

Chapter

**TREATMENT OF REVERSE OSMOSIS
CONCENTRATE FROM SANITARY LANDFILL
LEACHATE BY COMBINED PROCESSES:
ELECTROCOAGULATION FOLLOWED BY
ELECTRO-FENTON**

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ABSTRACT

Municipal solid wastes are increasing worldwide and the most common method to dispose solid residues is landfilling. However, in landfills, there is the formation of a highly contaminated leachate that cannot be discharged directly into the environment due to its high toxicity. Some leachate treatment plants are adopting membrane technologies, but a leachate concentrate that requires posterior treatment is obtained. In this chapter, the results obtained in the oxidation of a concentrate from reverse osmosis (chemical oxygen demand of $10\pm 1 \text{ g L}^{-1}$) of a sanitary landfill leachate are discussed. A combined treatment of electrocoagulation (EC) followed by electro-Fenton (EF) was applied. EC was performed using iron consumable anodes and the influence of the applied current intensity, process duration, initial pH and stirring speed was assessed. The EF experiments of the electrocoagulated samples were performed using a boron doped diamond (BDD) anode and a carbon-felt cathode. Since at the end of the EC assays dissolved iron was not enough to perform EF experiments, extra iron was supplied by anodic dissolution of iron electrodes. For the EF assays, the influence of the initial dissolved iron concentration and of the applied current density were evaluated. The results obtained with EF oxidation were compared with the results achieved by anodic oxidation of similar electrocoagulated samples, performed with a BDD anode and a stainless-steel or a carbon-felt cathode. Specific energy consumptions for the different assays were calculated. Ecotoxicological evaluation was assessed with the model organism *Daphnia magna*. The combined electrocoagulation and electro-Fenton processes showed to be adequate for the treatment of reverse osmosis concentrate from sanitary landfill leachate since it reduces drastically the organic load of the concentrate, as well as the sludge to be discarded.

Keywords: Reverse osmosis concentrate, Sanitary landfill leachate, Electrocoagulation, Electro-Fenton, Toxicity

INTRODUCTION

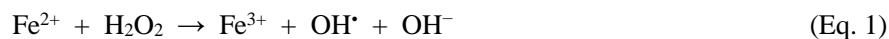
Landfilling is the most common method used for municipal solid wastes treatment. However, it presents serious environmental constrains, such as the generation of a highly polluted effluent - the sanitary landfill leachate. Sanitary landfill leachate is very difficult to treat due to its variable composition and because it may exhibit acute and chronic toxicity [1,2].

During the past years, several treatment methods have been studied for sanitary landfill leachate depuration, such as biological processes [3,4], membrane technologies [5,6], advanced oxidation processes [7-9], electrocoagulation [10,11], coagulation-flocculation [12,13], adsorption [14,15], among others. Most biological and physicochemical processes are unsuitable for treating leachate efficiently and, as a result, are complemented with/or even fully replaced by membrane technologies. Indeed, reverse osmosis (RO) has been increasingly applied worldwide for wastewater treatment, despite the expensive investment and maintenance costs. RO technology generates a high-quality water stream, but also a large volume of concentrate, which is its main disadvantage [16]. This reverse osmosis concentrate (ROC) contains the entire pollutant load presented in the leachate (salts, organics, inorganic, biological constituents, etc.) [16,17]. Generally, ROC is managed improperly, being discharged into evaporation ponds or recirculated to the sanitary landfills, threatening the leachate quality.

Many studies have focused on ROC management, either by integrating treatment technologies to RO systems [18,19], or by finding suitable treatment technologies to decontaminate ROC [16,17,20]. Among the different technologies studied to treat ROC, electrochemical processes have received great attention, since they offer many advantages, such as, operating at ambient temperature and pressure, the high chloride concentration in ROC that enhances the indirect oxidation and the high salinity, which promotes an excellent electric conductivity, reducing energy consumptions [16,21,22].

Electrocoagulation (EC), electro-Fenton (EF) and anodic oxidation (AO) are the most studied electrochemical processes for sanitary landfill leachate treatment [23]. EC, known for its ability to remove suspended, emulsified and dissolved contaminants, at relatively low costs, is a process that uses consumable anodes to supply ions to the solution/suspension. Iron and aluminum are the most widely used EC electrode materials, since they are cheap, readily available and effective [23]. 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 anode corrosion [23]. Nevertheless, there are some drawbacks associated to the application of this technology to the effluents treatment, namely the sludge that is formed during the process, which will have in its content significant amounts of iron or aluminum. Integration of the EC process with other treatment methods can be a possible solution to overcome this drawback. There are several studies describing the integration of EC and AO processes, where EC is used as a first step, to remove colloidal and suspended particles, and AO is utilized to eliminate the remaining dissolved persistent organic compounds [24-26]. Although AO is, according to literature, the most popular electrochemical

procedure for removing organic pollutants from wastewaters, it presents high operating costs, due to the high energy consumption, since electricity is basically the only consumable in the electrochemical oxidation [23]. On the other hand, the EF process, another attractive emerging electrochemical technique, promotes the oxidation of organic compounds via an indirect electrochemical oxidation through hydroxyl radicals produced in the Fenton reaction (Eq. 1), yielding good treatment efficiencies, and, according to literature, can promote the oxidation of the organic matter at lower energetic costs than AO, when the sample mainly consists of dissolved matter [22].



One of the main advantages of the EF process, is that, using a suitable cathode, like carbon-felt, H_2O_2 can be electrogenerated *in situ*, according to Equation 2 [27,28].



Furthermore, in the EF process, the reaction described by Equation 1 is electrocatalyzed, since Fe^{2+} ions are regenerated from the reduction of Fe^{3+} ions at the cathode, through Equation 3 [22,28].



According to the literature, EF efficiency can be further enhanced if it is used a high O_2 -overpotential anode, such as BDD, since it will accelerate the degradation of the organic matter, which can also be oxidized by adsorbed hydroxyl radicals (BDD(OH^\bullet)), formed as an intermediate of the anodic water discharge [22].

The aim of this work was to study the application of electrocoagulation and electro-Fenton processes as a combined treatment for reverse osmosis concentrates from sanitary landfill leachate, and to evaluate the efficacy of the treatment method in the simultaneous reduction of organic load and toxicity towards the model species *Daphnia magna* (Straus, 1820). EC was used as a first step, to remove mainly the colloidal and suspended particles, and it was followed by EF to eliminate the remaining dissolved persistent organic compounds. In both EC and EF assays different experimental conditions were tested. EF results were compared with the results achieved by AO at similar experimental conditions.

METHODS

Sample characterization

The ROC sample used in this study was collected at a Portuguese intermunicipal sanitary landfill site. The leachate treatment used in this landfill site comprises two reverse osmosis systems followed by a stripping column. The sample was collected in the reverse osmosis concentrate reservoir, and its physicochemical characteristics are presented in Table 1.

Table 1. Physicochemical characteristics of the reverse osmosis concentrate of the sanitary landfill leachate

Parameter	Value \pm SD
COD (g L ⁻¹)	10 \pm 1
DOC (g L ⁻¹)	4.2 \pm 0.7
DIC (g L ⁻¹)	2.2 \pm 0.4
TDN (g L ⁻¹)	3.2 \pm 0.1
Ammonium (g L ⁻¹)	3.80 \pm 0.04
Sulfate (g L ⁻¹)	2.97 \pm 0.02
Chloride (g L ⁻¹)	4.01 \pm 0.03
Total dissolved iron (mg L ⁻¹)	9 \pm 2
Dissolved iron (II) (mg L ⁻¹)	9 \pm 2
Acute toxicity (EC ₅₀ (48 h) / TU)	1.63% / 61.3
pH	8.3 \pm 0.4
Conductivity (mS cm ⁻¹)	30 \pm 1

SD - standard deviation, TU - toxic units (TU = 100/EC₅₀,
10 < TU < 100: very toxic [29])

Electrochemical experiments

EC assays were performed in batch mode, using an undivided electrochemical cell, equipped with iron anode and cathode, with a 7 mm gap between them and both with immersed dimensions of 25x60x3 mm. The electrodes were dipped into the cell containing 0.5 L of ROC sample. The influence of applied current intensity, EC duration, initial pH and stirring conditions in the EC efficiency was assessed.

Experiments were run at 2 and 3 A, with durations of 1, 2, 3 and 4 hours, with and without stirring at 200 rpm, using effluent at natural pH and at initial pH of 7. After EC treatment, samples were centrifuged in a high frequency induction motor centrifuge (Meditronic BL-S), at 5000 rpm, during 5 min, and the supernatant liquid was collected for the analytical determinations.

Attending to the results achieved in the EC study, a set of EC experimental conditions (2 A, 2 h, pH 7, without stirring) was chosen to proceed for EF and AO experiments. At these conditions, several EC assays were performed to produce the volume of pretreated sample required to run all the EF and AO assays. The centrifuged pretreated samples were mixed together to ensure that the composition of the electrocoagulated ROC used in all subsequent experiments was similar.

EF and AO experiments were conducted in batch mode with stirring, for 8 h, at imposed current densities (j) of 50, 100 and 200 A m⁻², using 200 mL of the electrocoagulated ROC. For the EF assays, the pH of the pretreated sample was adjusted to 3, which is, according to the literature, the optimum pH for the EF process [23].

EF assays were performed with a carbon-felt (CF) cathode (Carbone Loraine), with a thickness of 0.5 cm and an immersed area of 60 cm², and a BDD (Neocoat) anode, with an immersed area of 20 cm². The anode was centered in the electrochemical cell and surrounded by the cathode, which covered the inner wall of the cell. Continuous O₂ saturation at atmospheric pressure was ensured by bubbling compressed air through a fritted glass diffuser, at a flow rate of 1 L min⁻¹, starting 10 min before electrolysis, to reach a steady O₂ concentration. In order to ensure that H₂O₂ was being properly produced and was in sufficient amount to react with iron, H₂O₂ determinations were performed along the assays. Since dissolved iron concentration in the electrocoagulated ROC was not enough to promote an effective EF process (3.7 mg L⁻¹), previously to the EF assays extra iron was supplied to the solution by anodic dissolution of iron electrodes. For this purpose, iron electrodes, with dimensions 20x50x3 mm, were dipped in 210 mL of electrocoagulated ROC, acidified at pH 3, and an applied current intensity of 1 A was applied during 70 and 85 s, in order to reach a dissolved iron concentration of approximately 60 and 80 mg L⁻¹, respectively.

AO assays were performed using a BDD anode (the same utilized in the EF experiments) and a stainless-steel (SS) cathode, with similar immersed area to the BDD anode. The electrodes were disposed in parallel with a distance between them of 3 mm. AO experiments using BDD anode and carbon-felt cathode (the same used in EF experiments) were also performed.

A resume of the experimental conditions utilized in EF and AO experiments is presented in Table 2.

In all electrochemical experiments, a constant current intensity in the electrochemical cell was maintained using a DC power supply (GW, Lab DC, model GPS-3030D, 0-30V, 0-3 A). To acidify the samples, a H₂SO₄ concentrated solution was utilized.

Table 2. Experimental conditions utilized in the EF and AO experiments

Process	Anode / cathode	Initial pH	Initial dissolved iron concentration / mg L ⁻¹	Current density / A m ⁻²	
EF	BDD / CF	3	60	50	
				100	
				200	
				80	50
					100
					200
AO	BDD / SS	9.4 (natural)	3.7 (natural)	50	
				100	
				200	
	BDD / CF	9.4 (natural)	3.7 (natural)		200

Toxicological assays

The freshwater crustacean *Daphnia magna* cultured in the laboratory, under standardized conditions, was used to perform the toxicological assays. Adult females of *D. magna* (30 individuals per 1 L jar) were maintained in ASTM (American Society of Testing Materials) hard water under controlled temperature and light conditions (T=20±1 °C; photoperiod: 12:12 h light:dark). The culture media (supplemented with seaweed extract) was changed 3 times per week and the daphnids were feed daily with *Raphidocelis subcapitata* (3.0x10⁵ cells mL⁻¹). The 2nd to the 5th broods were used to perform toxicity tests.

Prior to the tests with the real samples a 24-h acute toxicity test with K₂Cr₂O₇ was performed, according to OECD Guideline 202 recommendation [30], to assess the sensitivity of the organisms. K₂Cr₂O₇ solutions (6 different concentrations) were prepared in ASTM hard water and tested in quadruplicate, ASTM hard water was used as control. For each replicate, 5 neonates with less than 24 h were exposed to the test solution during 24 h, then the number of immobilized daphnids was

registered and the concentration responsible for 50% of immobilization (EC_{50}) calculated using the Sigmaplot software package (v12.5).

The acute toxicity tests were performed in neonates with less than 24 h from the 2nd to the 5th brood in accordance with the OECD Guideline 202 [30]. Five replicates, with 5 neonates each, were tested on a set of dilutions (5 to 7 different dilutions per sample) with concentrations ranging from 0.31 up to 10%. Immobilized daphnids were registered after 24 and 48 h of exposure and EC_{50} calculated. All the tests were performed within 1 month of the electrochemical assays and the samples were maintained under dark conditions at 4 °C.

Physicochemical determinations

The samples collected before, during and after the electrochemical assays were analyzed, according to the procedures described in the Standard Methods [31], for the following parameters: chemical oxidation demand (COD), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and total dissolved nitrogen (TDN).

COD determinations were made using the closed reflux titrimetric method adapted to samples containing high concentrations of chloride [31,32]. The digestion of the samples occurred in strongly acid solution with a known excess of potassium dichromate, with addition of a silver compound as catalyst, to promote the oxidation of resistant organic compounds, and mercury sulfate, to reduce interferences from the oxidation of chloride ions. The samples closed reflux digestion was performed in a thermoreactor Merck Spectroquant TR 420, during 2 h at 150 °C. After digestion, the remaining unreduced dichromate was titrated with ferrous ammonium sulfate, using ferroine as indicator, to determine the amount of dichromate consumed, which is equivalent to the amount of oxygen required to oxidize the organic matter.

A Shimadzu TOC-VCPH analyzer combined with a TNM-1 unit was used to determine DOC, DIC and TDN. Before DOC, DIC and TDN determinations, samples were filtered through 0.45 μm membrane filters.

For ROC sample characterization, ammonium, sulfate and chloride ions concentrations were determined by ion chromatography using a Shimadzu 20A Prominence HPLC system that was equipped with a Shimadzu CDD 10Avp conductivity detector. To determine the NH_4^+ , an IC YK-A Shodex (4.6 mm ID×100 mm) cation column was utilized. The analysis was performed at isocratic mode and the mobile phase was an aqueous solution containing 5.0 mM tartaric acid, 1.0 mM dipicolinic acid and 24 mM boric acid, at a flow rate of 1.0 mL min⁻¹.

¹. The column temperature was 40 °C. To evaluate SO₄²⁻ and Cl⁻ concentrations, an IC I-524A Shodex (4.6 mm ID × 100 mm) anion column was employed. The mobile phase consisted of an aqueous solution of 2.5 mM of phthalic acid and 2.3 mM of tris(hydroxymethyl) aminomethane at a flow rate of 1.5 mL min⁻¹. The column temperature was 40 °C. All solutions for chromatographic analysis were prepared with ultrapure water obtained with Milli-Q[®] equipment. All eluents were HPLC grade and supplied by Sigma-Aldrich.

Total dissolved iron and dissolved iron (II) concentrations were determined using a spectrometric method with 1,10-phenanthroline [33]. Since samples absorbed at 511 nm, the absorbance of samples collected during the assays was measured before and after the addition of 1,10-phenanthroline and the difference between the values was converted into iron concentration.

H₂O₂ concentration was determined by the colorimetric metavanadate method [34]. The method is based on the reaction of H₂O₂ with ammonium metavanadate in acidic medium, which results in the formation of a red-orange colour peroxovanadium complex, with maximum absorbance at 450 nm. Since samples absorbed at 450 nm, the absorbance of the samples collected during the assays was measured before and after the addition of metavanadate and the difference between the values was converted into H₂O₂ concentration.

The pH was measured using a HANNA pH meter (HI 931400). The conductivity was determined using a Mettler Toledo conductivity meter (SevenEasy S30K).

RESULTS AND DISCUSSION

EC experiments

With the aim of determine the most suitable EC experimental conditions for the ROC sample pretreatment, different EC assays were performed where applied current intensity, sample initial pH, stirring speed and assay duration were varied. Figure 1 presents COD removals and iron and energetic consumptions for the EC assays performed at different experimental conditions. 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_{removed})⁻¹, presented in Figure 1 c) and d), were calculated according to Equations 4 and 5, where I is the current intensity, in A, t is the EC duration, in s, M_{Fe} is the iron molar mass, in g mol⁻¹, F is the Faraday constant, 96485 C mol⁻¹, n is the number of electrons involved in the

oxidation of Fe to Fe²⁺, V is the volume of the sample, in L, ΔCOD is the decay in COD and U is the cell voltage, in V.

$$Fe_{sp} = \frac{I \cdot t \cdot M_{Fe}}{F \cdot n \cdot V} \quad (\text{Eq. 4})$$

$$E_{sp} = \frac{U \cdot I \cdot t}{3.6 \cdot \Delta COD \cdot V} \quad (\text{Eq. 5})$$

Current intensity and assay duration are key factors in the EC process, since they exert a significant influence on the reaction kinetics and energy consumption. Increasing applied current intensity or assay duration, the extent of anodic dissolution of the consumable electrodes increases, resulting in an increase in the formation of hydroxide flocs that promote pollutants removal. However, the energy consumption is greatly increased by the increase in current intensity and assay duration. So, an optimum current intensity vs. EC duration must invariably involve a balance between energy consumption and efficient use of the introduced coagulant [23]. From data shown in Figure 1, it can be seen that, increasing applied current intensity from 2 to 3 A, COD removal increased, in average, 14±7%, but specific energy consumption increased 83±25%, with an increase in specific iron consumption of 50%. Regarding the influence of assay duration on EC efficiency, it can be observed that both COD removal and specific energy consumption increased with EC duration. However, with the increase in assay duration, COD removal rate became less pronounced and specific energy consumption deeply increased. These results indicated that an EC duration of 2 h at an applied current intensity of 2 A were the most suitable conditions for the ROC pretreatment.

The pH of the solution is another important operating factor that influences EC process performance. According to the literature, higher COD removal efficiencies are obtained at neutral pH conditions, whereas in acidic or alkaline medium COD removal is lower [23]. Thus, EC assays were performed at two initial pH conditions: natural pH (8.3) and pH of 7. Results obtained (Figure 1) show that higher COD removals and lower specific energy consumptions were achieved when assays were run at pH 7, in accordance with the results described in the literature [23].

The effect of mechanical stirring on EC process has been studied and different results have been achieved [23]. EC process is performed by the mobilization of ions by means of applied electrical charge, and mixing operation will influence the movement of the 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 ions mobilization and the breakup of the formed flocs. In this study, EC assays were performed without stirring and with stirring at 200

rpm. According to the results obtained (Figure 1), stirring had a negative effect on COD removal and on specific energy consumption, indicating that stirring make the aggregation more difficult, delaying the precipitation of the suspended and dissolved matter.

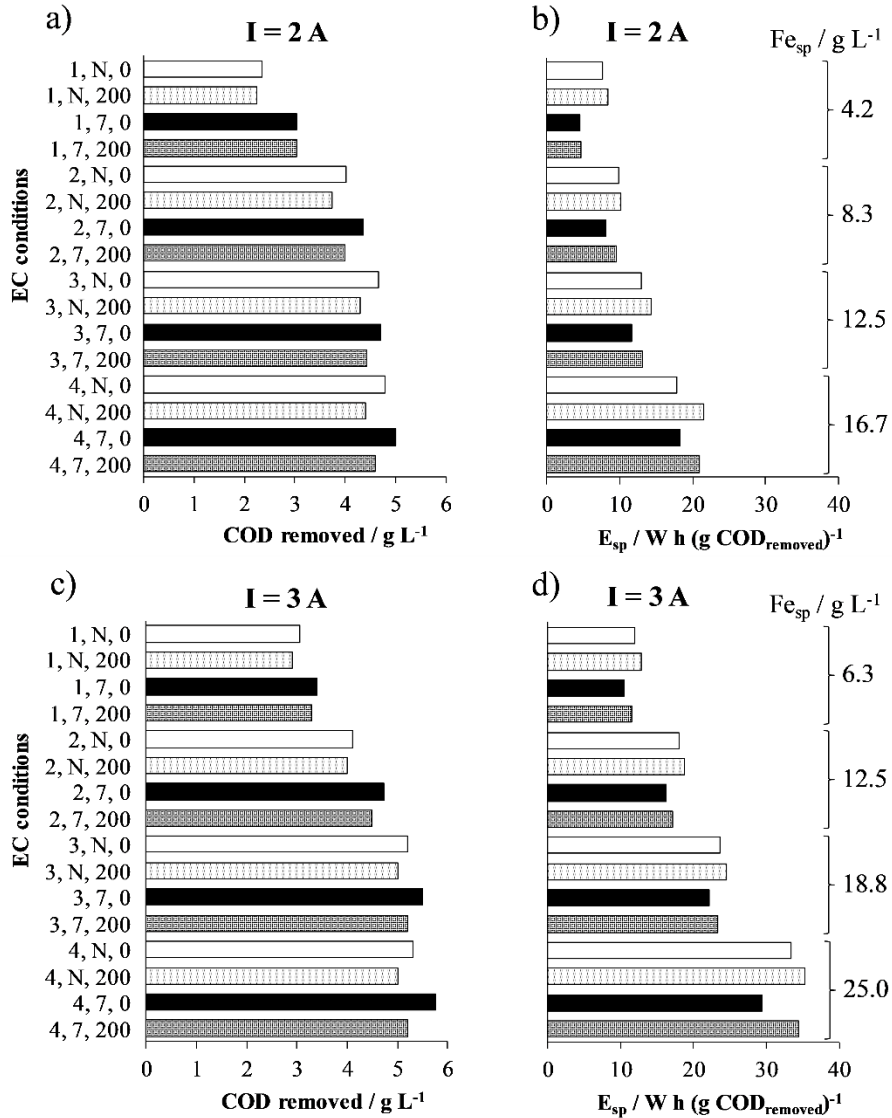


Figure 1. (a) and (c) Chemical oxygen demand removed in the EC experiments performed at applied current intensities of 2 and 3 A, respectively, at different:

assays duration (1, 2, 3 and 4 h); initial pH conditions (N-natural and 7); and stirring speed (0 or 200 rpm). (b) and (d) Specific energy and iron consumptions of the EC experiments performed at the applied current intensities of 2 and 3 A, respectively, using the experimental conditions described for (a) and (c).

Regarding the dissolved iron concentration at the final of the EC process, determined in the supernatant liquid of the centrifuged electrocoagulated sample, values between 0.8 and 6.1 mg L⁻¹ were obtained, showing that very little dissolved iron remained in the pretreated sample and that practically all the iron introduced during the EC process stayed in the sludge. The pH of the final samples varied between 8.9 and 10.9, being the highest pH values found in the assays performed at higher applied current intensities and EC durations.

Attending to the results attained in the EC experiments, the best EC experimental conditions to pretreat the ROC samples are: initial pH of 7, without stirring, at an applied current intensity of 2 A, during 2 hours.

EF and AO experiments

Using the ROC samples pretreated by EC at the best experimental conditions, EF assays were performed using different initial ferrous iron concentrations (60 and 80 mg L⁻¹ [35]), at the optimal pH of 3 and different applied current densities, 50, 100 and 200 A m⁻². Figure 2, a) to c), shows the COD removed along the time for the assays performed at different applied current densities and dissolved iron concentrations. It can be seen that, for both dissolved iron concentrations studied, COD removal increased with applied current density, showing that the process must be under current control. When applied current density was increased from 50 to 100 A m⁻², an increment in the average COD removal of 58±10% was achieved. However, increasing applied current density from 100 to 200 A m⁻² led to increases in COD removal of 29±14%. When specific energy consumption for previously described assays are analyzed (Figure 2 d)), it is observed that when the applied current density was increased from 100 to 200 A m⁻², the increase in the specific energy consumption was much more pronounced than the one observed when applied current density was increased from 50 to 100 A m⁻², showing a loss of current efficiency for the highest applied current density. In fact, the increase from 50 to 100 A m⁻² resulted in average specific energy consumptions increases of 48±8%, whereas the increase from 100 to 200 A m⁻² resulted in specific energy consumptions increases of 117±6%. This behavior has been reported in literature and is associated to competitive electrode reactions, such as oxygen discharge at

the anode and hydrogen evolution at the cathode, that increase under high applied currents and inhibit the main reactions [17,36].

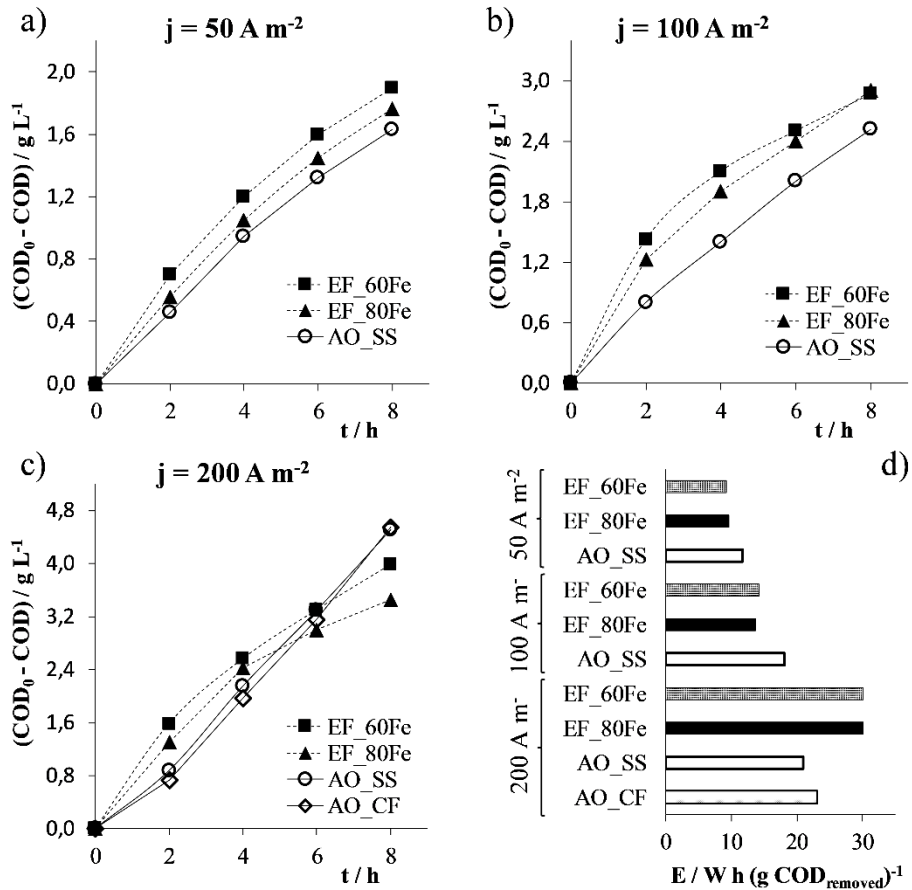


Figure 2. (a) to (c) - Variation with time of COD removed in the EF experiments (with 60 and 80 mg L⁻¹ of dissolved iron) and in the AO experiments (with SS and CF cathodes) performed at the applied current densities of 50, 100 and 200 A m⁻², respectively. (d) Specific energy consumptions of the EF and AO experiments described in (a), (b) and (c).

Dissolved iron (II) and total iron concentrations were also monitored along the EF experiments. Results, presented in Figure 3, corroborate the loss of current efficiency by side reactions at higher applied currents, since at 200 A m⁻², a significant amount of dissolved iron (III) is found in solution, especially at the last

hours of the assays. The presence of iron (III), also detected in the assays performed at 100 A m^{-2} , but in a much lower concentration, indicates that Fe^{2+} was not being properly regenerated at the cathode via Equation 3.

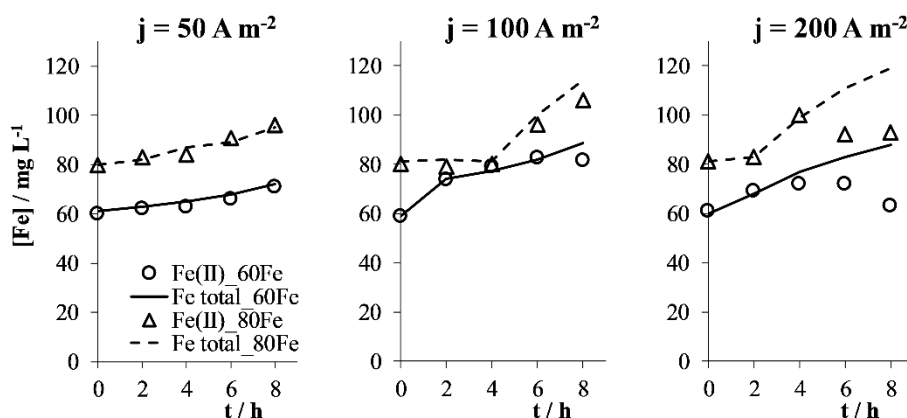
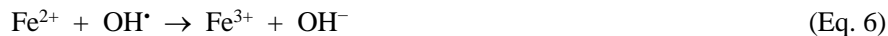


Figure 3. Variation with time of the dissolved iron (II) and total iron concentrations in the EF experiments performed with initial dissolved iron concentrations of 60 and 80 mg L^{-1} , at applied current densities of 50, 100 and 200 A m^{-2} .

Regarding the influence of the initial dissolved iron concentration, results obtained show that, for the assays performed with 80 mg L^{-1} , for all current densities tested, COD removal rate decreased, compared with the assays performed with 60 mg L^{-1} (see Figure 2 a) to c)). This decrease has already been reported in the literature and can be due to the scavenging reaction between iron and hydroxyl radicals (Equation (6)), which is enhanced by the excess of ferrous iron in solution and consumes the hydroxyl radicals available for the oxidation of the organic compounds [17,36,37].



Despite COD removal rates decrease for higher initial dissolved iron concentrations, specific energy consumptions were not increased (Figure 2 d)). This can be explained by the higher conductivity values presented by the pretreated samples with higher iron concentration that led to lower cell voltages for the same applied current density.

When dissolved iron evolution along the EF assays is analyzed (Figure 3), an increase in iron concentration can be observed, which is more pronounced at the

highest applied current density and the highest initial dissolved iron concentration. This could be a consequence of the existence of non dissolved iron in the pretreated sample, which was gradually dissolved as the EF treatment proceeded, as already described in the literature [37].

Attending to the results obtained in the EF experiments, the most favorable conditions are the applied current density of 100 A m^{-2} and the initial dissolved iron concentration of 60 mg L^{-1} . At these conditions, 2.9 g L^{-1} of COD was removed in 8 h of EF process, with a specific energy consumption of $14.2 \text{ W h (g COD}_{\text{removed}})^{-1}$.

To compare EF and AO performances, AO experiments were run at the same applied current densities used in the EF study, at natural iron and pH conditions. Two different electrochemical cells were utilized: BDD anode and stainless-steel cathode, the most applied in AO studies, and BDD anode and carbon-felt cathode, the same used in EF assays. Results, presented in Figure 2, show that, for applied current densities of 50 and 100 A m^{-2} , the AO process presents lower performance than EF, with lower COD removals and higher specific energy consumptions. However, at 200 A m^{-2} , COD removal in AO was higher than the one achieved in the EF process and the specific energy consumption was lower. In AO process, pollutants oxidation may occur on the electrode surface, by mediation of hydroxyl radicals continuously formed during water discharge, and on the bulk of the solution, by other powerful electrogenerated oxidants, such as active chlorine, persulfate, etc. [23]. At low applied current densities, the formation of oxidized active species that can promote pollutants oxidation in the bulk of the solution is low and, thus, pollutants' oxidation occurs mainly at the anode surface, by mediation of hydroxyl radicals, under weak oxidative conditions, since the pollutants are in excess compared to the available hydroxyl radicals. With the increase in applied current density, the formation of hydroxyl radicals and other oxidized active species is enhanced, promoting an effective oxidation of pollutants at the anode surface and in the bulk of the solution.

Regarding the influence of cathode material in AO performance (Figure 2, c) and d)), results show that, when carbon-felt cathode was employed, COD removal rate was slightly lower and specific energy consumption was higher, indicating that this cell configuration did not benefit the AO process.

Attending to the results achieved in both EF and AO studies, combined EC and EF processes showed to be the most economical solution to treat reverse osmosis concentrate from sanitary landfill, since it allowed the removal of organic load at lower energy consumption.

In order to evaluate the influence of the electrochemical processes on the acute toxicity of the ROC sample studied, ecotoxicity tests towards *D. magna* were

performed. Since the highest COD removals were achieved when EF and AO assays were performed at 100 and 200 A m⁻², only the final samples obtained using these applied current densities were evaluated. Results are presented in Table 3.

Table 3. *Daphnia magna* acute toxicity of the treated samples by combined EC/EF and EC/AO.

Secondary process (experimental conditions)	48 h EC ₅₀ / %	TU
EF (I = 100 A m ⁻² , [Fe] = 60 mg L ⁻¹)	2.76	36.2
EF (I = 100 A m ⁻² , [Fe] = 80 mg L ⁻¹)	1.97	50.7
AO (I = 100 A m ⁻² , SS)	2.05	48.7
EF (I = 200 A m ⁻² , [Fe] = 60 mg L ⁻¹)	3.01	33.2
EF (I = 200 A m ⁻² , [Fe] = 80 mg L ⁻¹)	2.57	39.0
AO (I = 200 A m ⁻² , SS)	2.61	38.3
AO (I = 200 A m ⁻² , CF)	2.06	48.5

EC₅₀: concentration responsible for 50% of immobilization, expressed as dilution.

TU: toxic units (TU = 100/EC₅₀, 10 < TU < 100: very toxic [29])

Considering the toxicity of the initial ROC sample, presented in Table 1, with an EC₅₀ of 1.63% (61.3 TU), it can be seen that after the electrochemical treatment the toxicity was reduced, for all the experimental conditions evaluated, although the treated samples were still very toxic, according to the toxicity classification based on toxic units (TUs) reported by Pablos et al. [29]. It can also be observed that the highest reductions in toxicity were achieved in the EF assays performed with the lowest iron concentration. Toxicity removal increased with the applied current density, which can be due to the high COD removal. However, for the AO assays performed at 200 A m⁻², whose COD removal presented the highest values, the decrease in toxicity was not the highest. This result can be consequence of the formation of organochlorinated compounds during AO treatment, as already reported in the literature [8].

CONCLUSION

The results of this study indicate that the combined processes, electrocoagulation followed by electro-Fenton, can be used to eliminate the recalcitrant organic load from sanitary landfill leachate concentrates and to decrease their toxicity.

On evaluating the effects of different operating parameters on COD removal efficiency, optimal experimental conditions of EC pretreatment and subsequent EF process were: 2 h of EC at a current intensity of 2 A and initial pH of 7, without stirring, followed by 8 h of EF at a current density of 100 A m⁻² and with an initial dissolved iron concentration of 60 mg L⁻¹. Under these optimal conditions, a COD removal of 7.3 g L⁻¹ was accomplished, along with a decrease of 69% in the acute toxicity towards *D. magna*, with a specific energy consumption of 10.6 W h (g COD_{removed})⁻¹.

Thus, this combined process can be used to treat reverse osmosis concentrates from sanitary landfill leachate, leading to a treated effluent with low content in recalcitrant organic and inorganic compounds, but still with significant organic load and toxicity, which can be sent to further treatments in urban wastewater treatment plants.

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