



## Electrochemical oxidation of stabilized landfill leachate on DSA electrodes

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### ABSTRACT

The electrochemical oxidation of stabilized landfill leachate with 2960 mg L<sup>-1</sup> chemical oxygen demand (COD) over a Ti/IrO<sub>2</sub>–RuO<sub>2</sub> anode was investigated in the presence of HClO<sub>4</sub> as the supporting electrolyte. Emphasis was given on the effect of electrolysis time (up to 240 min) and temperature (30, 60 and 80 °C), current density (8, 16 and 32 mA cm<sup>-2</sup>), initial effluent's pH (0.25, 3, 5 and 6), HClO<sub>4</sub> concentration (0.25 and 1 M) and the addition of NaCl (20 and 100 mM) or Na<sub>2</sub>SO<sub>4</sub> (20 mM) as source of extra electrogenerated oxidants on performance; the latter was evaluated regarding COD, total carbon (TC), total phenols (TPH) and color removal. Moreover, the anode was studied by scanning electron microscopy and cyclic voltammetry. The main parameters affecting the process were the effluent's pH and the addition of salts. Treatment for 240 min at 32 mA cm<sup>-2</sup> current density, 80 °C and the pH adjusted from its inherent value of 0.25 (i.e. after the addition of HClO<sub>4</sub>) to 3 yielded 90% COD, 65% TC and complete color and TPH removal at an electricity consumption of 35 kWh kg<sup>-1</sup> COD removed. Comparable performance (i.e. 75% COD reduction) could be achieved without pH adjustment but with the addition of 100 mM NaCl consuming 20 kWh kg<sup>-1</sup> COD removed.

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### 1. Introduction

Landfilling in sanitary landfills is the most common method employed to dispose of municipal solid wastes worldwide. Biological processes convert the organic matter into an environmentally harmful leachate and landfill gas. The former is a complex wastewater often containing both biodegradable and resistant organic compounds, heavy metals, suspended solids, chlorinated compounds and inorganic salts and exhibiting acute and chronic toxicity [1,2]. The composition of landfill leachates typically varies depending on the nature of the landfilled solid wastes, the active microbial flora, the rainfall patterns and the age of the landfill [3]. If poorly managed, a landfill may become a source of hydrological contamination due to the risk of leachate infiltrating into soil and groundwater.

Biological degradation is very effective for the treatment of landfill leachates with high values of biological oxygen demand (BOD), but it is not entirely efficient if recalcitrant compounds are present; therefore, alternative processes have been pursued like physico-chemical ones [4]. Examples of physico-chemical methods

employed for leachate treatment include chemical precipitation [5], Fenton reaction [6], Ozonation [7], Photocatalysis [8], Ultrasound irradiation [9] or combinations of the above [10]. Moreover, electrochemical oxidation has been proved capable of oxidizing most of the leachate organic content and removing color [11,12].

Electrochemical methods have attracted a great deal of attention basically due to the increased efficiencies that can be achieved using easy to operate and control, compact bipolar electrochemical reactors. Oxidizing agents such as hypochlorite, oxygen-based radicals, ozone and nitrogen oxides can be generated in situ in the electrochemical reactors [13]. During these processes, organic pollutants typically found in industrial wastewaters can be destroyed by direct or indirect oxidation. However, the reactions that take place during the electrochemical treatment are rather complicated, and the electrochemical removal mechanisms of organic pollutants are not fully clarified [14].

The electrochemical oxidation of various wastewaters has been investigated widely in recent years [13–17]. In particular, the use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological developments, thus reducing operational and investment costs [18,19]. DSA electrodes exhibit high electrocatalytic activity, high stability to anodic corrosion, and excellent mechanical stability. In these electrodes, oxidation can occur by direct oxidation, i.e. electron exchange between the contaminant and the electrode surface, or by indirect generation of reac-

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**Table 1**  
Main characteristics of stabilized leachate (mean values).

| Parameter  | Value |
|--|-------|
| pH   | 8     |
| COD (mg L <sup>-1</sup> )                            | 2960  |
| BOD <sub>5</sub> (mg L <sup>-1</sup> )               | 120   |
| TC (mg L <sup>-1</sup> )                             | 1150  |
| IC (mg L <sup>-1</sup> )                             | 667   |
| TPh (mg L <sup>-1</sup> )                            | 90    |
| BOD <sub>5</sub> /COD ratio                          | 0.04  |
| N-NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> ) | 14    |
| N-NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> ) | 44    |
| Cl <sup>-</sup> (mg L <sup>-1</sup> )                | 6150  |
| SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )  | 1850  |

tive species with high oxidizing power, such as H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and active chlorine, which are able to promote contaminant oxidation [20]. The most common anodes mentioned in literature are Ti/RuO<sub>2</sub>-TiO<sub>2</sub> [2], SPR (Sn-Pd-Ru oxide-coated titanium) [11], Fe [12], Al [12], graphite carbon [21,22], Ti/PbO<sub>2</sub> [23,24], Ti/Pt [25], Ti/TiO<sub>2</sub>-RuO<sub>2</sub>-IrO<sub>2</sub> [26] and boron-doped diamond [27].

Although the electrochemical oxidation of leachate has received recently considerable attention, the use of DSA binary electrodes based on IrO<sub>2</sub> and RuO<sub>2</sub> has not been evaluated before. Therefore, the goal of this work was to investigate the main parameters affecting the efficiency of electrochemical leachate oxidation including electrolysis time and temperature, current density, initial pH and electrolyte type and concentration. Treatment efficiency was evaluated in terms of chemical oxygen demand (COD), total carbon (TC), total phenolic (TPh) compounds and color removal. This work differs from previous electrochemical studies since the leachate contains only biorecalcitrant compounds coming from a bioreactor landfill which operated for over a year. According to the literature, the majority of the studies deal with concentrated fresh leachates with high BOD/COD ratios coming from sanitary landfills.

## 2. Materials and methods

### 2.1. Leachate

The leachate was collected from a laboratory scale, bioreactor landfill operating in sequential aerobic-anaerobic-aerobic conditions for over a year [28,29]. The leachate was stored in a refrigerator and filtered (with a 190 μm screen filter) in order to remove most of the suspended solids. The main physicochemical characteristics of the leachate are shown in Table 1. Due to its high pH value (>7.5) and low BOD<sub>5</sub>/COD value (<0.1), the leachate can be ascribed as stabilized [7].

### 2.2. Ti/IrO<sub>2</sub>-RuO<sub>2</sub> electrode preparation and characterization

The Ti/IrO<sub>2</sub>-RuO<sub>2</sub> working electrode was prepared by thermal decomposition of 250 mM H<sub>2</sub>IrCl<sub>6</sub>-H<sub>2</sub>RuCl<sub>6</sub> (Acros Organics, 40%) metal precursor dissolved in isopropanol (Fluka, 99.5%), on a titanium support. The titanium substrate was sandblasted to ensure good adhesion of the deposit on its surface. Following sandblasting, the substrate was treated using 1 M oxalic acid solution to clean its surface from residual sands. The substrate was then dried in an oven at 70 °C and weighed. The precursor solution was spread on the titanium substrate forming a thin film layer on the electron surface. Afterwards, the sample was treated in an oven for 10 min to allow solvent evaporation. This step was followed by treatment in the furnace for the thermal decomposition of the precursor solution at 500 °C in air for 10 min. The same procedure was repeated five times and, after the last IrO<sub>2</sub>-RuO<sub>2</sub> coating, the electrode remained at 500 °C for 60 min. The final IrO<sub>2</sub>-RuO<sub>2</sub> loading was 0.4 mg cm<sup>-2</sup>.

The anode electrode was characterized by cyclic voltammetry (CV) using a single-compartment, three-electrode cell described in previous study [31]. The electrolyte volume in the compartment was 40 mL. A platinum wire served as the counter electrode, while Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (MSE) (Ref-621, Radiometer Analytical) with a potential of 0.64 V vs SHE (Standard Hydrogen Electrode) was employed as the reference electrode. The surface morphology of the IrO<sub>2</sub>-RuO<sub>2</sub> was also studied by scanning electron microscopy (SEM) using a JEOL JMS-6300-F microscope.

### 2.3. Electrochemical oxidation experiments

Batch experiments were performed in a laboratory scale electrolytic cell purchased from Metrohm. The electrochemical reactor was a glass pot comprising a Ti/IrO<sub>2</sub>-RuO<sub>2</sub> anodic electrode with a working surface of 12.5 cm<sup>2</sup> and a pair of zirconium cathodes. The electrodes were placed vertically and parallel to each other with a gap of 1 cm between them. The reactor was loaded with 120 mL of the leachate and continuously stirred with a magnetic stirrer. A DC power supply (Elektro Automatik, EA-PS 3065-03B) was used to apply constant current. The temperature remained constant using a temperature control unit. More details about the experimental setup can be found elsewhere [18]. All experiments were carried out with HClO<sub>4</sub> as the supporting electrolyte, while, in some cases, NaCl or Na<sub>2</sub>SO<sub>4</sub> were also added as secondary electrolytes. If necessary, the effluent's pH was adjusted adding a measured volume of concentrated NaOH solution.

### 2.4. Analytical measurements

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution (Merck, Germany) and the mixture was then incubated for 120 min at 150 °C in a COD reactor (Spectroquant TR420 Merck). COD was measured colorimetrically using a Spectroquant Nova 60 spectrophotometer (Merck). Prior to COD determination, appropriate dilutions were applied in order to keep the concentration of chlorides below 2 g L<sup>-1</sup> since greater concentrations interfere positively with the standard COD test. TPh were determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin-Ciocalteu protocol as described in the standard procedure 5500B [30]. A Shimadzu 5050A carbon analyzer was employed to measure first TC and then the inorganic carbon (IC) of the effluent. Effluent's pH was measured using a Crison pH-meter. Moreover, its absorbance was scanned in the range of 400–800 nm on a Shimadzu UV 1240 spectrophotometer; changes in sample absorbance at 450 nm were recorded to assess the extent of decolorization that had occurred.

## 3. Results and discussion

### 3.1. Electrode characterization

Surface morphology of the IrO<sub>2</sub>-RuO<sub>2</sub> film was studied by scanning electron microscopy. SEM images (Fig. 1) reveal that the Ti surface is highly porous mainly due to sandblasting and the subsequent chemical treatment of the support. The deposition of IrO<sub>2</sub>-RuO<sub>2</sub> via thermal treatment at 500 °C led to the development of metal oxide islands on the porous surface. These islands were not uniform and their surface was in the order of μm<sup>2</sup>. According to the SEM, the two oxides appear as alloy rather than two distinguished phases. In general, the observed morphology of the surface was similar with that reported by Song et al. [32] using IrO<sub>2</sub>-RuO<sub>2</sub> films deposited on TiO<sub>2</sub>/Ti substrate.

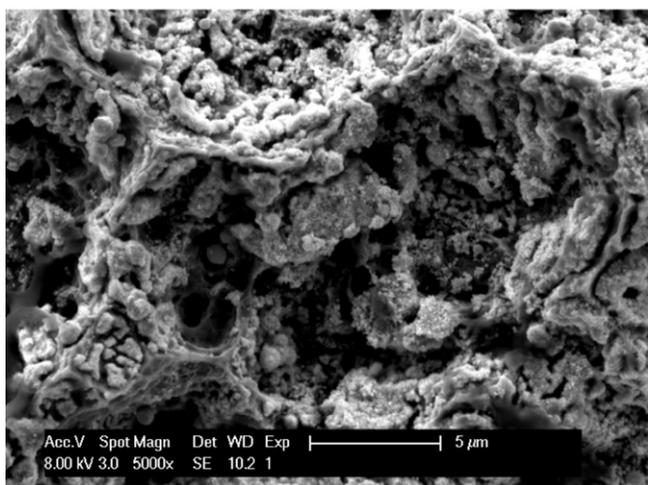
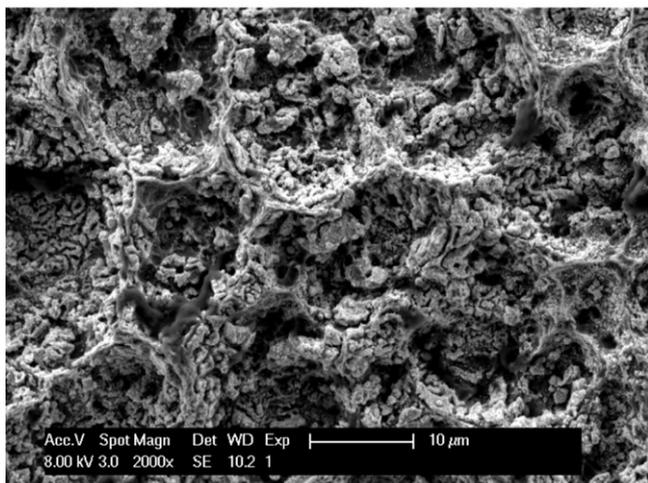
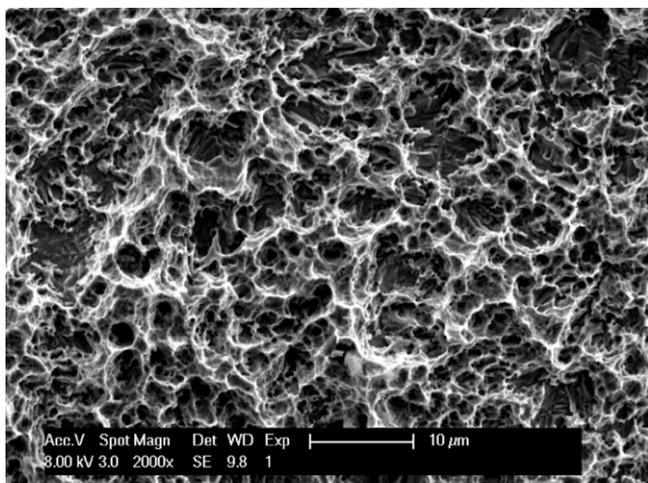


Fig. 1. SEM images of Ti support (top) and Ti/IrO<sub>2</sub>-RuO<sub>2</sub> film at two magnifications (middle and bottom).

CV was also used to characterize the electrochemical behavior of the electrode. Fig. 2 shows typical voltammograms of the Ti/IrO<sub>2</sub>-RuO<sub>2</sub> electrode recorded at 30 and 100 mV s<sup>-1</sup> in 1 M HClO<sub>4</sub> at 25 °C between -600 mV and +700 mV against MSE. The voltammograms exhibit broad waves consistent with the shape of voltammograms reported for IrO<sub>2</sub> and RuO<sub>2</sub> DSA electrodes in previous studies [33,34]. The non-distinguished oxidation and reduction peaks can be ascribed to the oxidation of IrO<sub>2</sub> and RuO<sub>2</sub> to higher oxides as the potential is increased and to their reduc-

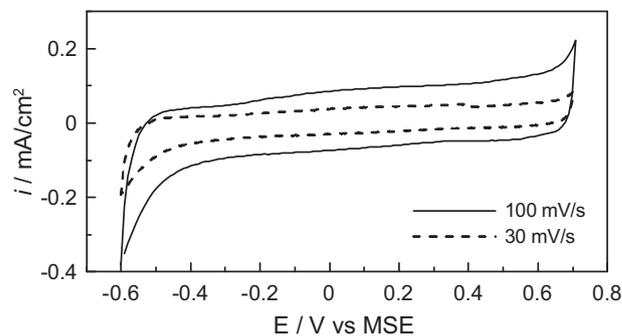


Fig. 2. Typical cyclic voltammogram of Ti/IrO<sub>2</sub>-RuO<sub>2</sub> electrode recorded at 30 and 100 mV s<sup>-1</sup> in 1 M HClO<sub>4</sub> at 25 °C between -600 mV and +700 mV against MSE.

tion during the backward scan. As the potential for every oxidation and/or reduction is very close to each other the final voltammogram appeared with broad waves.

### 3.2. Effect of operating conditions

HClO<sub>4</sub> was chosen as the main electrolyte because no oxidizing species liable to react with organic carbon are generated during electrolysis in contrast with other electrolytes such as NaCl and Na<sub>2</sub>SO<sub>4</sub> where production of active chlorine (Cl<sub>2</sub>, HClO, ClO<sup>-</sup>) and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> takes place, respectively. As soon as HClO<sub>4</sub> was added in the effluent, its pH dropped rapidly to values below unity and, consequently, IC was partly removed from the liquid phase in the form of CO<sub>2</sub>. As a matter of fact, IC reduction was about 70%, thus resulting in a TC value (prior to electrolysis) of about 683 mg L<sup>-1</sup>; it should be noted here that this value was taken as the starting concentration to compute TC conversion.

In order to explore the effect of electrolyte concentration on degradation, experiments were conducted at 0.25 and 1 M HClO<sub>4</sub> concentration. Fig. 3 shows that the effect of electrolyte concentration on degradation is negligible regardless the parameter studied. This can be explained by the fact that pH in both cases is low (~0.25), thus the extent of IC removal is similar and, consequently, the initial effluent conditions before electrolysis are nearly identical. Nonetheless, working at higher electrolyte concentrations would

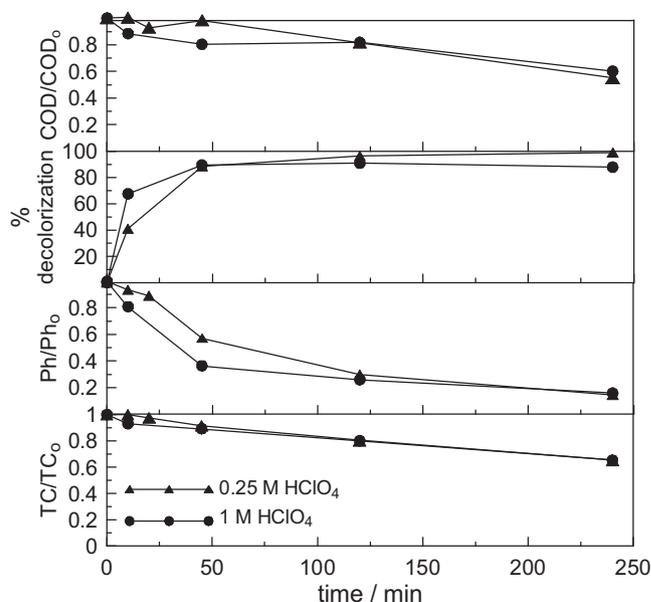
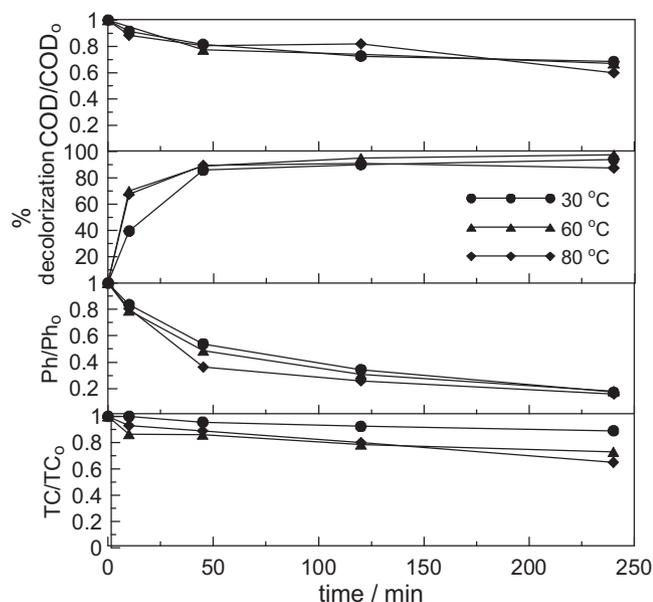


Fig. 3. Evolution of TC, COD, TPh and color as a function of electrolysis time and HClO<sub>4</sub> concentration (0.25 and 1 M). T = 80 °C, pH = 0.25, i = 32 mA cm<sup>-2</sup>.



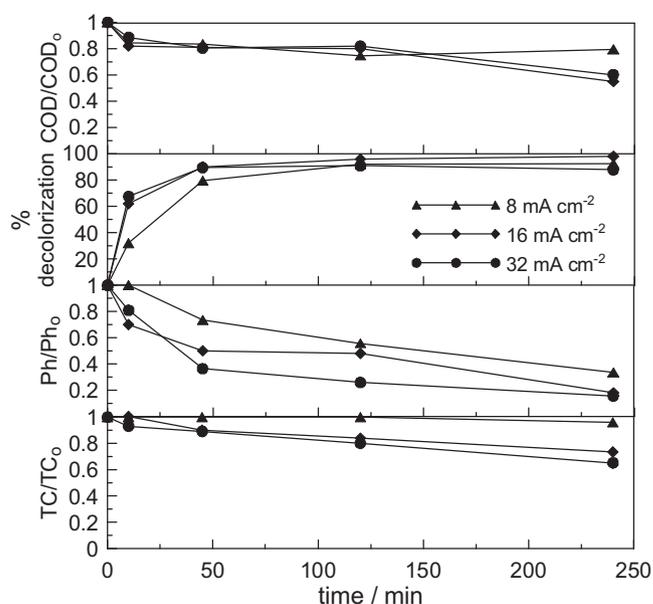
**Fig. 4.** Evolution of TC, COD, TPh and color as a function of electrolysis time and temperature (30, 60 and 80 °C).  $i = 32 \text{ mA cm}^{-2}$ ,  $\text{pH} = 0.25$ ,  $1 \text{ M HClO}_4$ .

result in lower energy consumption since the potential applied to operate at  $32 \text{ mA cm}^{-2}$  was 4 and 7 V at 1 and 0.25 M  $\text{HClO}_4$ , respectively. Therefore, all subsequent experiments were performed at 1 M  $\text{HClO}_4$ .

Fig. 4 shows the effect of temperature (30, 60 and 80 °C) on degradation. Although the final (i.e. after 240 min) removal is independent of the temperature, the latter appears to have a beneficial effect during the early stages of treatment (i.e. <60 min) and this is more pronounced for decolorization and TC removal. For example, the extent of decolorization was 40% at 30 °C and  $70 \pm 2\%$  at 60 °C or 80 °C after 10 min of treatment. At the same time, TC removal was negligible at 30 °C and almost 15% at 60 °C. Given that electrochemical oxidation is an exothermic process, high operating temperatures may be sustained without additional cost. Therefore, all subsequent experiments were performed at 80 °C.

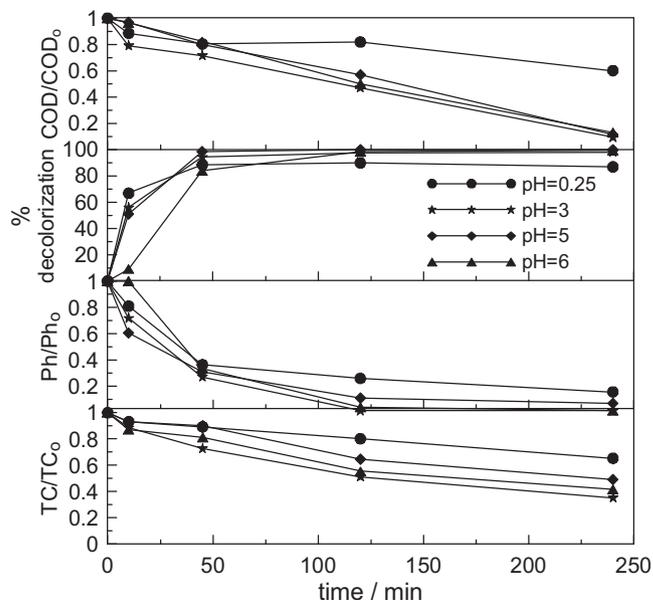
Fig. 5 shows the effect of applied current (8, 16 and  $32 \text{ mA cm}^{-2}$ ) on treatment performance at 80 °C. Although COD removal seems to be independent of the applied current (for  $t < 120 \text{ min}$ ), higher current densities result in faster TC removal reaching 35% after 240 min at  $32 \text{ mA cm}^{-2}$ . The relatively low values of TC removal even after prolonged treatment could be attributed to the selective, partial conversion of the organic compounds originally present in the leachate to other organic intermediates that are resistant to mineralization to carbon dioxide and water. The oxidation power of anodic materials in acidic media is strongly related to the competition between reactions of organics with electrogenerated hydroxyl radicals and the side reaction of the anodic discharge of these radicals to oxygen [35]. It has been proposed that the weaker the interaction between the hydroxyl radicals and the electrode surface, the lower the electrochemical activity towards oxygen evolution (high overvoltage anodes) and the higher the chemical reactivity towards organics oxidation [35]. Based on this approach, the  $\text{Ti/IrO}_2\text{-RuO}_2$  electrode could be characterized as anode with low oxidation power.

The effect of changing effluent's pH in the range 0.25–6 on degradation was also studied and the results are shown in Fig. 6. The lower efficiency was achieved at highly acidic conditions ( $\text{pH} = 0.25$ ), while the greater was observed at pH 3 with COD and TC removal being 90% and 65%, respectively after 240 min of electrolysis; furthermore, complete color and TPh removal occurred



**Fig. 5.** Evolution of TC, COD, TPh and color as a function of electrolysis time and applied current density (8, 16 and  $32 \text{ mA cm}^{-2}$ ).  $\text{pH} = 0.25$ ,  $T = 80^\circ\text{C}$ ,  $1 \text{ M HClO}_4$ .

after about 45 and 120 min of reaction; respectively. Li et al. [36], who studied the electrochemical oxidation of leachate at various pH values, reported that treatment at pH 4 gave 20% higher COD removal than at pH 8 after 240 min of reaction. In other studies, Vlyssides et al. [37] reported that the effect of pH on the oxidation of leachate was far more significant than the concentration of  $\text{Cl}^-$  or  $\text{SO}_4^-$ , applied current, temperature and flow rate. Furthermore, Cossu et al. [4] found that the COD pseudo-first order rate constant had a slight increase at pH 3 compared with that at pH 8.3. Other studies [11,38] suggested that pH higher than 4 has no or little effect on COD removal. This is in agreement with this study since pH values higher than 5 give comparable degradation rates. Indeed, acidic conditions decrease the concentration of  $\text{CO}_3^-$  and  $\text{HCO}_3^-$  which are generated at the anode and act as scavengers of hydroxyl radicals [36].



**Fig. 6.** Evolution of TC, COD, TPh and color as a function of electrolysis time and initial pH (0.25, 3, 5, 6).  $T = 80^\circ\text{C}$ ,  $i = 32 \text{ mA cm}^{-2}$ ,  $1 \text{ M HClO}_4$ .

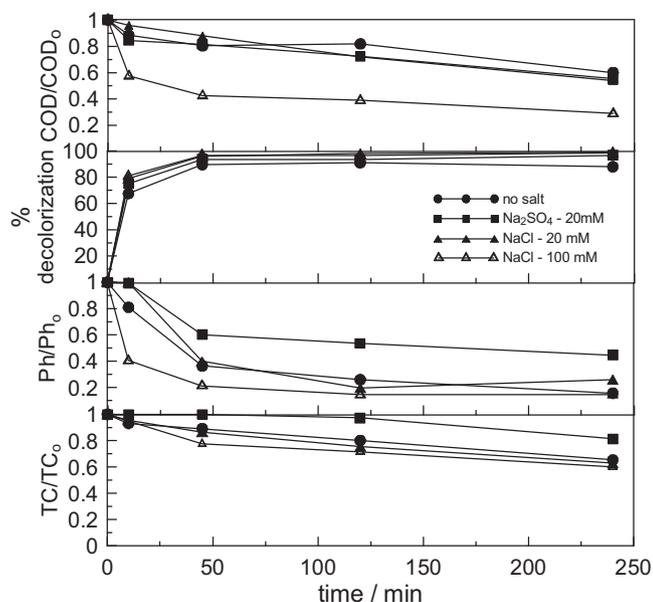


Fig. 7. Evolution of TC, COD, TPh and color as a function of electrolysis time in the presence of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ .  $T = 80^\circ\text{C}$ ,  $i = 32\text{ mA cm}^{-2}$ ,  $1\text{ M HClO}_4$ ,  $\text{pH} = 0.25$ .

In a final set of experiments, the effect of adding extra electrolytes (NaCl and  $\text{Na}_2\text{SO}_4$ ) was investigated. The rationale behind this was to enhance indirect leachate oxidation through the generation of additional oxidants such as chlorine, hypochlorite,  $\text{S}_2\text{O}_8^{2-}$  etc. As seen in Fig. 7, addition of 20 mM NaCl gave similar results with the experiment where no salt was externally added; this is possibly due to the fact that the effluent already contains about 175 mM of chlorides (Table 1) and, therefore, increasing  $\text{Cl}^-$  concentration by only about 10% had a marginal effect on indirect oxidation. Conversely when NaCl concentration increased to 100 mM, performance was improved and this was more pronounced for COD removal; for instance, its extent after 240 min of reaction was 75% and 43% at 100 and 0 mM of externally added NaCl, respectively. According to the literature [11,38], the critical value of  $\text{Cl}^-$  concentration depends strongly on the applied current density. Although addition of  $\text{Cl}^-$  can improve the oxidation efficiency, the production of organochlorinated organic compounds can be significantly enhanced giving a final solution with high ecotoxicity [39,40].

Unlike NaCl, addition of 20 mM  $\text{Na}_2\text{SO}_4$  had a detrimental effect on degradation and this was more pronounced for TC and TPh removal; for instance, their removal decreased to 3% and 47%, respectively, after 120 min of treatment, while the corresponding values without extra electrolyte were 20% and 74%. The inhibitory action of  $\text{SO}_4^{2-}$  could be related to the enhancement of the side reaction of oxygen evolution which can limit the chlorine/hypochlorite electrogeneration.

### 3.3. Energy consumption

To assess the cost implications related to leachate treatment by electrochemical oxidation, specific energy consumption (SEC) was computed and representative results are shown in Fig. 8. SEC, which is defined as the energy required to remove a unit mass of pollutant (i.e. COD), is about  $35\text{ kWh kg}^{-1}$  COD to remove 90% COD at pH 3 (other conditions as in Fig. 6) and  $20\text{ kWh kg}^{-1}$  COD to remove 75% COD in the presence of 100 mM NaCl (other conditions as in Fig. 7); as a rough estimate, the electricity cost would be  $1\text{--}2\text{ € kg}^{-1}$  COD removed if the treatment unit operated in Greece.

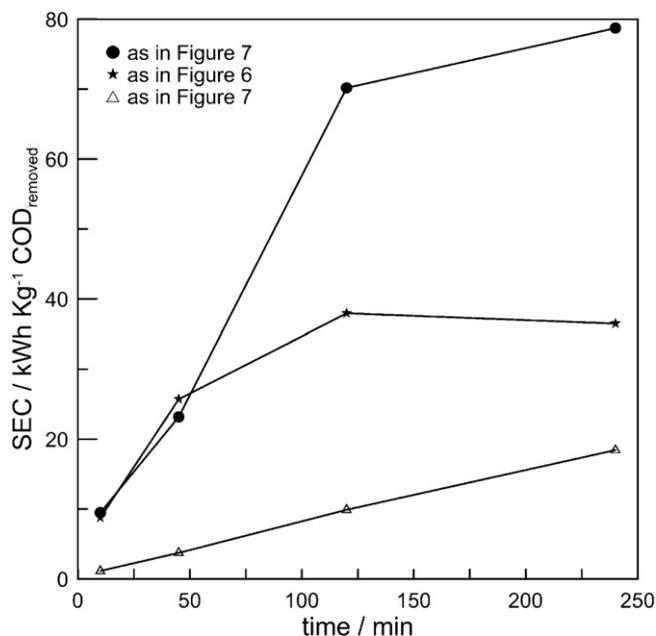


Fig. 8. Evolution of SEC as a function of electrolysis time for leachate treatment at various conditions.

## 4. Conclusions

This work investigated the behavior of a  $\text{Ti/IrO}_2\text{-RuO}_2$  anode for the electrochemical oxidation of landfill leachate under various operating conditions including treatment time and temperature, current density, effluent's pH and the type and concentration of supporting electrolyte. At the conditions in question, the main parameters affecting the process were effluent's pH and the concentration of  $\text{Cl}^-$ . Quantitative COD removal accompanied by 65% TC elimination and complete decolorization could be achieved after 240 min of operation at  $80^\circ\text{C}$ ,  $32\text{ mA cm}^{-2}$  and pH 3; such performance would require an energy consumption of about  $35\text{ kWh kg}^{-1}$  COD removed; this could almost be halved by adding 100 mM of sodium chloride presumably due to the decrease of electrical resistance in the effluent.

In this respect, this work may form the basis to develop and optimize a sustainable advanced oxidation process for the treatment of effluents containing substantial biorefractory organic compounds.

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