



Anodic oxidation of a biologically treated leachate on a boron-doped diamond anode

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ABSTRACT

In the present study, the anodic oxidation of a leachate from an intermunicipal sanitary landfill was evaluated using a boron-doped diamond anode as a possible post-treatment to the biological one, in order to diminish the remaining bio-refractory organic matter. The influence of the dilution of the leachate sample and the applied current density on the performance of electrochemical oxidation was investigated.

For the different assays performed, a comparison between the theoretical kinetic model for organic mineralization, proposed in the literature, and experimental data was done and the best correspondences were attained at lower applied current density for sample without dilution and at higher applied current density for the more diluted sample. However, the energetic most favourable treatment is attained for sample without dilution at very low current density. The DOC/COD ratio was also analysed and apparently, the mineralization of the organic matter improves with the dilution of the leachate samples.

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1. Introduction

Due to its properties and composition, landfill leachate is one of the major environmental problems concerning water pollution [1,2]. Optimal leachate treatment, in order to fully reduce the negative impact on the environment, is today a challenge [3]. Over the past 30 years, there are several studies reporting the application of technologies based on oxidation processes to water and wastewater treatment [4–7]. Electrochemical oxidation has received great attention due to its effectiveness and ease in operation: no chemicals are used; only electrical energy is consumed [8]. Different types of anode materials (i.e., $\text{TiO}_2/\text{RuO}_2$, $\text{PbO}_2/\text{SnO}_2$, Ti/Pt , Ti/PbO_2 and boron doped diamond (BDD)) and the effect of several operating factors have been assessed [9–11]. BDD anodes present the best results. This material has unique chemical, electrochemical and structural stabilities that allow its use at high potentials where most organic pollutants can be oxidized [12,13]. In fact, the BDD anode enable the production of weakly adsorbed and consequently highly reactive hydroxyl radicals which can promote unselectively the mineralization of a wide range of organic pollutants. Even for complex wastewaters like landfill leachates, electrochemical oxidation using BDD anodes has been applied as a post-treatment method [14–21]. Cabeza et al. [14] study the feasibility of removing ammonium from landfill leachates by electrochemical oxidation, using a BDD electrode as anode. Experimental results showed very good

ammonium removal. Also, it was observed that when additional Cl^- was provided, the treatment efficiency increased. The effect of chloride ions in the treatment of landfill leachates was also conducted by Anglada et al. [15,19], at a pilot plant with BDD anodes, and they showed that the concentration of chloride has an effect on the oxidation of ammonia and chloride ions compete with organic matter to be oxidized at the anode. Moreover, organic matter and ammonia oxidation are highly influenced by the applied current density; a change in the mechanism of organic matter oxidation is observed when high current densities are applied [15]. A BDD electrode was also used in a comparative study between coagulation and activated carbon adsorption vs. electrochemical oxidation with a landfill leachate that had previously undergone biological treatment [16]. Experimental results showed that 50% removal of chemical oxygen demand (COD) was achieved by coagulation and 80% by activated carbon adsorption, when applied after coagulation treatment, while electrochemical oxidation led to a COD removal of 90%, without the formation of solid residues.

Integration of oxidation processes (Fenton and electrooxidation) in the conventional treatment of mature landfill leachates was also reported [17], showing that Fenton treatment allowed an important reduction in the COD level. However, it was ineffective in the abatement of ammonium content while electrooxidation with BDD anodes allowed the elimination of residual COD and ammonium.

The effect of various operating conditions, such as treatment time, current intensity, initial pH and initial concentration of chloride ions, were studied for electrochemical oxidation of landfill leachate with BDD anodes [19,21]. It was found that chloroform,

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Table 1
Physicochemical characteristics of raw and biologically pretreated leachates.

Property	Mean value (\pm SD)	
	Raw leachate	Biologically pretreated leachate
Chemical oxygen demand (g L^{-1})	13.7 \pm 0.4	5.8 \pm 0.1
Dissolved organic carbon (g L^{-1})	5.3 \pm 0.1	0.83 \pm 0.08
Dissolved inorganic carbon (g L^{-1})	1.38 \pm 0.06	0.31 \pm 0.05
Total Kjeldahl nitrogen (g L^{-1})	2.32 \pm 0.09	1.47 \pm 0.02
Total ammonia nitrogen (g L^{-1})	1.88 \pm 0.07	1.21 \pm 0.05
Chloride (g L^{-1})	2.5 \pm 0.3	4.4 \pm 0.4
Suspended solids (g L^{-1})	0.95 \pm 0.07	1.77 \pm 0.04
Dissolved solids (g L^{-1})	18.7 \pm 0.2	20.9 \pm 0.2
pH	7.5 \pm 0.3	8.4 \pm 0.4
Conductivity (mS cm^{-1})	17.4 \pm 0.1	22.1 \pm 0.1

dichloroacetonitrile, 1,2-dichloroethane and 1,1-dichloroacetone were the main chlorinated organic compounds formed as a result of organic matter oxidation and their concentration increase continuously with treatment time. Acidic conditions are found to favour the formation of haloacetonitriles and halo ketons [21].

An evaluation of the technical and economic feasibility of electrochemical oxidation for landfill leachate treatment showed that electrochemical oxidation with BDD anodes can compete with Fenton oxidation in terms of operation results and treatment costs [18]. Also, Zhao et al. [20] proposed a synergistic combination of the biochemical treatment and electrochemical oxidation of landfill leachate with sectional treatment on a BDD electrode that was highly efficient and energy-saving due to the high total organic carbon (TOC) removal and the low energy cost on the BDD electrode.

Besides all the problems associated with the composition of the sanitary landfill leachates, its seasonality and the consequent variation in the concentration of its immense pollutants introduces a new variable in any proposed treatment. This can be an advantage for the electrochemical treatment, since experimental conditions can easily be adjusted to the daily needs. The aim of this work is to study the influence of the real leachate dilution and the applied experimental conditions on the electrochemical degradation of a biologically pretreated leachate from a sanitary landfill using a BDD anode.

2. Experimental

2.1. Leachate characterization

The landfill leachate used in this study was collected in March 2011 from the intermunicipal sanitary landfill facility. This site, which serves a population of over 220,000 inhabitants in thirteen municipalities, has an onsite facility capable of treating daily up to 50 m³ of leachate. The raw leachate was initially treated on site by an activated sludge process. The characteristics of the biologically pretreated leachate are presented in Table 1. According to data in Table 1, most of the carbon present in the sample is in the organic form and about 80% of total Kjeldahl nitrogen (TKN) is ammonia nitrogen (NH₃-N).

2.2. Electrodegradation experiments

Experiments were conducted in batch mode, with stirring, and using 200 mL of solution. A BDD Diachem[®] anode, with an immersed area of 10 cm², and a stainless steel cathode, with identical area, were used. A GW, Lab DC, model GPS-3030D (0–30V, 0–3 A), was used as power supply. The electrodegradation assays were performed in a double-wall cell that enabled the recirculation of water from a thermostatic bath, set to 25 °C. Different current

intensities were tested, between 0.05 and 0.7 A. The biologically pretreated leachate (1:1) and several dilutions of this wastewater, between 1:2 and 1:16, were studied, being the concentration expressed as (volumes of raw leachate:volume of total sample). 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 (Pronalab, PA), was added in those experiments. All assays were performed in triplicate.

Degradation tests were followed by chemical oxygen demand, dissolved organic carbon (DOC), dissolved inorganic carbon, total Kjeldahl nitrogen, total ammonia nitrogen and UV-vis absorption spectrophotometry.

3. Analytical methods

COD determinations were made using closed reflux and titrimetric method [22]. TKN and NH₃-N were determined according to standard procedures using a Kjeldatherm block-digestion-system and a Vapodest 20s distillation system, both from Gerhardt [22]. Suspended solids (SS) and dissolved solids (DS) analysis were performed following the analytical procedure from standard methods [22].

Dissolved organic and inorganic carbons were measured in a Shimadzu TOC-V CSH analyser. Before these determinations, the samples were filtrated through 0.45 μm glass microfiber filters.

Chloride determinations were made by ion chromatography following the analytical procedure 4110C from Standard Methods [22].

UV-vis absorbance was measured from 200 to 800 nm using a Shimadzu UV-1800 spectrophotometer. pH was measured using a pH meter HANNA (HI 931400). Conductivity was determined using a conductivity meter Mettler Toledo (SevenEasy S30K).

4. Results and discussion

The effect of the landfill leachate dilution on the rate of electrochemical oxidation was studied by performing the electrodegradation assays using the biologically pretreated leachate without any dilution (1:1) and diluting it since 1:2–1:16. Fig. 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 behavior is observed, since at least part of the assay is controlled by the diffusion of the species undergoing degradation towards the electrode surface.

Fig. 2 shows the DOC results for the assays, which COD are presented in Fig. 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 behavior, 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 [23]; (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.

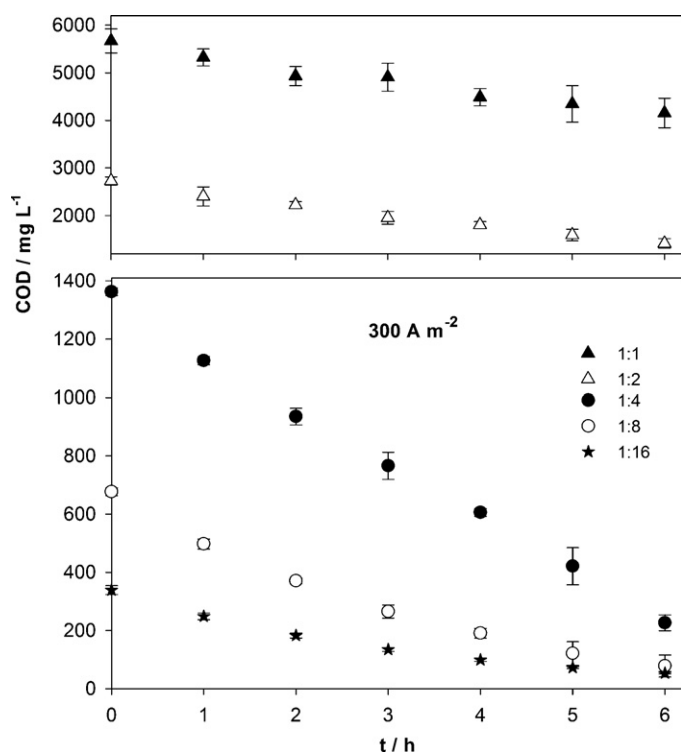


Fig. 1. Variation of COD with time for the electrodegradation assays performed without dilution and with different initial dilutions of the biologically pretreated leachate, at a current density of 300 A m^{-2} . Error bars refer to the standard deviation of the COD mean values.

In Table 2 the COD, DOC, TKN, $\text{NH}_3\text{-N}$ and absorbance (275 nm) removals are shown after 6 h of electrooxidation 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 behavior, 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 2), COD percentage removals above 85% were achieved and lead to final COD values below the Portuguese legal discharge limit (150 mg L^{-1}) [24]. For these dilutions, the increase in COD removal with concentration

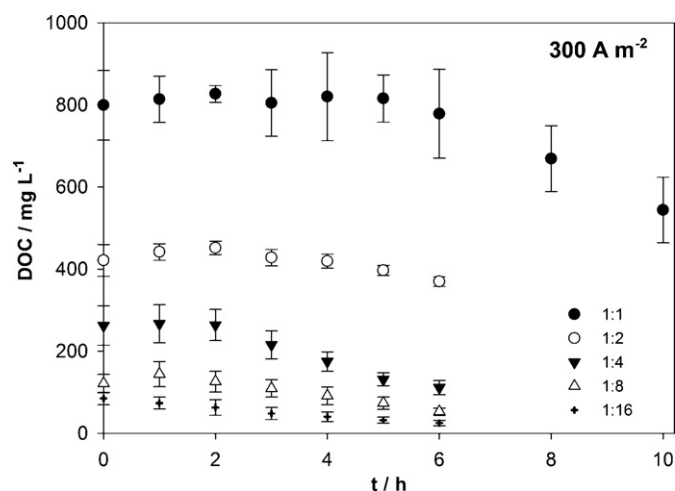


Fig. 2. Variation of DOC with time for the electrodegradation assays performed without dilution and with different initial dilutions of the biologically pretreated leachate, at a current density of 300 A m^{-2} . Error bars refer to the standard deviation of the DOC mean values.

observed presents the typical behavior of a diffusion controlled process [25]. In all cases, after 6 h 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. Regarding the absolute TKN and $\text{NH}_3\text{-N}$ 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 $\text{NH}_3\text{-N}$ 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 [4,26].

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 2, samples with higher dilutions (1:8 and 1:16) presented higher absorbance decays (around 88%), showing good removal of aromatic compounds after 6 h of electrolysis.

The influence of current density on the electrodegradation rate of biologically pretreated leachate, without dilution, was studied for current densities between 50 and 500 A m^{-2} and is presented in Fig. 3 and Table 3. Data reported, showed that COD removal rate increased with current density, achieving 44% after 6 h of electrolysis with an applied current density of 500 A m^{-2} . The regular

Table 2
Initial values of COD, DOC, TKN and $\text{NH}_3\text{-N}$ for the samples used in the assays performed at 300 A m^{-2} , their respective removals and absorbance removal 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
$\text{NH}_3\text{-N}$	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

Table 3

COD and DOC removals 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	–
DOC removal ($mg\ L^{-1}$)	–	–	–	20	251	303	–
Dilution 1:16							
COD removal ($g\ L^{-1}$)	–	–	0.30	0.30	0.32	–	0.32
DOC removal ($mg\ L^{-1}$)	–	–	29	40	48	–	50

linear decay, observed in Fig. 3 for all the applied current densities, indicates that electrolysis is mainly under current control.

According to the model previously proposed in the literature for electrolysis under current limited control [25], the trend of COD during electrochemical oxidation can be predicted by Eq. (1), where I is the current intensity, in A, F is the Faraday constant and V is the volume, in m^3 .

$$COD(t) = COD_0 - \frac{I}{4FV}t \quad (1)$$

Theoretical slopes, $I/4FV$, can be calculated, using Eq. (1), 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 Fig. 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 electrooxidation 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

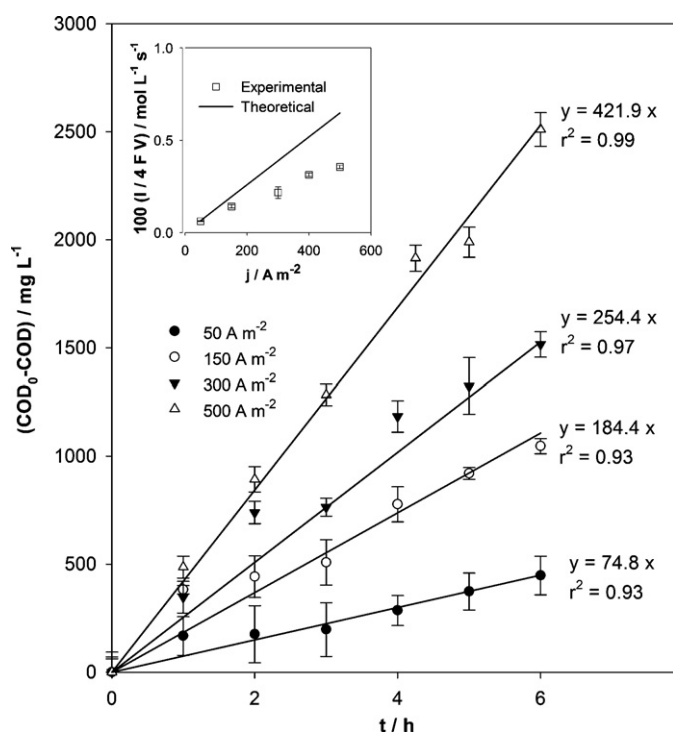


Fig. 3. COD removal with time for the electrodegradation assays performed with biologically pretreated leachate, without dilution, at different current densities and fittings of Eq. (1). Error bars refer to the standard deviation of the COD mean values. Inset: experimental (from the main figure) and theoretical (from Eq. (1)) values of $I/4FV$ vs. current density.

the reduction in COD, the control of the oxidation process can be mainly diffusive.

If data from Fig. 1 for dilutions 1:2 and 1:4 are adjusted to Eq. (1), zero order kinetic constants can be calculated for those assays run also in current control, at the current density $j = 300\ A\ m^{-2}$, and their values are: dilution 1:2–213 $mg\ L^{-1}\ h^{-1}$; dilution 1:4–184 $mg\ L^{-1}\ h^{-1}$. In fact, these values are further away from the theoretical value 448 $mg\ L^{-1}\ h^{-1}$ than the one obtained for the raw leachate in similar experimental conditions (254.4 $mg\ L^{-1}\ h^{-1}$, see Fig. 3), showing that, there is also a decrease in COD removal rate with dilution.

As showed in Table 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.

Apparently, the results presented in Fig. 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 Fig. 4 and Table 3. As it can be seen in Fig. 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 [25], given by Eq. (2), where A represents the geometric area of the electrode, in m^2 , and using data obtained at 400 and 700 $A\ m^{-2}$, allowed the determination of the medium mass transport coefficient, $k_m = 2.74 \times 10^{-5}\ m\ s^{-1}$. This value is higher than that presented in the literature ($1.75 \times 10^{-5}\ m\ s^{-1}$)

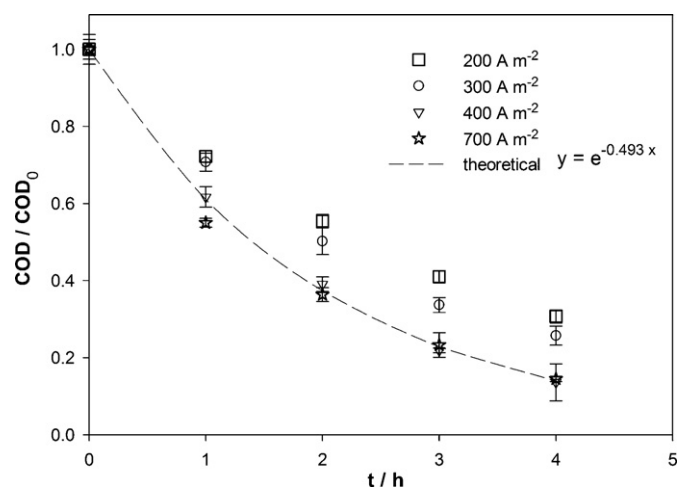


Fig. 4. Normalized COD variation with time for the electrodegradation assays performed with biologically pretreated leachate diluted at 1:16, at different current densities. Error bars refer to the standard deviation of the COD mean values.

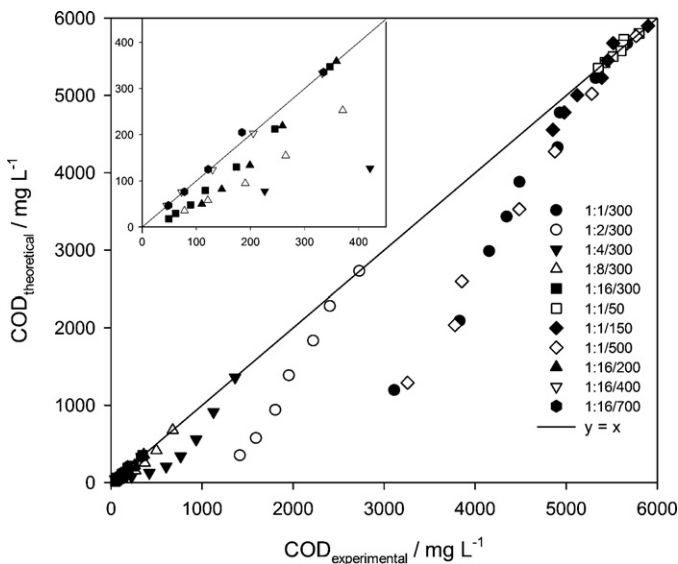


Fig. 5. COD parity plot for the assays performed with the biologically pretreated leachate and with its different dilutions at several current intensities [dilution/(current intensity/mA)].

[21], determined using the limiting current technique with a ferricyanide/ferrocyanide/ Na_2CO_3 electrolyte solution.

$$\text{COD}(t) = \text{COD}_0 \exp \left[- \left(\frac{Ak_m}{V} \right) t \right] \quad (2)$$

The medium mass transport coefficient obtained can be used in Eq. (3) to calculate the critical COD, COD_{cr} , that depends on the current intensity and has the value of 908 mg L^{-1} for $I=0.3 \text{ A}$.

$$\text{COD}_{\text{cr}} = \frac{I}{4AFk_m} \quad (3)$$

This COD_{cr} value indicates that, for $I=0.3 \text{ A}$, which corresponds to $j=300 \text{ A m}^{-2}$ (Fig. 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, j_{lim} , is calculated by means of the following equation [25]:

$$j_{\text{lim}} = 4Fk_m \text{COD}_0 \quad (4)$$

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.

Table 3 shows that for current densities higher than 400 A m^{-2} , 95% of COD removal and 85% of DOC removal were achieved after 6 h. After 2 h, COD values were below the legal discharge limit.

The agreement between the theoretical models, Eqs. (1) and (2), and experimental data can be visualized in a COD parity plot (Fig. 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.

Another aspect that may be interesting to analyse is the influence of leachate dilution on the ratio of DOC/COD (Fig. 6). If a linear regression is made with data collected at 300 A m^{-2} for 1:8 and 1:16 dilutions, a $\text{DOC}/\text{COD}=0.3$ was obtained. However, this

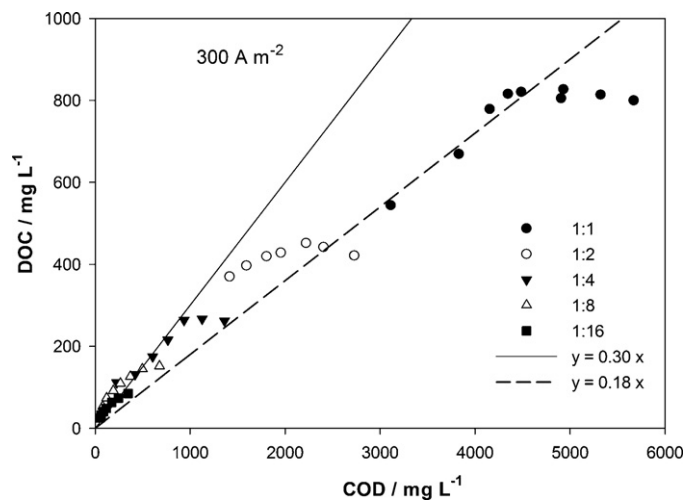


Fig. 6. DOC/COD experimental ratio (points) for the electrodegradation assays performed with different initial dilutions at a current density of 300 A m^{-2} and DOC/COD curve fittings for the assays performed without dilution (1:1) and with dilution 1:16 (lines).

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 specific energy consumptions, E_{sp} , in W h (g COD)^{-1} , for the different assays were calculated, by means of Eq. (5):

$$E_{\text{sp}} = \frac{UI\Delta t}{3600V\Delta \text{COD}} \quad (5)$$

where U is the cell voltage, in V, resulting from the applied current intensity I , in A, Δt is the duration of the electrolysis, in s, V is in L and ΔCOD is the removed COD, in mg L^{-1} , during Δt . The obtained E_{sp} values, divided by the lowest value found, are represented in Fig. 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 minimal.

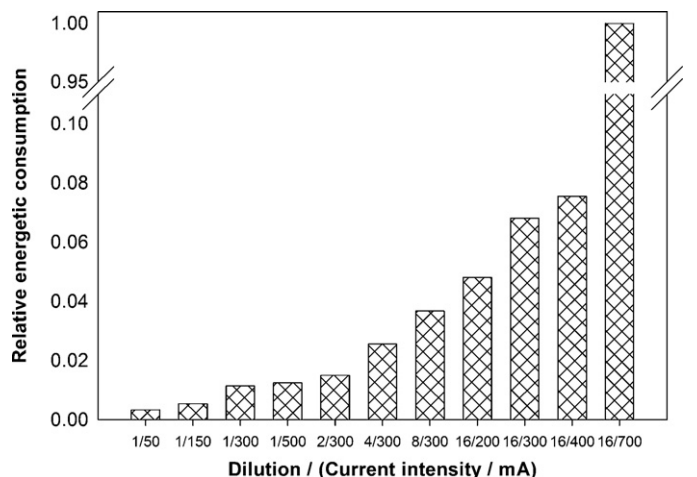


Fig. 7. Relative energetic consumption for the different assays performed.

Although after 6 h 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 h 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 $(5.8-1.52)=4.28 \text{ mg L}^{-1}$ and for the sample treated with an initial dilution of 1:16 is $(0.33-0.3)=0.03 \text{ mg L}^{-1}$. This procedure, although less expensive, would also increase the net amount of COD discharged in the environment.

5. Conclusions

With the obtained results it seems feasible the application of the electrochemical technology as a tertiary treatment of leachates from sanitary landfills, after a biological process, to eliminate the remaining organic load. The applicability of the theoretical models developed for the electrochemical degradation of effluents containing only organic matter is limited, and the situations 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. It was also found that an increase in the dilution or in the current intensity greatly increases the energy consumption. However, the mineralization of the organic matter improves with the dilution of the leachate.

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References

- [1] C.B. Öman, C. Junestedt, Chemical characterization of landfill leachates – 400 parameters and compounds, *Waste Manag.* 28 (2008) 1876–1891.
- [2] T. Eggen, M. Moeder, A. Arukwe, Municipal landfill leachates: a significant source for new and emerging pollutants, *Sci. Total Environ.* 408 (2010) 5147–5157.
- [3] A.A. Abbas, G. Jingsong, L.Z. Ping, P.Y. Ya, W.S. Al-Rebaki, Review on landfill leachate treatments, *J. Appl. Sci. Res.* 5 (2009) 534–545.
- [4] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41.
- [5] C.A. Martínez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- [6] C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, *Appl. Catal. B: Environ.* 87 (2009) 105–114.
- [7] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, *Chem. Rev.* 109 (2009) 6541–6569.
- [8] C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poullos, D. Mantzavinos, Advanced oxidation processes for water treatment: advances and trends for R&D, *J. Chem. Technol. Biotechnol.* 83 (2008) 769–776.
- [9] A. Anglada, A. Urriaga, I. Ortiz, Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications, *J. Chem. Technol. Biotechnol.* 84 (2009) 1747–1755.
- [10] M. Panizza, M. Delucchi, I. Sirés, Electrochemical process for the treatment of landfill leachate, *J. Appl. Electrochem.* 40 (2010) 1721–1727.
- [11] D. Ghernaout, M.W. Naceura, A. Aouabeda, On the dependence of chlorine by-products generated species formation of the electrode material and applied charge during electrochemical water treatment, *Desalination* 270 (2011) 9–22.
- [12] M. Panizza, G. Cerisola, Application of diamond electrodes to electrochemical processes, *Electrochim. Acta* 51 (2005) 191–199.
- [13] M. Fryda, D. Herrmann, L. Schäfer, C.P. Klages, A. Perret, W. Haenni, C. Comninellis, D. Gandini, Properties of diamond electrodes for wastewater treatment, *New Diamond Front. Carbon Technol.* 9 (1999) 229–240.
- [14] A. Cabeza, A. Urriaga, M.J. Rivero, I. Ortiz, Ammonium removal from landfill leachate by anodic oxidation, *J. Hazard. Mater.* 144 (2007) 715–719.
- [15] A. Anglada, A. Urriaga, I. Ortiz, Pilot scale performance of the electro-oxidation of landfill leachate at boron-doped diamond anodes, *Environ. Sci. Technol.* 43 (2009) 2035–2040.
- [16] C. Papastavrou, D. Mantzavinos, E. Diamadopoulos, A comparative treatment of stabilized landfill leachate: coagulation and activated carbon adsorption vs. electrochemical oxidation, *Environ. Technol.* 30 (2009) 1547–1553.
- [17] A. Urriaga, A. Rueda, A. Anglada, I. Ortiz, Integrated treatment of landfill leachates including electrooxidation at a pilot plant scale, *J. Hazard. Mater.* 166 (2009) 1530–1534.
- [18] A. Anglada, D. Ortiz, A.M. Urriaga, I. Ortiz, Electrochemical oxidation of landfill leachates at pilot scale: evaluation of energy needs, *Water Sci. Technol.* 61 (2010) 2211–2217.
- [19] A. Anglada, A.M. Urriaga, I. Ortiz, Laboratory and pilot plant scale study on the electrochemical oxidation of landfill leachate, *J. Hazard. Mater.* 181 (2010) 729–735.
- [20] G. Zhao, Y. Pang, L. Liu, J. Gao, B. Lv, Highly efficient and energy-saving sectional treatment of landfill leachate with a synergistic system of biochemical treatment and electrochemical oxidation on a boron-doped diamond electrode, *J. Hazard. Mater.* 179 (2010) 1078–1083.
- [21] A. Anglada, A. Urriaga, I. Ortiz, D. Mantzavinos, E. Diamadopoulos, Boron-doped diamond anodic treatment of landfill leachate: evaluation of operating variables and formation of oxidation by-products, *Water Res.* 45 (2011) 828–838.
- [22] A. Eaton, L. Clesceri, E. Rice, A. Greenberg, M.A. Franson, *Standard Methods for Examination of Water and Wastewater*, twenty-first ed., American Public Health Association, Washington, DC, 2005.
- [23] P. Mazellier, E. Leroy, J. Laat, B. Legube, Transformation of carbendazim induced by the $\text{H}_2\text{O}_2/\text{UV}$ system in the presence of hydrogenocarbonate ions: involvement of the carbonate radical, *New J. Chem.* 26 (2002) 1784–1790.
- [24] Decreto-Lei no. 236/98, *Diário da República*, I Série-A, no. 176, 3676–3722, 1998.
- [25] M. Panizza, P.A. Michaud, G. Cerisola, C. Comninellis, Anodic oxidation of 2-naphthol at boron-doped diamond electrodes, *J. Electroanal. Chem.* 507 (2001) 206–214.
- [26] Y. Deng, J.D. Englehardt, Electrochemical oxidation for landfill leachate treatment, *Waste Manag.* 27 (2007) 380–388.