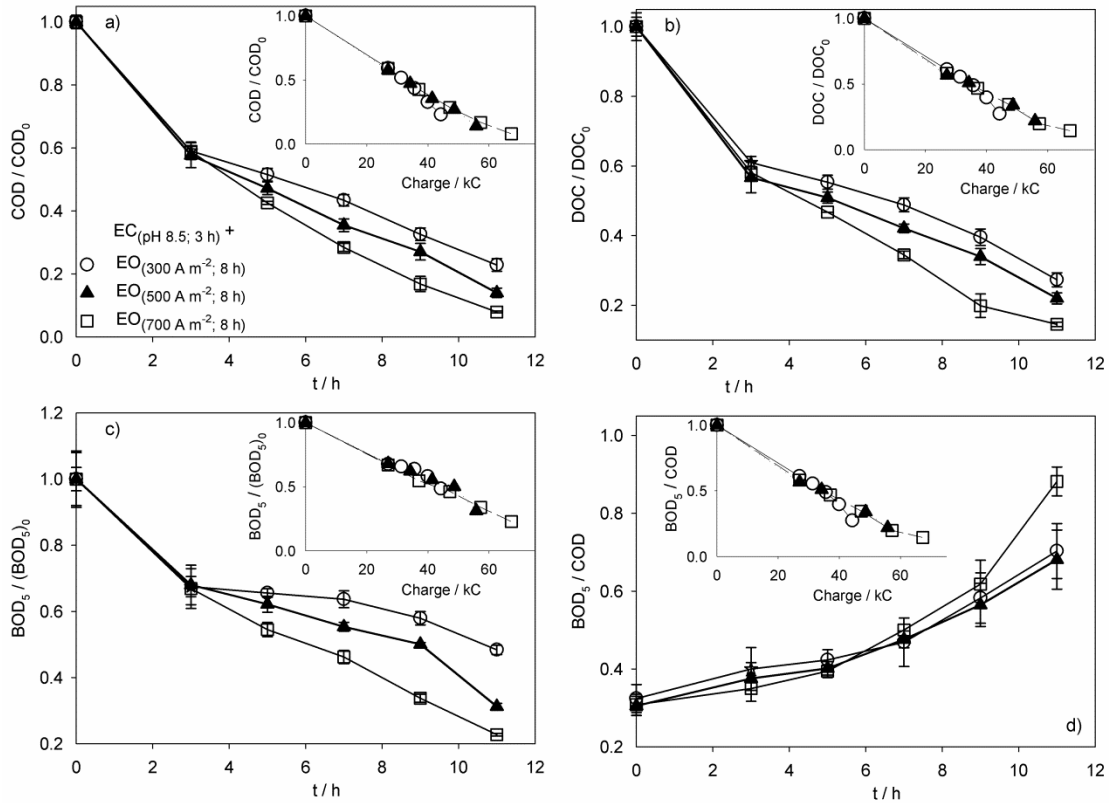


Figure 6.11 - Variation with time and with applied charge (insets) of the normalized (a) COD, (b) DOC and (c) BOD₅ and of the (d) BOD₅/COD ratio for the EC + EO experiments. EC conditions: natural initial pH, 3 h duration, 2.5 A current intensity; EO conditions: current densities of 300, 500 and 700 A m⁻², 8 h duration. Error bars refer to the standard deviation of the normalized mean values.

Figure 6.12 shows the results obtained for nitrogen removal at the different intensities of the applied current. For all forms of the nitrogen measured, at the same applied charge, the higher applied current intensities are associated with lower nitrogen removal rates. These results are not in agreement with some reported in literature [29,40,78], but leachates used in this work possess much higher organic load content and were subjected to an electrocoagulation pre-treatment, which may justify this different behaviour.

To analyse the effect of the different experimental conditions on the energy consumption, the instantaneous specific energy consumption, IE_{sp} , in $W h (g COD)^{-1}$, was calculated using Equation (2.7). Determination of $\partial E / \partial t$ and $\partial(\Delta COD) / \partial t$ was performed by adjusting the polynomial equations to the variations of E and ΔCOD with time, and calculating the corresponding derivatives. Figure 6.13a reports the instantaneous specific energy consumption as a function of time for the assays performed with different initial EC experimental conditions.

Although the energy consumption during the electrocoagulation process at the natural pH is higher for the assays with 3 hours duration, it leads to an extra reduction in the specific

energy consumption during the electrochemical oxidation process, indicating that the extra hour of EC can be beneficial for the entire combined process.

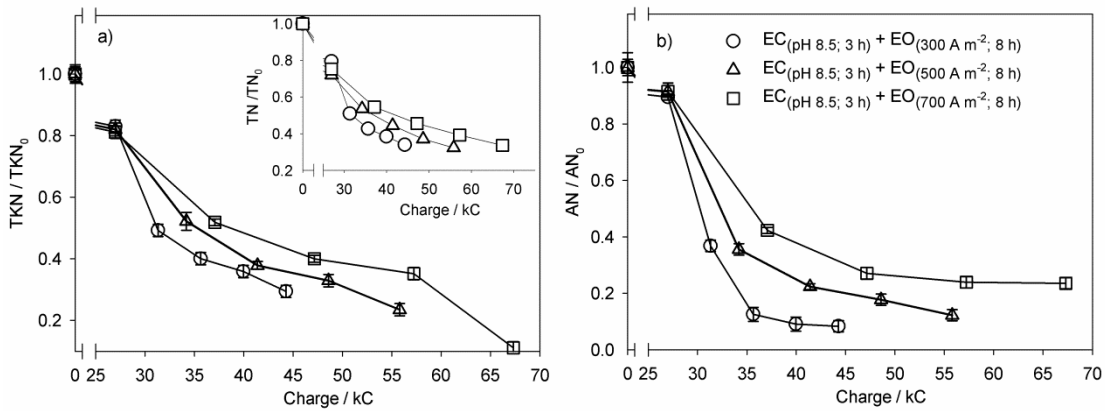


Figure 6.12 - Variation of the normalized (a) TKN, TN (inset) and (b) AN with the applied charge for the EC + EO experiments. EC conditions: natural initial pH, 3 h duration, 2.5 A current intensity; EO conditions: current densities of 300, 500 and 700 A m⁻², 8 h duration. Error bars refer to the standard deviation of the normalized mean values.

However, for these two assays the medium specific energy consumption, E_{sp} , determined as the ratio between the total energy consumption and the total COD removed, is almost equal: 15.1 and 15.4 W h (g COD)⁻¹, for a 2 and 3 hours EC pre-treatment, respectively. For the assays performed with 2 hours of electrocoagulation, the adjustment of the initial pH to 6 promoted a higher organic load removal rate compared with the assay run at an initial pH of 8.5 and presented a more favourable IE_{sp} . This assay shows the lowest medium specific energy consumption of 11.2 W h (g COD)⁻¹. The least favourable E_{sp} result, 17.5 W h (g COD)⁻¹, was obtained for the combined assay with an initial pH of 6 and 3 hours of electrocoagulation. In this case, the extra hour of EC treatment did not lead to a posterior specific energy consumption reduction.

The IE_{sp} values associated with the assays performed at different applied current densities were also calculated, and the IE_{sp} values that corresponded to the EO treatment are presented in Figure 6.13b. The energy costs increase with the current density. For the applied densities of 300 and 500 A m⁻², the energy consumption decreases with time, showing a higher slope for the lowest density. For the highest applied density, the IE_{sp} value increases with time, most likely because at this high current density, the oxidation of most of the organic compounds in solution are diffusion controlled, leading to a lower current efficiency. For these assays, the medium specific energy consumption increases with the applied current density as shown in the following data: 15.4, 21.3 and 21.4 W h (g COD)⁻¹ for the current densities of 300, 500 and 700 A m⁻², respectively.

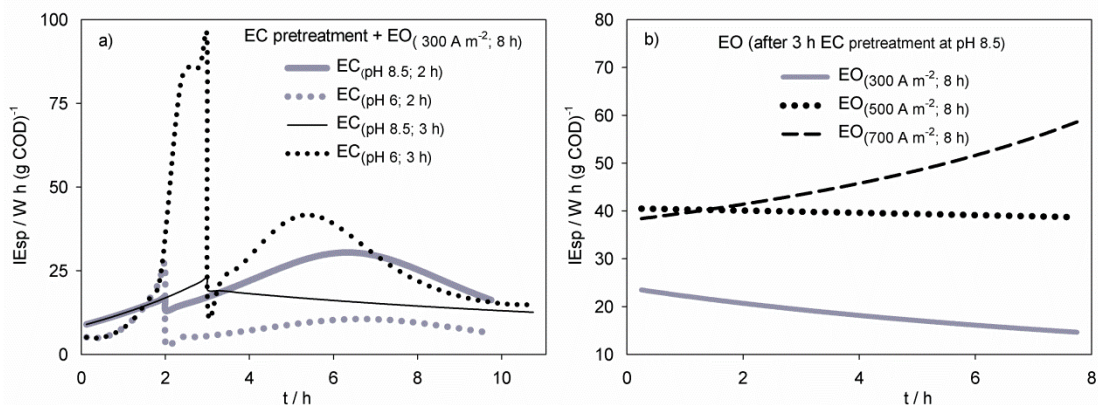


Figure 6.13 - Instantaneous specific energy consumption, I_{Esp} , for the assays performed under the following experimental conditions: (a) EC at an initial pH of 6 or the natural pH (8.5), 2 or 3 h duration, at an applied current intensity of 2.5 A; EO at a current intensity of 300 A m⁻², 8 h duration; and (b) EO at a current density of 300, 500 and 700 A m⁻², 8 h duration, after 3 h of EC pre-treatment, at the natural pH, at an applied current intensity of 2.5 A.

The iron, chromium and zinc concentrations were also monitored. Figure 6.14 presents their variation during the experiments. The variation in iron concentration showed an initial increase followed by a decrease during the EC experiments (Figure 6.14a and b). This fluctuation is mainly due to the iron hydroxide formation and posterior precipitation of the suspended/dissolved matter from the leachate, which is followed by shorter, identical cycles. Similar behaviour was also reported in the literature [85]. The initial increase in the iron concentration is higher in the assay performed at an initial acidic pH, due to an extra dissolution of the electrode by the acid effect. This effect leads to a shorter time for the decay in iron concentration in solution. Figure 6.14a and b shows that the conductivity trend follows the iron concentration evolution in time for both of the initial pH conditions studied. The results of the variation of the iron concentration during EO (insets of Figure 6.14a and b) showed an initial sharp decrease followed by a slow, continuous decrease. The correction of the initial pH to 6 leads to a slower removal of the iron from solution. The results of the variation of the chromium and zinc concentrations during EC and EO (Figure 6.14c, d and insets) showed a decrease in concentration during both processes. The decrease in the chromium and zinc concentrations in EC is due to the simultaneous precipitation with the formed flocs and also due to the reduction in the cathode, with the corresponding deposition of metals on the cathode surface; the concentration decrease in EO is mainly due to the latter process.

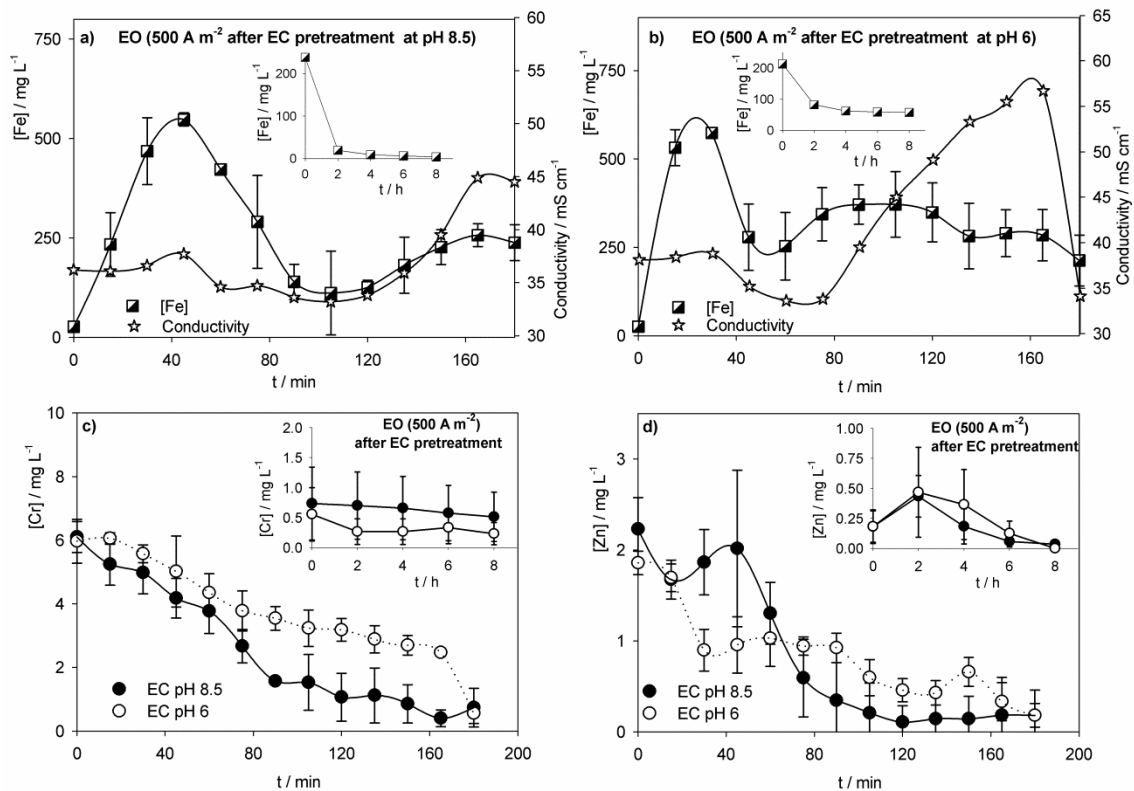


Figure 6.14 - Variation of the iron concentration and conductivity (a and b) and chromium (c) and zinc (d) concentrations with time for the EC + EO experiments. EC was performed at an initial pH of 6 or the natural pH (8.5), for a 3 h duration, at an applied current intensity of 2.5 A; EO (insets) performed at a current intensity of 500 A m⁻², for a 8 h duration. Error bars refer to the standard deviation of the mean values.

Attending to the aim of this case study, which was to evaluate the feasibility of a combined EC/EO process to improve the biodegradability of leachates, the following conclusions can be drawn:

- ✓ The application of two combined electrochemical techniques, electrocoagulation and electrochemical oxidation, can be used to eliminate the recalcitrant organic load from sanitary landfill leachates and to increase their biodegradability. For the most favourable experimental conditions applied (3 h of EC at the natural initial pH followed by 8 h of EO at a current density of 700 mA cm⁻²), an increase in the BOD₅/COD ratio from 0.3 to almost 0.9 was observed, with a 95% COD removal.
- ✓ Cathodic processes can be used to treat the heavy metal content in leachate, because this process reduces the metal ions and deposits them over the cathode. Thus, this combined process can be used to obtain treated leachates, with low content in recalcitrant organic and inorganic compounds, but still with significant organic load, that can be sent to urban wastewater treatment plants comprising biological steps.

- ✓ The combined electrochemical treatments resulted in very high removals of all forms of nitrogen, although the pH correction during EC did not result in enhanced nitrogen removal. Nevertheless, lower nitrogen removal during EC was compensated because the nitrogen removal increased during EO when EC pre-treatment was run at pH of 6.

The work described in this case study led to the publication of a paper in an international scientific journal with scientific arbitration [86] and to two oral scientific communications [87,88].

Chapter 7

Application of Ti/Pt/PbO₂ anodes for the EO of leachates

To evaluate the performance of Ti/Pt/PbO₂ anodes in the electrooxidation of sanitary landfill leachates, experiments with this anode material were run and are presented in Case studies 7 and 8. This chapter gives a description of the experimental conditions used, the obtained results and the main conclusions withdrawn from these case studies. BDD anodes were also used in similar experimental conditions, in order to compare the behaviour of both anode materials.

7.1 Case study 7

Ti/Pt/PbO₂ vs. BDD anode for the EO treatment of a biologically pre-treated sanitary landfill leachate and simulated samples

With the aim of comparing the oxidation ability of Ti/Pt/PbO₂ and BDD anodes in the treatment of a biologically pre-treated sanitary landfill leachate, experiments were performed under the same experimental conditions, using both anode materials. Assays were conducted at an applied current density of 300 A m⁻², at room temperature (22-25 °C), with stirring and using 200 mL of leachate Sample H, at natural pH, and without the addition of a background electrolyte, being electrolysis time 6 hours. The physicochemical properties of the leachate samples used are presented in Table 3.1. Also, to understand the elimination of the different forms of nitrogen present in the leachate samples, assays were also conducted with simulated samples without organic matter. Simulated samples were prepared as follows: NH₄NO₃ - 0.232 g, NH₄Cl - 1.605 g, CaCl₂ - 0.7 g, MgCl₂·6H₂O - 1.42 g, NaCl - 2.472 g and KCl - 2.0986 g and distilled water up to 1 L.

Figure 7.1 presents the results for the variation with time of the normalized COD and DOC obtained from the experiments performed with real leachate and for the two anode materials used in this case study. The variation of the normalized COD with electrical energy consumption is also presented. For both anodes, the DOC removal was less than that of the

COD removal. This behaviour has been reported previously in the literature and in Case study 1 and has been explained by the formation of low molecular mass organic compounds with high degrees of oxidation that resist further oxidation [29]. Despite this behaviour, for the experiments with the BDD anode (Figure 7.1b), the difference between the COD and DOC removal is less pronounced than for the Ti/Pt/PbO₂ anode, suggesting that the BDD anode more easily promotes the complete combustion of the organic matter. Due to the inert surface of BDD anodes, hydroxyl radicals, the main species that mediates the oxidation of the organic compounds, are very weakly adsorbed; consequently, they are very reactive toward the complete oxidation of organics. Alternatively, for Ti/Pt/PbO₂, hydroxyl radicals are expected to be more strongly adsorbed on the surface; consequently, they promote the conversion of the organic matter into more oxidized by-products rather than resulting in mineralization.

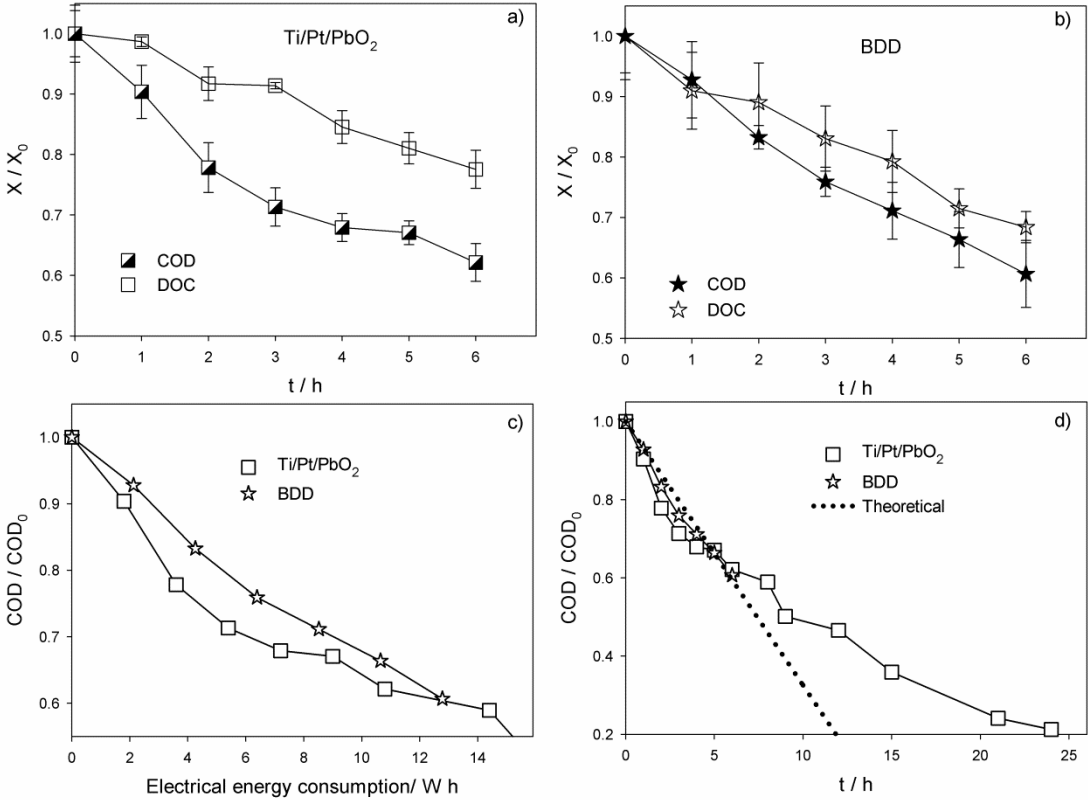


Figure 7.1 - Variation with time of the normalized COD and DOC for the EO experiments performed with real leachate using (a) Ti/Pt/PbO₂ and (b) BDD anodes. Variation of the normalized COD with electrical energy consumption (c) and with time (d) for the two anode materials. Error bars refer to the standard deviation of the normalized mean values.

Comparing the COD evolution with time for both anode materials studied (Figure 7.1d), a similar type of decay was found. When these results are compared with the theoretical trend of COD during electrochemical oxidation, calculated by Equation (2.33), for the first hour's assay, it can be seen that the results obtained with BDD lie over the theoretical line, whereas

the results obtained at Ti/Pt/PbO₂ are slightly better. This result is due to the electrocatalytic effect of the platinum because despite being covered by the metal oxide, platinum peaks are always detected by X-ray diffraction [63], probably due to the porosity of the oxide film.

When the normalized COD is plotted against the electrical energy consumption (Figure 7.1c) calculated based on the potential difference mean values for the assays run with each anode material, which are 6.0 and 7.1 V for Ti/Pt/PbO₂ and BDD, respectively, the best results are obtained for the anode of the metallic oxide. This happens for two main reasons: the lower potential difference presented by the metal oxide for equal applied intensity because it is more conductive than BDD, and the electrocatalytic effect presented by the oxide.

Figure 7.2 shows the results obtained for the nitrogen removal in the experiments performed with real leachate. AN removal is more pronounced for the Ti/Pt/PbO₂ anode, especially in the last hours of the assays. The results obtained for the experiments performed with the BDD anode (Figure 7.2b) show enhanced TKN removal, but both TN and AN demonstrate reduced removal when compared with Ti/Pt/PbO₂ (Fig. 7.2a).

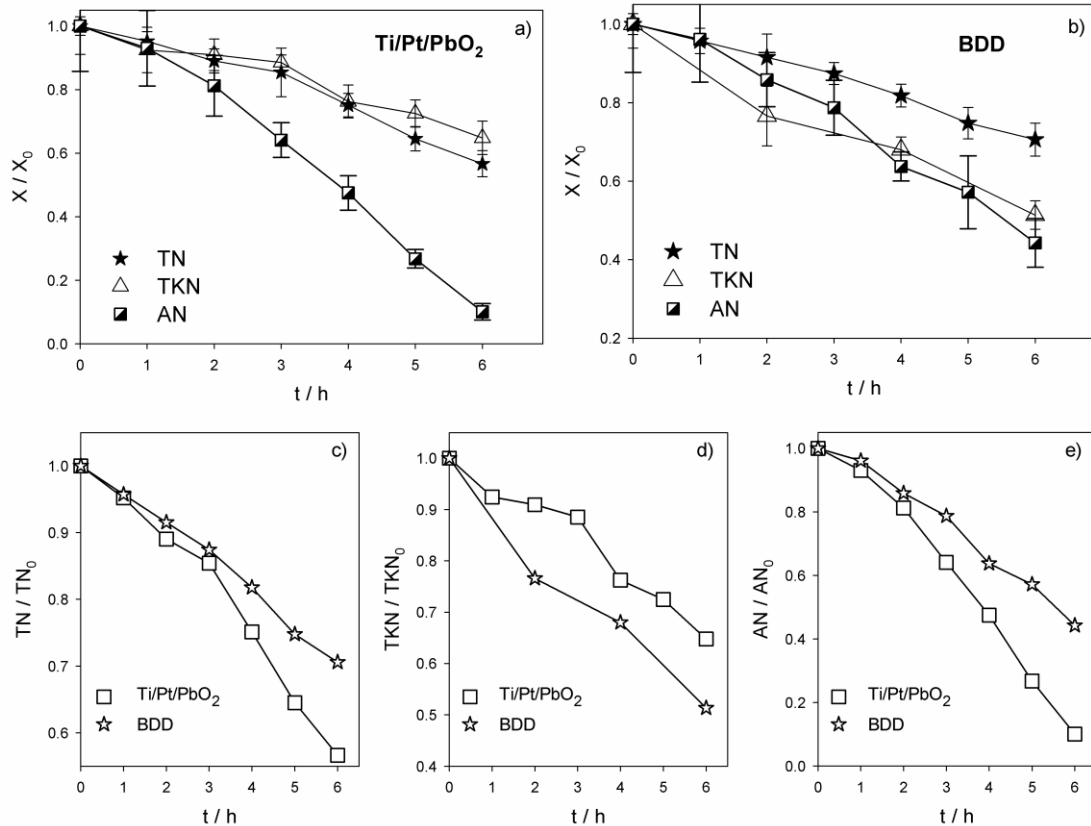
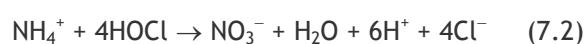
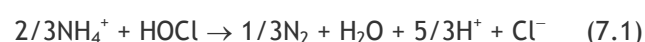


Figure 7.2 - Variation with time of the normalized TN, TKN and AN for the EO experiments performed with real leachate using (a) Ti/Pt/PbO₂ and (b) BDD anodes. Comparison of the results obtained using the two anode materials for (c) TN, (d) TKN and (e) AN. Error bars refer to the standard deviation of the normalized mean values.

At BDD, the TKN and AN decays were identical. This result indicates that BDD is more efficient in the removal of the organic nitrogen, whereas the metal oxide is mostly effective in the removal of the ammonium nitrogen. This finding agrees with the theory previously presented that hydroxyl radicals are weakly adsorbed on BDD and, consequently, they are more proficient in the oxidation of larger molecules with lower diffusion coefficients than metal oxides, which are more effective in the oxidation of smaller molecules with higher diffusion coefficients because their oxidation occurs at the electrode surface where the hydroxyl radicals are strongly adsorbed.

Comparing the COD (Figure 7.1a) and AN (Figure 7.2a) profiles during the EO runs for Ti/Pt/PbO₂, AN removal occurs at a slower rate than that of COD during the first 3 h of the assays. However, when the COD value decreases to approximately 70% of the initial concentration, the AN removal rate increases. Similar results can be found in the literature. Cossu *et al.* [19], using a Ti/Pt anode, reported that the removal rate of AN was lower than that of COD at the initial stage of electro-oxidation and that AN was substantially removed in the subsequent electrochemical oxidation stage when indirect oxidation became prevalent. This increase in indirect oxidation may be enhanced by the formation of chloride-based electrogenerated oxidants, which includes HOCl [25,47]. According to Pérez *et al.* [47], ammonium reacts with HOCl (Equations (7.1) and (7.2)), regenerating chloride ions.



The concentration of chloride, determined by HPLC, is higher for the assays performed with Ti/Pt/PbO₂ anode (Figure 7.3a), indicating that this ion may be involved in the oxidation of ammonium and may be regenerated after that process. Additionally, the metal oxide anode is the most effective in removing the total nitrogen (Figure 7.2c), showing that nitrogen gas is being formed at a higher rate than at the BDD anode, which is more effective at partially oxidizing ammonia to nitrate (Figure 7.3b) [25]. In fact, whereas BDD anode promotes the generation of hydroxyl radicals, the high content of chloride ions induces the simultaneous formation of free chlorine, responsible for the indirect oxidation of ammonium [78], and since chlorine evolution is enhanced at lower COD concentrations, it results in higher ammonium oxidation rates. Regarding nitrites (Figure 7.3c), they are completely eliminated during the electrochemical oxidation at both electrode materials.

The mass balance to all nitrogen forms determined during the assays performed with the two electrode materials is presented in Figure 7.3d. A discrepancy is observed only for the final period of the assays, although the value zero is always contained in the interval of the value \pm SD. This discrepancy must be related with the experimental errors of the techniques used to determine the different forms of nitrogen.

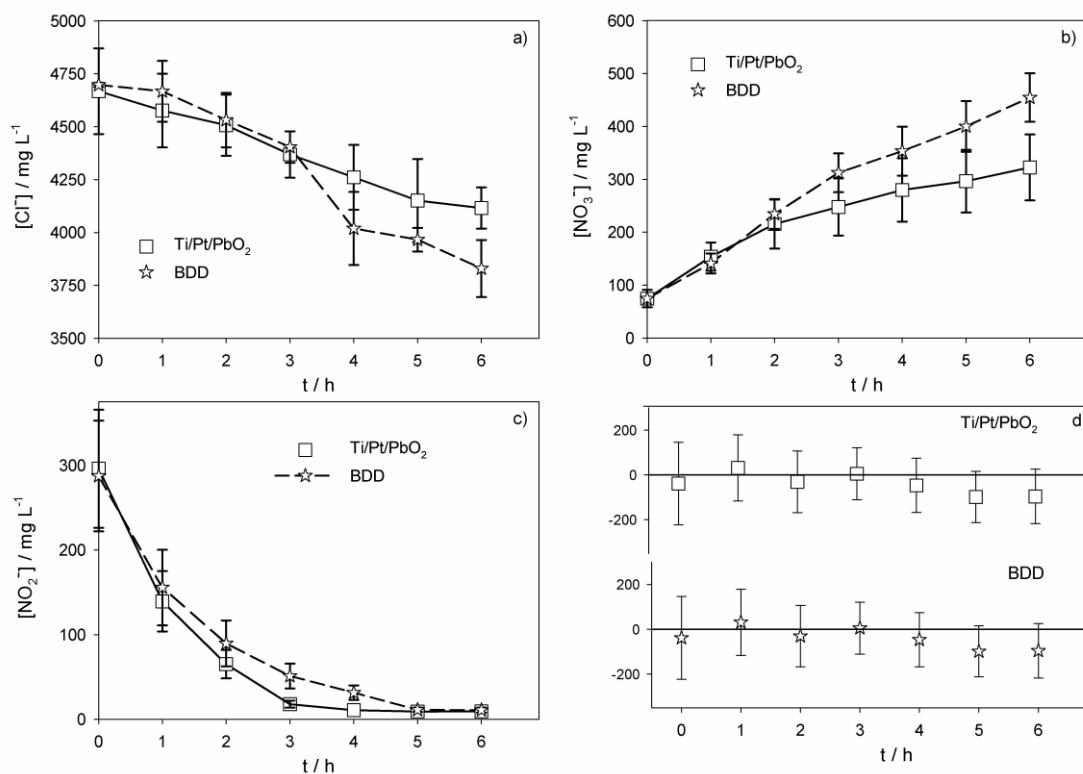


Figure 7.3 - Variation with time of (a) Cl⁻, (b) NO₃⁻ and (c) NO₂⁻ concentrations, determined by HPLC, for the EO experiments performed with real leachate using Ti/Pt/PbO₂ and BDD anodes. (d) Mass balance of the different forms of nitrogen determined in solution during the assays. Error bars refer to the standard deviation of the mean values.

Biochemical oxygen demand after 5 days of incubation was determined for samples obtained after 6 h of electrochemical treatment with Ti/Pt/PbO₂ anode, and the value of 0.50 ± 0.05 g L⁻¹ was obtained. This value led to the BOD₅/COD ratio of 0.13 ± 0.02 , indicating that the biodegradability of the samples after 6 h of EO did not improve. This issue occurs because matter that is more difficult to electrolyze is also less biodegradable and because the presence of chlorine/hypochlorite may alter the BOD₅ results, since these species can deactivate microorganisms responsible for the biodegradation.

After the electrochemical treatment, there were reductions of 45 and 43% in the absorbance measured at 275 nm and reductions of 9.1 and 9.5% in the conductivity for the assays performed with the Ti/Pt/PbO₂ and BDD anodes, respectively. The reduction in the absorbance is due to the ease of degrading the aromatic structures by electrochemical oxidation in materials with high oxygen evolution potentials that produce high concentrations of hydroxyl radicals [62], whereas the decrease in conductivity is due to metal deposition over the cathode caused by the cathodic reduction of the metal ions present in the leachate samples. Concerning the pH variation during the assays, no significant variation was found for both anode materials, being within an acceptable range for experimental error.

To understand the effect of organic matter on the elimination of ammonium nitrogen, assays were run with the two electrode materials using simulated solutions containing chloride, nitrates and ammonium in concentrations similar to those encountered in the leachate samples. The results are presented in Figure 7.4. The elimination rate of chloride is enhanced because there is no competition with the organic matter for oxidation. In contrast, hydroxyl radicals are free to convert ammonium, which does not participate in Equations (7.1) and (7.2) and which does regenerate chloride ions. The discrepancy between the nitrate formation rate for the two electrode materials increases, showing that BDD is more predisposed to oxidize ammonium to nitrates, whereas for Ti/Pt/PbO₂, ammonium and total nitrogen removal are increased and nitrate formation rate is decreased, showing that the metal oxide is more effective in the complete elimination of nitrogen from solution via the partial oxidation of ammonium to nitrogen. A decrease in nitrate concentration is observed during the first 30 minutes of the assays performed with the oxide anode that can be related to nitrate reduction to other nitrogen forms. This electrochemical reduction of nitrate using oxide anodes was already reported in literature [89].

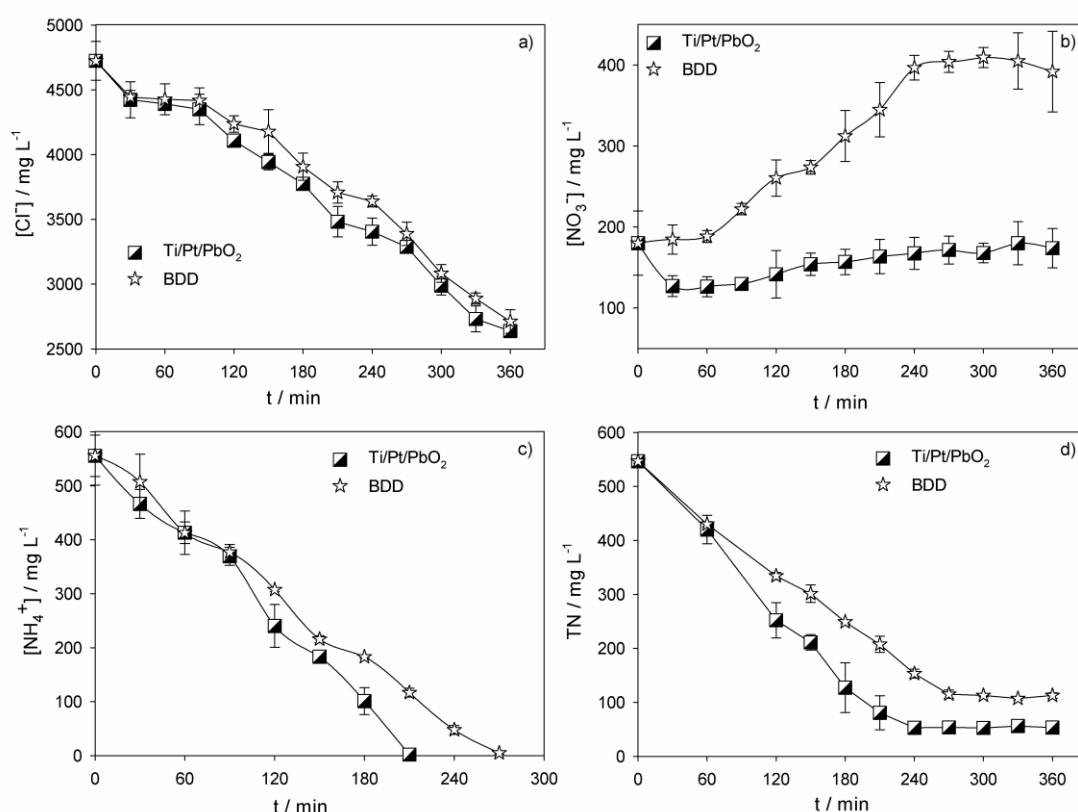


Figure 7.4 - Variation with time of (a) Cl⁻, (b) NO₃⁻, (c) NH₄⁺ and (d) TN concentrations for the EO experiments performed with the simulated sample using Ti/Pt/PbO₂ and BDD anodes. Error bars refer to the standard deviation of the mean values.

After the electrochemical treatment performed with this simulated solution, there were reductions in conductivity of approximately 20% for the assays performed with both anodes, due to the oxidation of species with high conductivity, such as ammonium and chloride, and the formation of nitrate, which has a lower conductivity than ammonium. The increase in pH (from 6.1 ± 0.1 to 7.8 ± 0.1 and 6.4 ± 0.1 for the Ti/Pt/PbO₂ and BDD anodes, respectively) also contributed to the decrease in conductivity.

Alongside this study, the feasibility of the application of a Ti/Pt/SnO₂-Sb₂O₄ anode was also evaluated, being the obtained results very similar to those found for Ti/Pt/PbO₂ anode [90].

From this case study, whose purpose was to evaluate the feasibility of the application of the Ti/Pt/PbO₂ anode in the treatment of a biologically pre-treated sanitary landfill leachate, comparing its oxidation ability with BDD anodes, the following outcomes can be highlighted:

- ✓ Ti/Pt/PbO₂ is a good alternative as anode material for the treatment of sanitary landfill leachates, yielding good results, mainly in terms of nitrogen removal. Although it makes the material more expensive, the Pt layer can strategically decrease the energetic consumptions and increase the electrode lifetime; the electrodes used in this work were tested for more than 1000 hours.
- ✓ Both Ti/Pt/PbO₂ and BDD anodes present similar COD removal kinetics, whereas the BDD anode promotes the highest DOC removal, leading to a higher mineralization degree due to its inert surface where hydroxyl radicals, which are responsible for the indirect oxidation, are less strongly adsorbed than at the metal oxide surface.
- ✓ Ti/Pt/PbO₂ promotes higher levels of TN and AN removals than BDD, whereas BDD shows the highest level of TKN removal. This effect occurs because for metallic oxides, the partial oxidation of ammonium to nitrogen gas occurs, whereas for BDD, ammonium is oxidized to nitrate, again indicating the ability of BDD to complete oxidation.
- ✓ Ti/Pt/PbO₂ anode lead to low energy consumptions since it is more conductive than BDD and also due to the electrocatalytic effect of the oxides.

The work described in this case study led to the publication of a paper in an international scientific journal with scientific arbitration [90].

7.2 Case study 8

Ti/Pt/PbO₂ vs. BDD anode for the EO of leachates and simulated samples: Influence of current density and chloride concentration

In this study, performed with a raw leachate and with simulated samples, the influence of the initial chloride concentration and of the applied current intensity on the electrodegradation performance, using BDD and Ti/Pt/PbO₂ anodes, was investigated. The characterization of the leachate used in this study is presented in Table 3.1, Sample I. Assays were performed at applied current densities of 300, 500 and 700 A m⁻², using raw leachate and leachate samples with addition of chloride (0.6 and 2 g L⁻¹). The increment of chloride ion was made by adding KCl.

Assays with simulated samples were also performed, to better understand the influence of the chloride on the organic load and nitrogen electrodegradation mechanisms at different applied current densities. Simulated samples were prepared with humic acid and inorganic salts, in order to replicate the COD and NH₄⁺ contents of leachate I, and having different Cl⁻ contents. Simulated samples without any chloride content were also studied. Table 7.1 summarizes the composition of the different simulated samples used in the experiments, as well as the experimental conditions tested. Assays were conducted at room temperature (22-25 °C) and natural pH. Electrolysis duration was 8 hours.

Table 7.1 - Composition of the simulated samples and experimental conditions tested in Case study 8 assays.

[Cl ⁻] _{intended} / g L ⁻¹	Simulated sample composition / L of solution	Applied current density / A m ⁻²
0	Humic acid - 3.300 g (NH ₄) ₂ SO ₄ - 10.278 g	
2.5	Humic acid - 3.300 g (NH ₄) ₂ SO ₄ - 5.618 g NH ₄ Cl - 3.768 g	300, 500, 700
4.5	Humic acid - 3.300 g (NH ₄) ₂ SO ₄ - 5.618 g NH ₄ Cl - 3.768 g KCl - 4.206 g	

Figure 7.5 presents the results for the variation with time of the normalized COD obtained from the experiments performed with real leachate with different Cl⁻ concentrations, and for the two anode materials used in this case study. In Figures 7.5 to 7.10 the chloride concentration of 2.5 g L⁻¹ corresponds to samples where no chloride was added, since this was the chloride concentration of the raw leachate. Figure 7.5 shows that, for both anode materials, COD removal rate increases with applied current density. This behaviour has been

reported in literature and has been explained by the increased production of the oxidizing species with the operating current density [18].

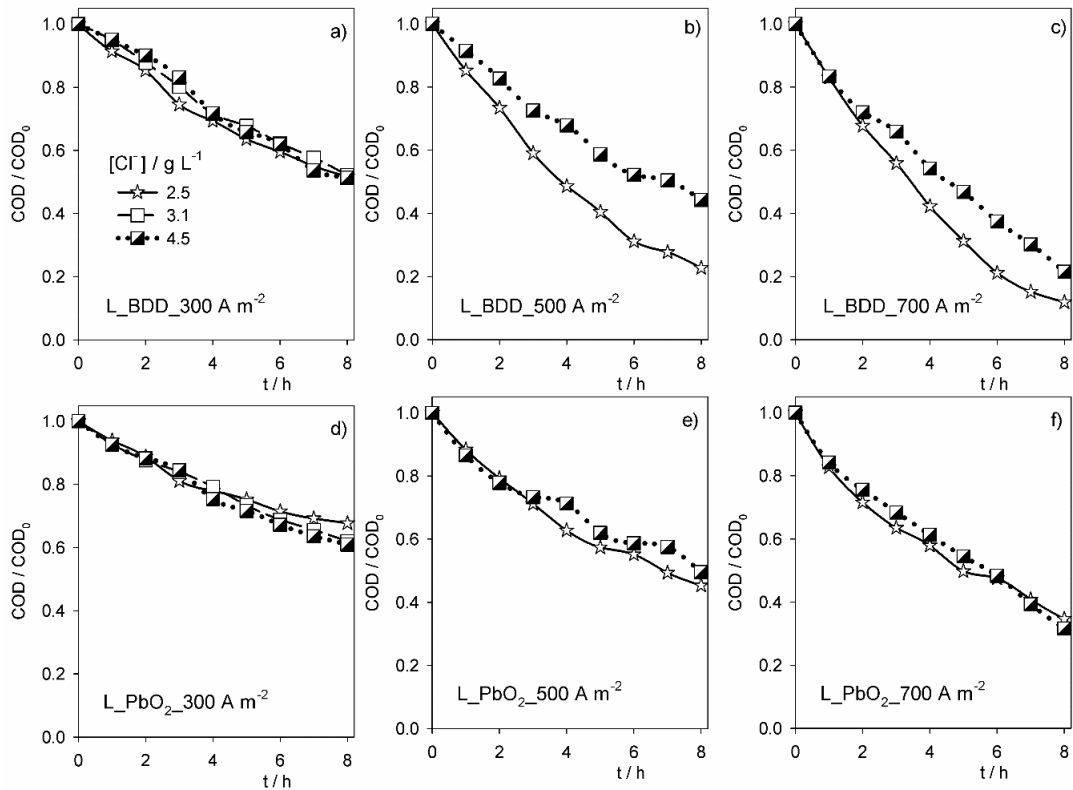


Figure 7.5 - Variation with time of the normalized COD for the EO experiments performed with real leachate (L) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/ PbO_2 anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

It can also be seen in Figure 7.5 that, for all the tested conditions, BDD anodes promoted higher COD removal rates than Ti/Pt/ PbO_2 anodes. This behaviour was not found in Case study 7, where a similar type of decay was found for both anode materials. However, in Case study 7 a young leachate was used and in the present case study an old leachate was assayed, with higher nitrogen content and lower chloride concentration than the young leachate used in Case study 7. A possible explanation for the difference found in COD removal rates between both anode materials could be the fact that hydroxyl radicals formed at BDD anodes are physically adsorbed, presenting high ability to oxidize organic matter, whereas hydroxyl radicals formed at Ti/Pt/ PbO_2 anodes are chemically adsorbed, mainly due to the Pt layer, and thus less available for the oxidation of the organic matter. Furthermore, Ti/Pt/ PbO_2 anodes are more prone to indirect oxidation through chlorine/hypochlorite, being more adequate for the elimination of nitrogen compounds. Since the leachate used in this case study presents high nitrogen concentrations, nitrogen removal would be dominant in the competition between nitrogen and COD removals by the indirect oxidation and, consequently, COD removal rate would be lower at Ti/Pt/ PbO_2 anodes.

Regarding the effect of initial chloride concentration on COD removal rate, for the range of chloride concentrations tested, no significant influence was found when the Ti/Pt/PbO₂ anode was used. But, with BDD anode, a loss in efficiency was observed at applied current densities of 500 and 700 A m⁻² when Cl⁻ concentration was increased, being this loss more pronounced at 500 A m⁻². This can be explained by the fact that, at higher current densities, chlorine generation will be enhanced and hence the organic matter anodic oxidation with hydroxyl radicals will be depressed. In the meantime, the nitrogen removal will be dominant in the competition between nitrogen and COD removal by the indirect oxidation and, consequently, COD removal rate will decrease with the decrease of current density [39,45]. When the nitrogen concentration is reduced, which will occur first at the higher current density, organic matter indirect oxidation will be enhanced, explaining the less pronounced loss of efficiency at 700 A m⁻². This explanation is corroborated by TN decays observed in the assays performed with real leachate, shown in Figure 7.6.

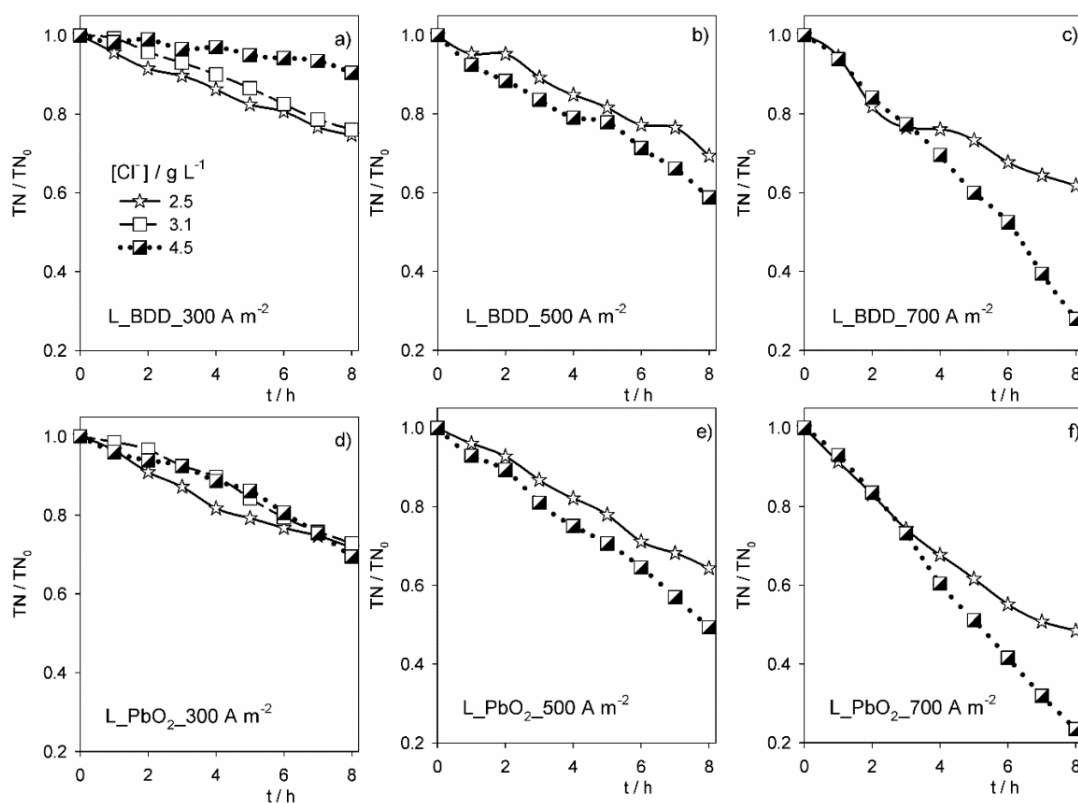


Figure 7.6 - Variation with time of the normalized TN for the EO experiments performed with real leachate (L) with different Cl⁻ concentrations, using BDD anodes at applied current densities of (a) 300 A m⁻², (b) 500 A m⁻² and (c) 700 A m⁻², and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m⁻², (e) 500 A m⁻² and (f) 700 A m⁻².

As expected, TN removal rates were higher when the Ti/Pt/PbO₂ anode was used, since, as explained above, this anode material is more prone to indirect oxidation through chlorine/hypochlorite and nitrogen removal should be dominant in the competition between nitrogen and COD removal by the indirect oxidation. When current density was increased, TN

removal rates increased for both anode materials, since at higher current densities, chlorine/hypochlorite production is enhanced [18], and in the case of BDD anodes, indirect oxidation through this species becomes more relevant.

At 300 A m^{-2} , the increase in chloride concentration presented a negative effect for both anode materials. In fact, when BDD anode was used, TN removal decreased significantly by increasing Cl^- concentration to 4.5 g L^{-1} . However, increasing the applied current density, the increase in the TN removal rate with Cl^- concentration becomes evident, which is due to the enhancement of the chlorine/hypochlorite production and the consequent nitrogen indirect oxidation.

Figure 7.7 shows the normalized $[\text{NH}_4^+]$ decays with time for the experiments performed with real leachate. At 300 and 500 A m^{-2} , identical $[\text{NH}_4^+]$ decays were observed for both anode materials. Also, at these applied current densities, no pronounced differences were found between the decays at different Cl^- concentrations. However, at 700 A m^{-2} , divergent results were found for both anode materials at different Cl^- concentrations.

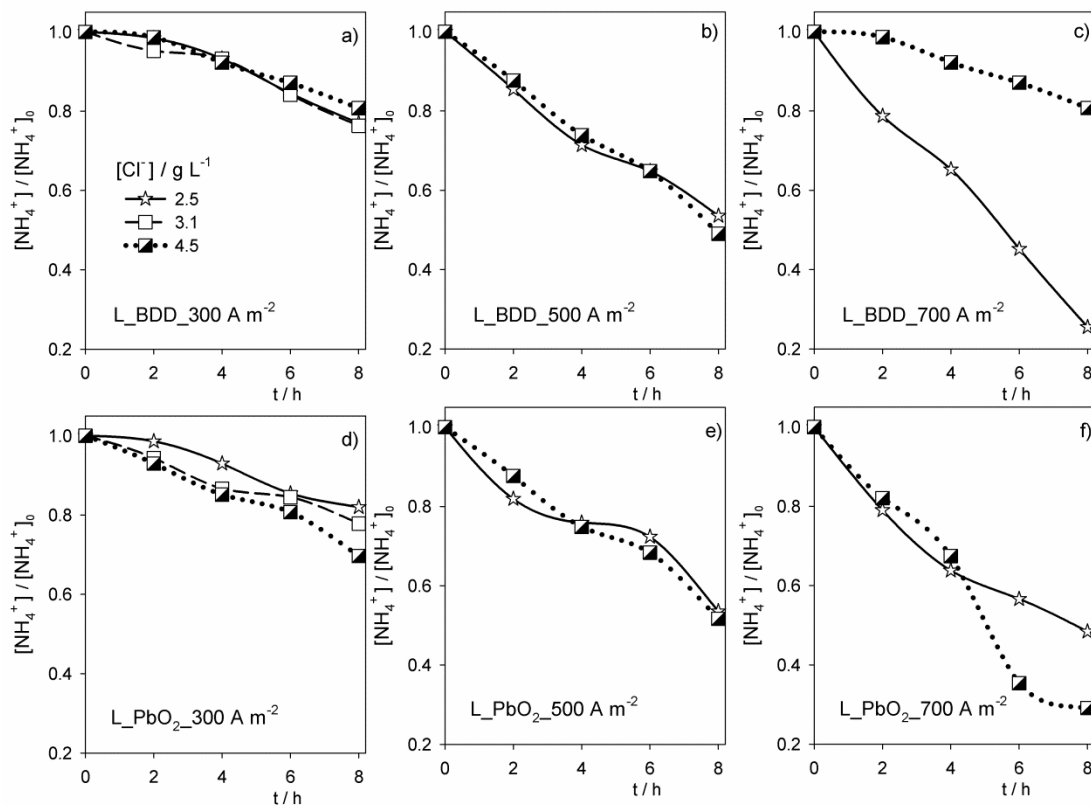


Figure 7.7 - Variation with time of the normalized AN for the EO experiments performed with real leachate (L) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

For the assays performed with the BDD anode, a sharp decrease in the NH_4^+ removal rate was observed when Cl^- concentration was increased. This behaviour can be explained attending to the TN removal decays (Figure 7.6) and the nitrate formation showed in Figure 7.8. According to the results, apparently, at the lowest Cl^- concentration, NH_4^+ oxidation is favoured and it is converted to NO_3^- . This can be due to the fact that NH_4^+ is a small molecule with high diffusion coefficient, being its oxidation at the electrode surface more favoured, since the amount of Cl^- is not enough to promote an efficient indirect oxidation. When Cl^- concentration is increased, the oxidation of the organic nitrogen becomes preferable, since the extra chlorine/hypochlorite produced makes more proficient the oxidation of larger molecules with lower diffusion coefficients.

When Ti/Pt/PbO₂ anode was used, the same trend was followed for the different Cl^- concentrations until the fourth hour assay, but after that a sharp increase in NH_4^+ removal rate was observed for assays performed at the highest initial Cl^- concentration. According to nitrate results (Figure 7.8), the enhanced indirect oxidation through higher chlorine/hypochlorite production efficiency caused by extra Cl^- addition, apparently enhanced the NH_4^+ oxidation to N_2 or other volatile N-containing molecules. Similar results are reported in literature for BDD anodes [47].

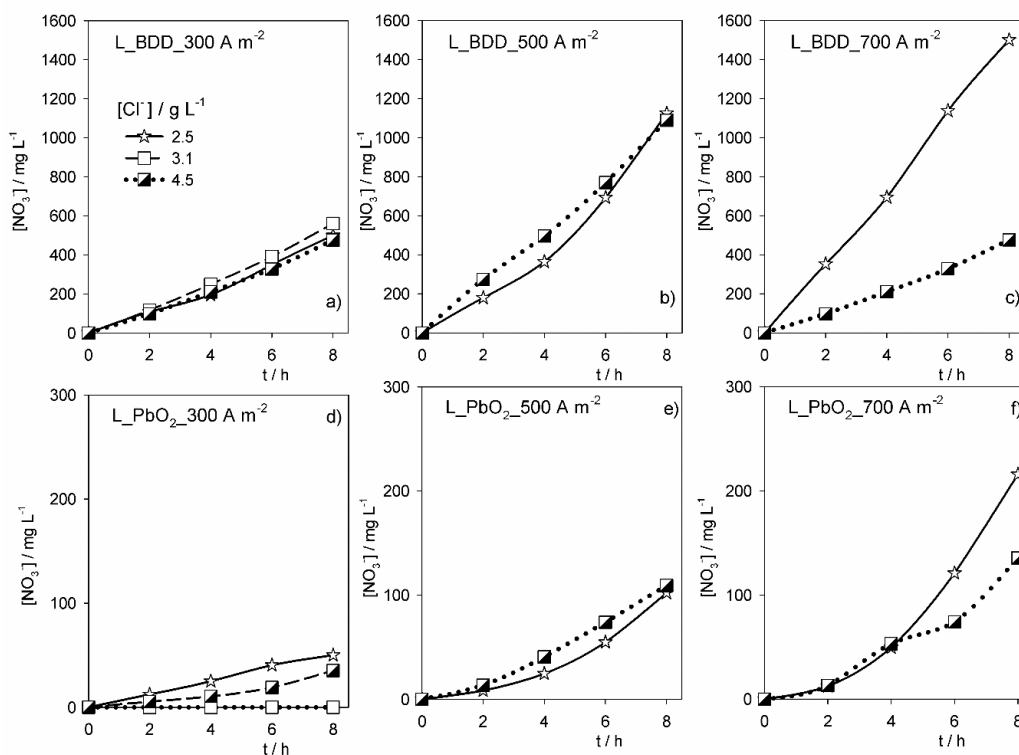


Figure 7.8 - Variation with time of nitrate concentration for the EO experiments performed with real leachate (L) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

From what can be observed in Figure 7.8, NH_4^+ oxidation to NO_3^- was favoured at BDD anodes. Again, Cl^- concentration showed no significant influence at applied current densities of 300 and 500 A m^{-2} , which can indicate that at these current densities extra chloride is not being converted into the oxidizing species, such as chlorine and hypochlorite.

Chloride concentration decays along the assays performed with real leachate are shown in Figure 7.9. The most significant decays were observed for Ti/Pt/PbO₂ anode and were more pronounced at the highest applied current density. This could indicate that indirect oxidation through chlorine/hypochlorite species was more prominent at Ti/Pt/PbO₂ anode, which is consistent with the data reported above.

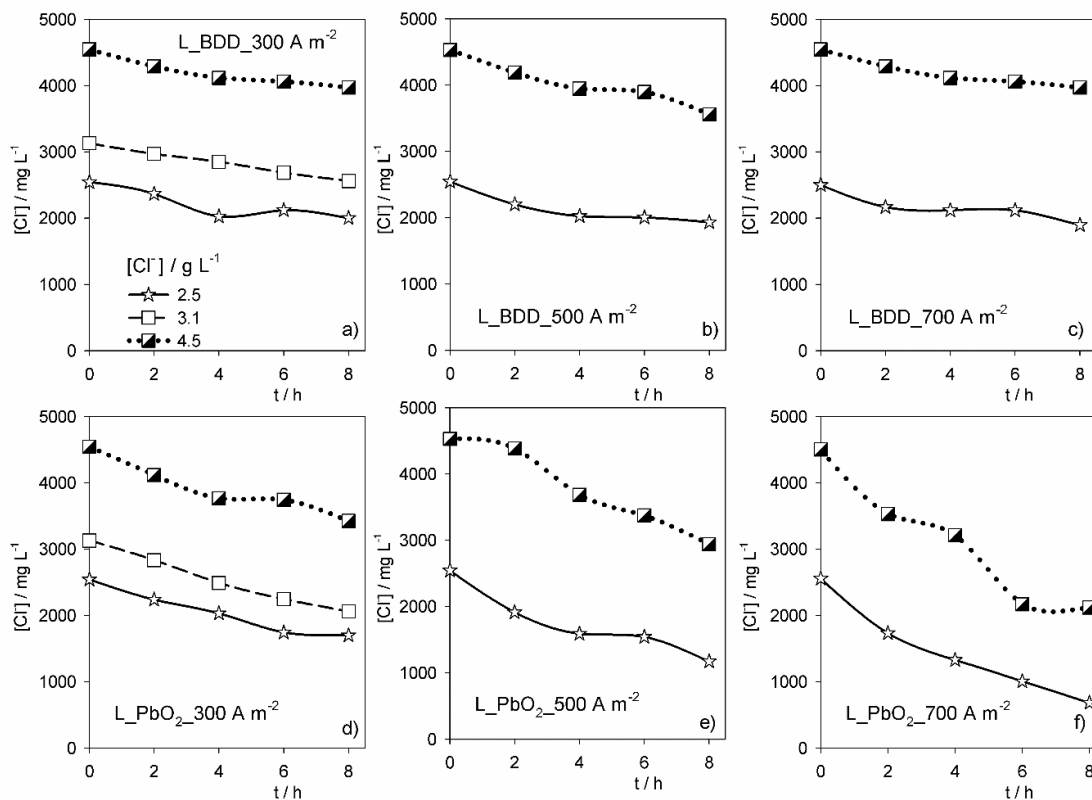


Figure 7.9 - Variation with time of chloride concentration for the EO experiments performed with real leachate (L) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

In Figure 7.10, DOC decays are presented for the assays performed with real leachate. For Ti/Pt/PbO₂ anode, DOC removal was lower than COD removal (Figure 7.5). This behaviour has been reported previously in the literature and in other case studies reported in this thesis and has been explained by the formation of low molecular mass organic compounds with high degrees of oxidation that resist to further oxidation [29]. An increase in initial Cl^-

concentration showed to slightly increase the DOC removal, indicating that the extra Cl^- added enhances the complete oxidation of the organic matter.

For the assays performed with BDD anodes, DOC removals were very close to COD removals, being the highest difference among them observed for assays performed with extra Cl^- concentration. This behaviour suggests that the BDD anode promotes the complete combustion of the organic matter. The reason for this has been explained in Case study 7 and is due to the inert surface of BDD anodes and the consequent reactivity of hydroxyl radicals toward the complete oxidation of organics. As already reported for COD, an increase in the initial Cl^- concentration led to a decrease in DOC removal, being the explanation for this the similar to that presented for the variation of COD removal with chloride concentration.

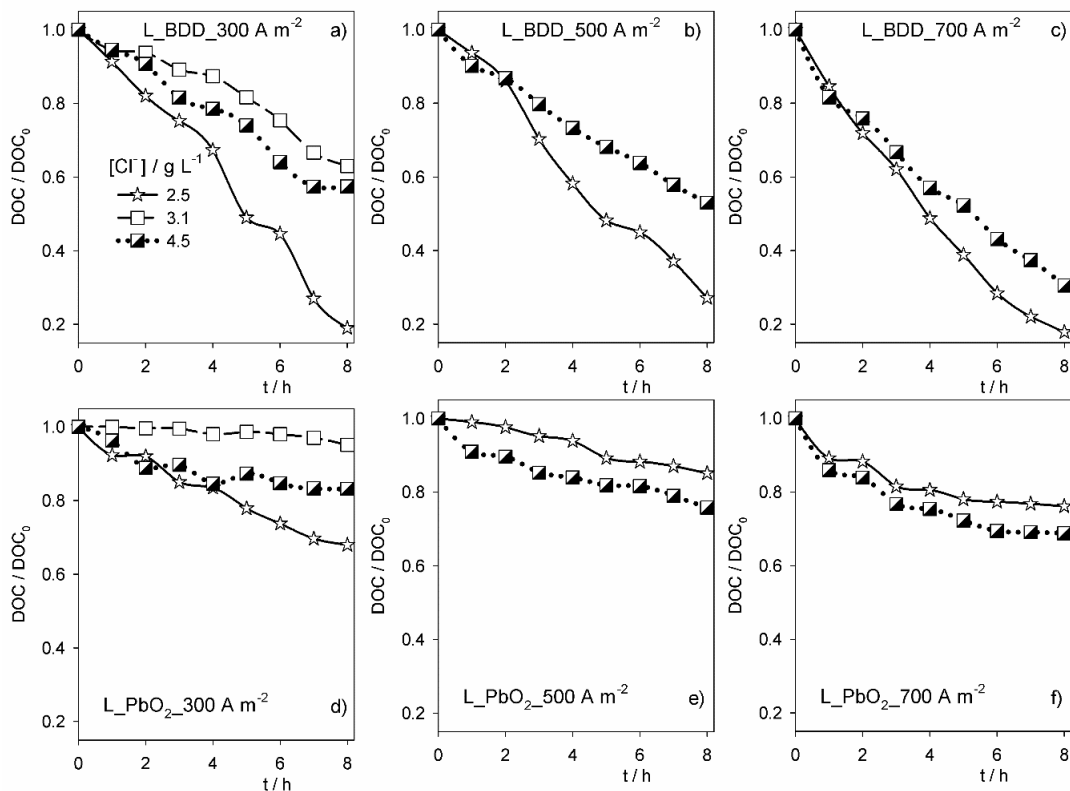


Figure 7.10 - Variation with time of the normalized DOC for the EO experiments performed with real leachate (L) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/ PbO_2 anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

To understand the effect of the initial Cl^- concentration and of the applied current density on the elimination of recalcitrant organic matter and ammonium nitrogen, assays were run with both electrode materials using simulated solutions prepared as described in Table 7.1. The obtained results are presented in Figures 7.11 to 7.16.

Regarding COD removals (Figure 7.11), the assays performed with BDD anode at 300 A m^{-2} have not shown a marked effect of the Cl^- concentration, meaning that indirect oxidation of the organic matter through chlorine/hypochlorite species was not very effective. For the assays performed with BDD anodes at 500 and 700 A m^{-2} , the presence of Cl^- influenced the COD removal, showing an increase in the oxidation through chlorine/hypochlorite with the increase in chloride content. Similar results were presented for the anodic oxidation at Ti/Pt/PbO_2 electrode, except in the case of the assay run at 300 A m^{-2} without addition of chloride ion, probably because of some fouling/polarization of the electrode surface, because of the porosity presented by this type of oxide electrodes. Similar to what was reported for the assays performed with real leachate, for the assays run with chloride, COD removal increases with applied current density, for both electrodes.

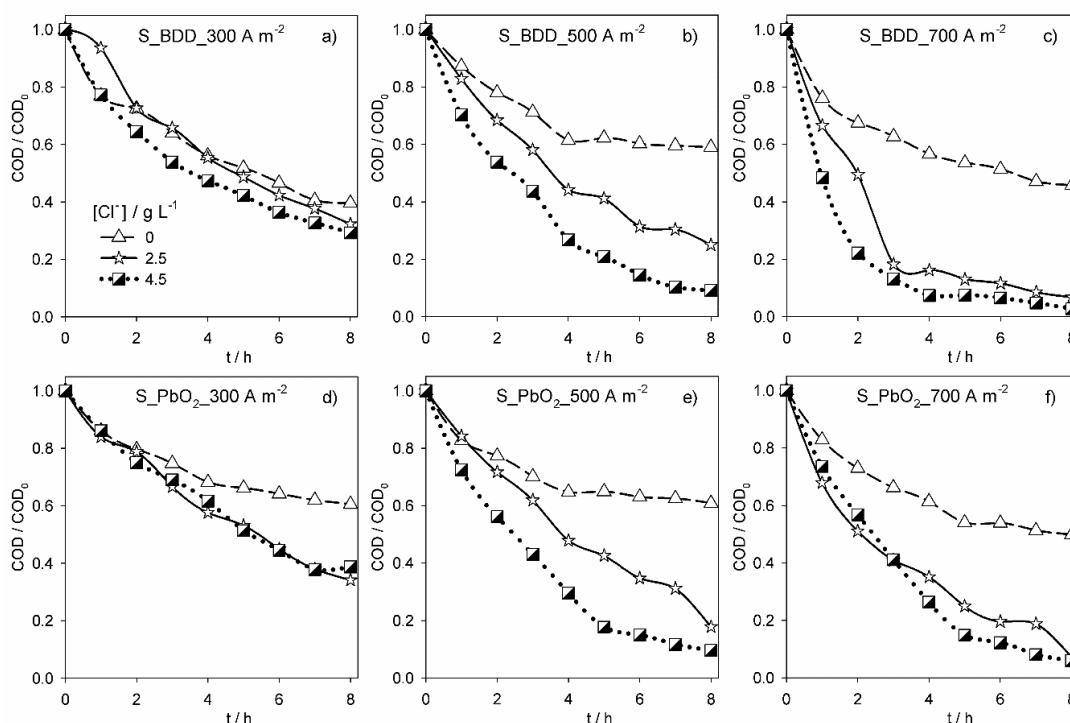


Figure 7.11 - Variation with time of the normalized COD for the EO experiments performed with simulated samples (S) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} and Ti/Pt/PbO_2 anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

DOC removal (Figure 7.12) followed similar behaviour to that reported for COD, except in the assays performed with BDD anode at 300 A m^{-2} , where Cl^- concentration showed to influence DOC removal. DOC removals obtained with the Ti/Pt/PbO_2 anode, using simulated samples, were much higher than those obtained with real leachate samples, indicating a higher mineralization degree for simulated samples. This fact may be due to some hindrance promoted by adsorption on the electrode surface of the species contained in the leachate

that are not present in the simulated samples or due to the presence of species more resistant to mineralization.

Despite the high DOC removals presented by Ti/Pt/PbO₂ anodes, they were even higher when BDD anodes were used. DOC removals obtained with BDD using simulated samples are slightly smaller than those obtained for leachate samples (Figure 7.10) for the chloride concentration of 4.5 g L⁻¹. However, for the lowest chloride concentration tested in the leachate samples, the DOC removals presented by the simulated samples are much smaller. The highest values presented by the leachate samples for the “natural” chloride content, i.e., no added chloride that corresponds to [Cl⁻]=2.5 g L⁻¹, may be interpreted as if the addition of extra chloride to raw leachate destabilizes the samples, maybe through the formation of organ-chloride species difficult to oxidize, phenomena that is not observed with simulated samples.

For all the applied current densities assayed, after some period of time, which decreases as the current density increases, DOC removal reaches a threshold and, after that, DOC removal rate decreases sharply, as if the organic matter present was more resistant to mineralization.

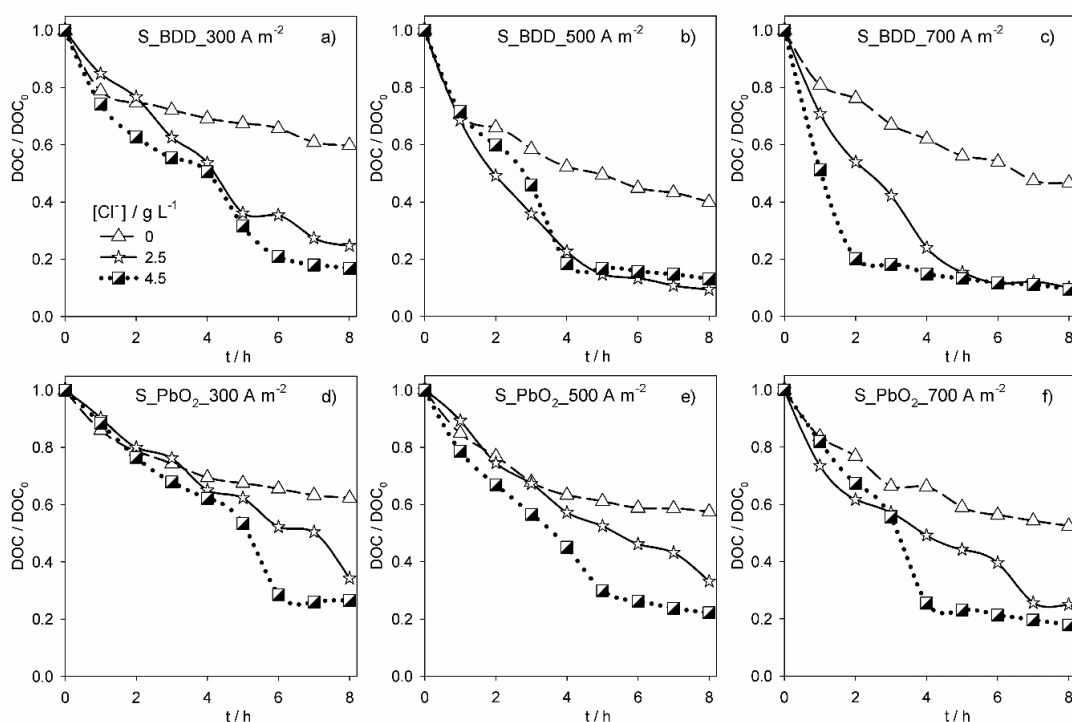


Figure 7.12 - Variation with time of the normalized DOC for the EO experiments performed with simulated samples (S) with different Cl⁻ concentrations, using BDD anodes at applied current densities of (a) 300 A m⁻², (b) 500 A m⁻² and (c) 700 A m⁻² and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m⁻², (e) 500 A m⁻² and (f) 700 A m⁻².

Regarding nitrogen forms evolution during the assays (Figures 7.13 to 7.15), it can be seen that, for simulated samples without Cl⁻, no changes in the different nitrogen form contents is

observed, at any applied current density and at both anode materials used. These results showed that NH_4^+ and TN removals take place mainly by indirect oxidation through chlorine/hypochlorite species.

Similar to what was reported for real leachate assays, for the highest Cl^- concentration, TN removal rates were higher when the Ti/Pt/PbO₂ anode was used. When initial Cl^- concentration is 2.5 g L⁻¹, TN removal rates are low, confirming that, at this concentration, the amount of Cl^- is not enough to promote an efficient indirect oxidation. Also, considering that TN and NH_4^+ removal rates are much lower than those obtained for COD, it can be assumed that COD removal was dominant in the competition between nitrogen and COD, indicating a change in the degradation mechanism comparing with real leachate. This must be due to the fact that, in simulated samples, nitrogen was almost all in the form of NH_4^+ . For the same reason, NH_4^+ removal rates presented in Figure 7.14 are similar to TN removal rates (Figure 7.13).

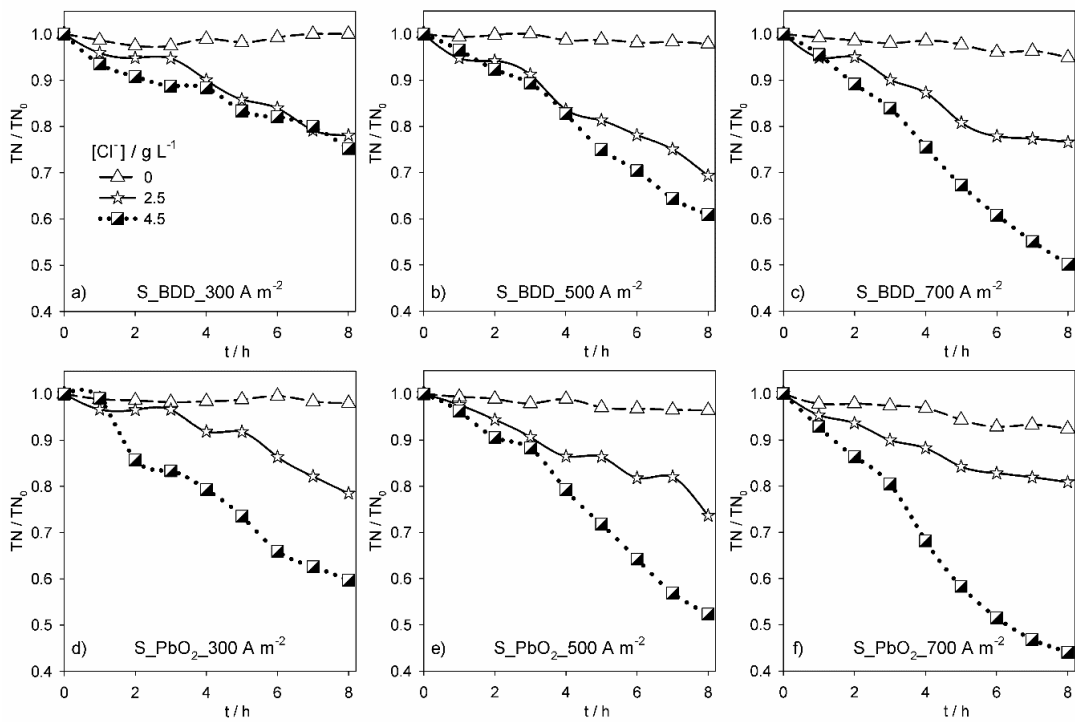


Figure 7.13 - Variation with time of the normalized TN for the EO experiments performed with simulated samples (S) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m⁻², (b) 500 A m⁻² and (c) 700 A m⁻² and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m⁻², (e) 500 A m⁻² and (f) 700 A m⁻².

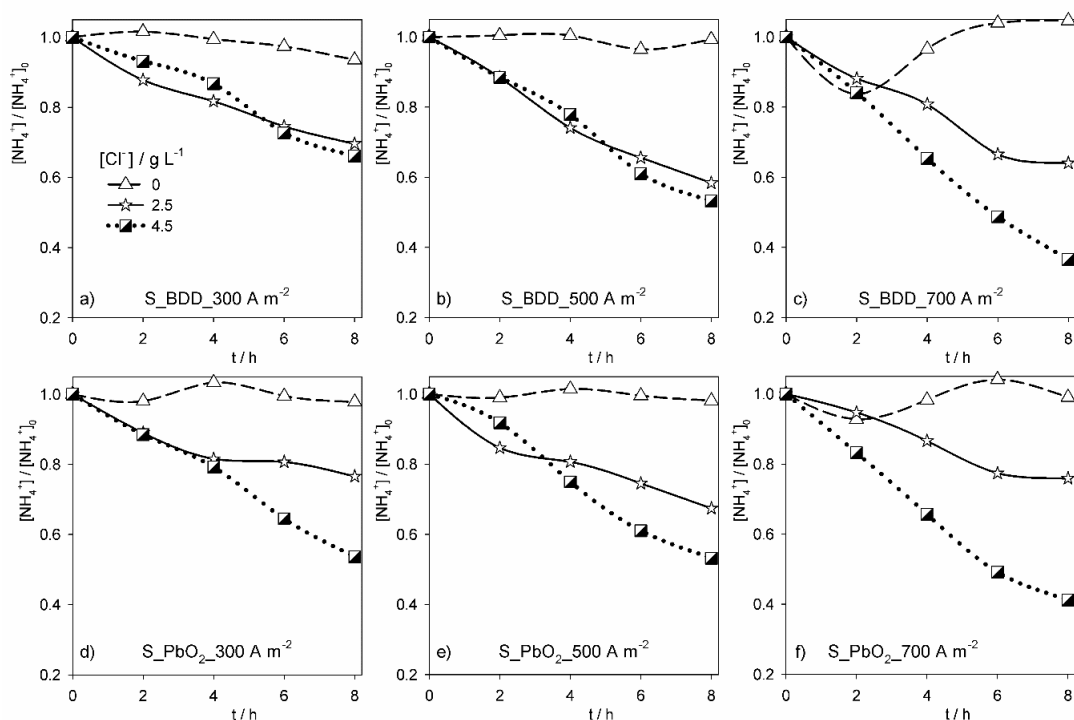


Figure 7.14 - Variation with time of the normalized $[\text{NH}_4^+]$ for the EO experiments performed with simulated samples (S) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} and Ti/Pt/ PbO_2 anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

Nitrate formation (Figure 7.15) describes a similar behaviour to the one described for real leachate samples, showing that at BDD anodes NH_4^+ is oxidized to nitrate and at Ti/Pt/ PbO_2 anodes NH_4^+ is oxidized to N_2 or other nitrogen volatile species.

Figure 7.16 shows Cl^- concentration decay along the assays performed with simulated samples. Decays were similar for both anode materials, despite the decays observed when Ti/Pt/ PbO_2 anode was used have shown to be slightly more pronounced when Cl^- concentration had its highest value. Regarding the simulated samples without added chloride, there was a residual chloride content, probably from acid humic or inorganic salts contaminants.

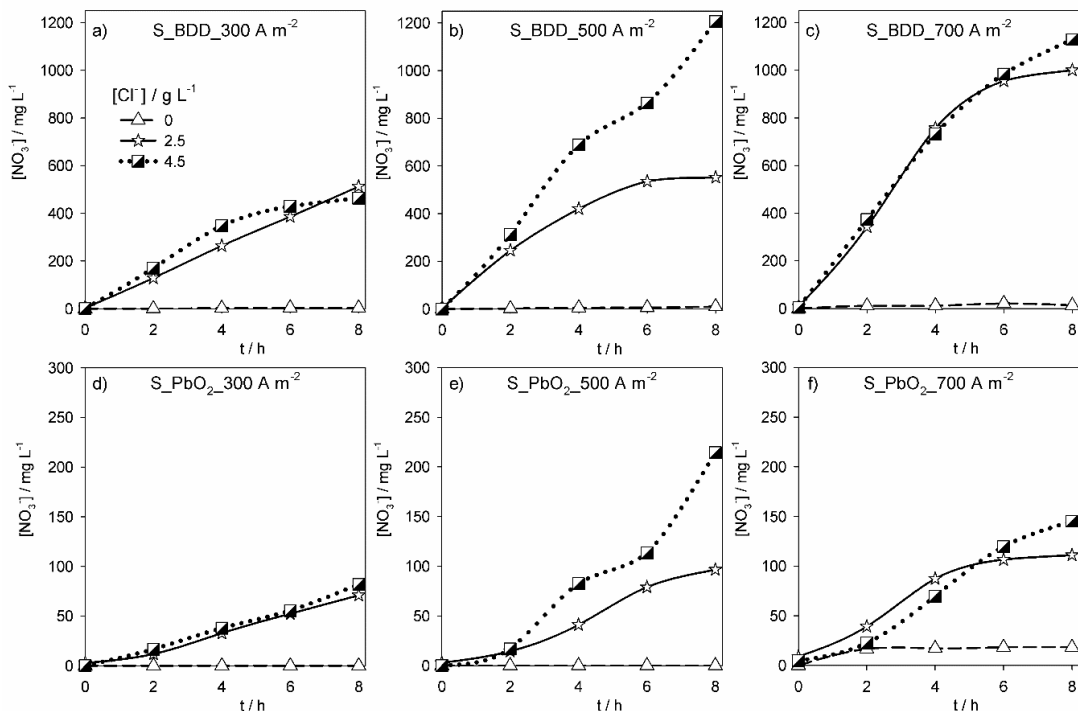


Figure 7.15 - Variation with time of the nitrate concentration for the EO experiments performed with simulated samples (S) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} , and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

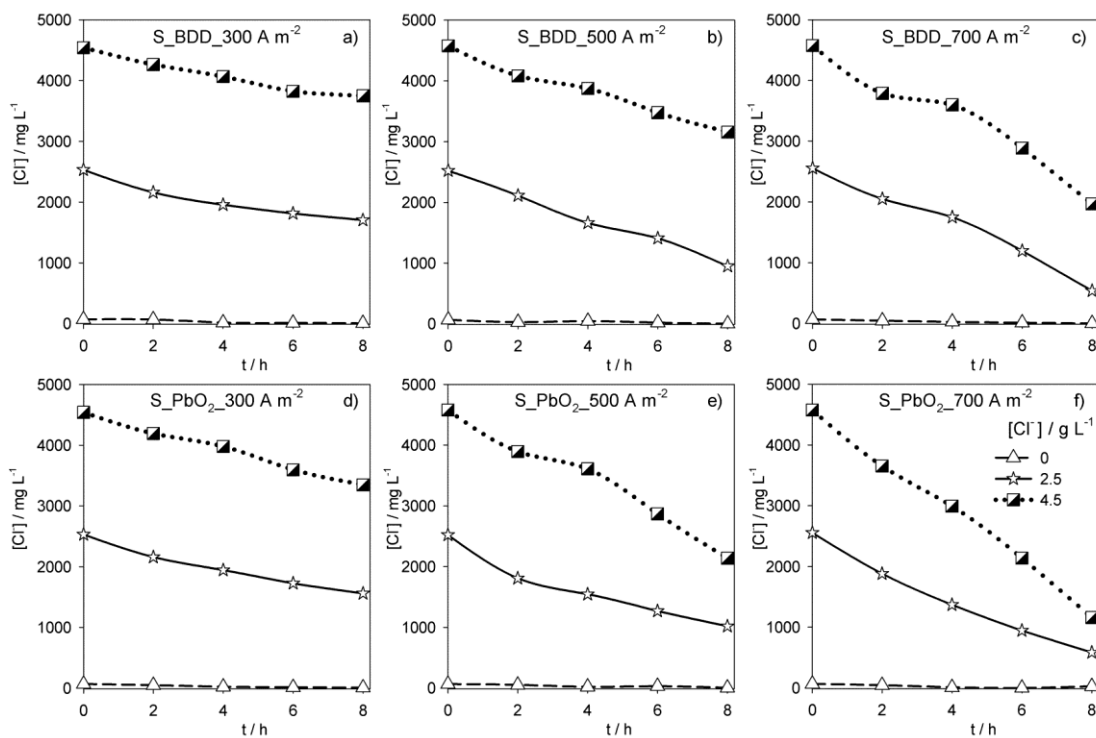


Figure 7.16 - Variation with time of the chloride concentration for the EO experiments performed with simulated samples (S) with different Cl^- concentrations, using BDD anodes at applied current densities of (a) 300 A m^{-2} , (b) 500 A m^{-2} and (c) 700 A m^{-2} and Ti/Pt/PbO₂ anodes at applied current densities of (d) 300 A m^{-2} , (e) 500 A m^{-2} and (f) 700 A m^{-2} .

According to the aims of this case study, which were investigate the effects of the applied current density and of the addition of extra chloride ion on the electrochemical oxidation of an old leachate and in simulated samples, using BDD and Ti/Pt/PbO₂ anodes, the following main conclusions can be drawn:

- ✓ For leachate and simulated samples, COD, TN and NH₄⁺ removals increased with applied current density, for both electrodes.
- ✓ For the assays performed with leachate samples, using BDD anodes, the addition of extra chloride ion to the leachate did not offer significant advantages regarding COD and DOC removals. In fact, at 500 and 700 A m⁻², COD and DOC removal rates decreased with initial Cl⁻ concentration.
- ✓ For the assays performed with simulated samples using BDD anodes, the presence of Cl⁻ influenced the COD removal, showing an increase in the oxidation through chlorine/hypochlorite species with the increase in initial chloride content.
- ✓ When Ti/Pt/PbO₂ anodes were used with leachate samples, the addition of extra chloride ion did not influence the COD removal. However, when simulated samples were assayed, the presence of Cl⁻ influenced the COD removal, showing an increase in the oxidation rate with the increase in chloride content, due to indirect oxidation by chlorine/hypochlorite species.
- ✓ For simulated samples without Cl⁻, no changes in the different nitrogen forms contents were observed, at any applied current density with both anode materials, showing that NH₄⁺ and TN removals took place mainly by indirect oxidation through chlorine/hypochlorite species.
- ✓ Using leachate samples, TN removal rates increased with initial Cl⁻ concentration and with current density, for both anodes since at higher applied current densities, chlorine/hypochlorite production is enhanced, and in the case of BDD anodes, indirect oxidation through this species became more relevant.
- ✓ For both leachate and simulated samples, using BDD anodes, NH₄⁺ oxidation was favoured and it was converted to NO₃⁻. For leachate samples assays, when initial Cl⁻ concentration was increased to 4.5 g L⁻¹, the oxidation of the organic nitrogen becomes preferable.
- ✓ Using Ti/Pt/PbO₂ anodes, for leachate and simulated samples, NH₄⁺ oxidation was enhanced, forming N₂ or other nitrogen volatile species.

Chapter 8

Concluding remarks and future trends

The main goal of this work was to present an efficient electrochemical solution for sanitary landfill leachates treatment, which could complement or partially replace the existing treatment systems. In order to accomplish this main goal, secondary goals were established and laboratory experiments were performed to achieve the proposed objectives. The performed experiments were grouped in four main parts, according to the goals proposed, being these main parts divided into case studies, in agreement with the outlined strategy. Along the “Results and discussion” chapters, the main conclusions were drawn for each of the case studies presented, according to the results obtained. Based on these remarks, an evaluation of the proposed goals is presented in this chapter. First, secondary goals are analyzed and then the main goal is evaluated. Finally, future perspectives for the application of the electrochemical processes in the treatment of sanitary landfill leachates are presented.

Secondary goals analysis is exposed in the next four paragraphs, one for each of the main goals proposed:

1. To evaluate the feasibility of an electrochemical oxidation treatment applied as a polishing step, after a biological process, to eliminate the remaining dissolved persistent organic compounds

This goal was accomplished, since electrochemical oxidation can be successfully employed as a polishing step, after a biological process. Although working at low current densities leads to high treatment durations, it is preferable to apply low current densities in order to increase the current efficiency and consequently to decrease energetic costs. Depending on the initial characteristics of the leachate and on the desired final values, operational conditions, such as recirculation flow rate, can be adjusted to lead the process to the desired final. For instance, in the experiments performed in this study, it was found that the mineralization of organic pollutants was enhanced by low pollutants concentration and by high recirculation flow rates. On the other hand, nitrogen removal was enhanced by low flow rates. Energy consumptions of 15 and 21 W h (g COD)⁻¹ were attained working at laboratory scale and semi-pilot scale, respectively, showing that electrochemical oxidation process can be competitive with other post treatment processes, without the disadvantage of sludge production.

2. To study the application of an electrochemical oxidation treatment to raw sanitary landfill leachates, determining the operational conditions that lead to higher treatment efficiencies

This goal was accomplished. Electrochemical oxidation can be an alternative to treat non-biodegradable sanitary landfill leachates, although the costs involved can significantly increase when higher pollutants removals are required. COD removals above 90% were achieved for a specific energy consumption of $78 \text{ W h (g COD)}^{-1}$. It was found that organic load removal rate increases with applied current density and also with recirculation flow rate. However, nitrogen removal decreases with recirculation flow rate and current efficiency decreases with applied current density. A reduction in energetic costs was achieved by reducing the applied current density along the electrochemical oxidation process and by increasing the recirculation flow rate. For the experimental conditions tested, batch electrochemical oxidation process using a feed-recirculated reactor has shown to be more effective than a stirred one.

3. To evaluate the introduction of an electrocoagulation process before the EO treatment

This goal was accomplished. The introduction of an EC process before the EO treatment can be a suitable solution to reduce the electrochemical treatment costs, since it allowed organic load removals of about 50% with specific energy consumptions of $2 \text{ W h (g COD)}^{-1}$. This combined electrochemical process can be successfully applied either as pre-treatment or as a polishing step. When applied to raw leachates, biodegradability is enhanced and thus the application of a biological post treatment is potentiated. In the experiments performed, an increase in the BOD_5/COD ratio from 0.3 to almost 0.9 was observed, with a 95% COD removal. Furthermore, cathodic processes can be used to treat the heavy metal content in the leachate, because this process reduces the metal ions and deposits them over the cathode. Thus, this combined process can be used to obtain treated leachates, with low content in recalcitrant organic and inorganic compounds, but still with significant organic load, that can be sent to urban wastewater treatment plants comprising biological steps.

4. To study the application of Ti/Pt/PbO_2 anodes for EO treatment of sanitary landfill leachates and to evaluate their performance and comparing it with boron-doped diamond (BDD) anodes behaviour.

This goal was accomplished. Ti/Pt/PbO_2 anodes can be successfully used for the treatment of sanitary landfill leachates, leading to lower energy consumptions than the attained with BDD anodes. Both Ti/Pt/PbO_2 and BDD anodes present similar COD removal kinetics. Despite BDD yields higher mineralization degree, Ti/Pt/PbO_2 promotes higher levels of TN and AN removals. When initial Cl^- concentration in the leachate is low, indirect oxidation can be enhanced by the addition of extra chloride ions at high current densities, resulting in an increase in TN removal.

Based on the results obtained, an efficient electrochemical solution for sanitary landfill leachates treatment, which can complement or partially replace the existing treatment systems, can be presented. Depending on the leachate characteristics, electrochemical treatments can be applied as pre-treatment or post treatment of biological processes. Here, biological processes are always the reference, since they are among the most economical treatment technologies and are implemented in most of the sanitary landfill treatment plants. Combination of biological processes with electrochemical technologies gives the most economic solution. For young leachates with high contents of organic matter, electrochemical processes should be applied after the biological processes, in order to remove the refractory organic matter remaining in the leachate after biological treatment. For old leachates or leachates with low biodegradability index, electrochemical treatment should be applied before the biological processes, in order to enhance the biodegradability of the effluent, improving the performance of the subsequent biological process. If leachate presents a high amount of solids, a combined EC/EO process is indicated, since the solids present in the leachate will reduce the efficiency of the electrochemical oxidation treatment. When solids content is low, it is preferable to apply only EO process, since it does not have the disadvantage of sludge production.

The work described in this thesis showed that electrochemical technologies can be efficiently applied in the treatment of sanitary landfill leachates. However, there are some drawbacks that need to be overcome before full scale implementation.

EC application requires simple equipment, being easy to operate and does not require chemicals addition. The main disadvantages associated to this process are: it needs the regular replacement of the “sacrificial electrodes”, since they are dissolved into the leachate as a result of oxidation; the increase in conductivity of the remaining effluent; the eventual formation of an impermeable oxide film on the cathode, disabling the EC unit; and, not less important, the sludge that is formed during the process that will have in its content significant amounts of iron and other recalcitrant pollutant species which need to be treated before its disposal. Moreover, some toxic chlorinated organic compounds and trihalomethanes may be formed *in situ* if chloride and high humic and fluid acid contents are present [56].

To increase the efficiency of the EC process and to reduce the increase in conductivity of the remaining effluent, attention has to be paid to the metal ions concentration in solution, avoiding unnecessary high metal contents. EC studies performed should be developed in more detail, and also using aluminium, to learn how to maintain the metal ions in solution in such a concentration that allows high efficiency without unnecessary waste of of the sacrificial anode.

Changing electrodes' polarity may help reducing the efficiency loss caused by the impermeable oxide film formed on the cathode. Also, constant applied current intensity

instead of constant applied potential decreases the electrodes' passivation, although it increases energy consumption, since, to keep the intensity when a passivating film is forming, higher overpotentials have to be applied. This increase in overpotential presents an extra feature that is the possibility of the direct oxidation of the organic matter present in the effluent. To find reliable ways of reducing electrode's passivation and the consequent inactivation of the EC landfill leachate treatment unit can pass also by the development of different electrode types and arrangements and more sophisticated reactor operational strategies.

To integrate EC process with other treatment methods can also be a possible solution to overcome some of the drawbacks, namely the solid-liquid separation and the sludge elimination. The EC technology can be designed to include membrane separation, reverse osmosis, electrofiltration, sludge dewatering, thermo-oxidation and other conventional technologies to enhance the recovery of fine particles and metal ions from wastewater [58]. This is an area in which urges to perform intensive work. Otherwise, EC will become just another way of transferring the problem, with the addition of metal ions to the final solution.

Integration of EC and EO processes, besides enhancing the treatment efficiency, also have the potential to eliminate possible toxic species, like chromium, zinc and part of the iron introduced during the EC process, as it was shown in Case study 6 [86]. However, this study has to be further developed, to include many other metal ions that were not included in this study. Research on the best experimental conditions that will lead to a more efficient recovery of the metals from solution, as well as the possibility of the selective recovery of the most dangerous metal ions or those that are present in higher concentration, are also welcome.

EO provides a simple, viable and promising method for the remediation of sanitary landfill leachates. In fact, this electrochemical method allows high treatment efficiencies without the disadvantage of sludge production. Under appropriate experimental conditions, it can remove most of the COD, almost all ammonia, and also significantly removes colour, without carrying out the accumulation of refractory organics. As a consequence of Cl^- presence in leachates, indirect electro-oxidation mediated by electrogenerated active chlorine occurs, increasing EO efficiency but at the same time promoting the possible production of undesirable toxic chlorinated by-products, which is one of the drawbacks of the EO application to landfill leachates treatment. Another drawback, possibly the most relevant, is the high operating costs due to the high energy consumption, since electricity is basically the only consumable in electrochemical oxidation. To overcome this problem, two paths can be taken: (1) the use of this technology in combination with other techniques as a pre-treatment or a polishing step; (2) the use of renewable energy sources to power electrochemical oxidation. There are several reports describing the application of combined methods involving EO to treat sanitary landfill leachates [10,32,46,91-96]. The encouraging results obtained so

far set the basis for future work. Regarding the use of renewable energy sources, the integration of photovoltaic modules in electrochemical wastewater treatment has been already reported [97]. Within this field, there is still a wide range of possibilities that can be explored. Development of a sustainable process based on the integration of efficient technologies is one of the key obstacles that have to be overcome before full-scale implementation of electrochemical oxidation.

Another major area for future research is the improvement of the electrocatalytic activity and electrochemical stability of new electrode materials, to develop better and more cost-effective electrodes, which will result in lower operational and capital costs. Despite the exceptional properties of BDD electrodes, already described, and the good results obtained when this electrode is used, its application has been mostly studied at Si-supported devices, which present difficulties related to their industrial transposition, due to the fragility and the relatively low conductivity of the Si substrate [17]. BDD films synthesized on Nb, Ta and W are promising, but their large-scale utilization is impossible due to the unacceptably high costs of these metal substrates [17]. On the contrary, titanium would possess all required features to be a good substrate material. There are already available in literature some studies reporting the use of Ti/BDD electrodes [98-103], but its use has never been reported in EO of sanitary landfill leachates. On the other hand, lead and stannous oxides have already proved to be very efficient in the leachates treatment, and there are already lead oxide electrodes commercially available. Maybe the next important step to implement EO technology is to perform pilot scale studies, in the in-situ plants, to deal with all daily constraints and changes, to find out if the only problem associated with this technology is, in fact, the cost.

In spite of the very good results obtained with electrochemical techniques on pollution abatement, electrochemical processes are often accused of being interfacial reactions and therefore difficult or impossible to apply to large volumes. The “interfacial problem”, in fact, is not a problem that has not already been solved by several industrial unit operations. However, it is a sort of a handicap that, to be efficiently overcome, needs pilot and semi-industrial scale studies. Also, to lower the energetic costs, these technologies should be applied to partial streams or as integrated processes with biological solutions. The energetic consumption can also be solved with green energy, like wind energy, tidal or solar, or using biogas from an anaerobic digestion reactor to produce energy to be used in the electrochemical reactor to polish the reactor effluent. Thus, incorporating renewable energy sources in the electrochemical treatment of sanitary landfill leachates closes with a flourish future prospects in this field.

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