

Electrochemical process for the treatment of landfill leachate

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Received: 21 December 2009 / Accepted: 23 February 2010 / Published online: 12 March 2010
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Abstract In this paper, the anodic oxidation of a real leachate from an old municipal solid waste landfill has been studied using an electrolytic flow cell equipped with a lead dioxide (PbO_2) anode and stainless steel as the cathode. The influence of several operation parameters such as (i) the applied current (from 0.5 to 3 A), (ii) liquid flow rate (from 50 to 420 L h^{-1}), (iii) temperature (from 25 to 50 °C), and (iv) pH (from 3.5 to 8.2) on the COD removal rate, current efficiency, and energy consumption has been evaluated. The galvanostatic electrolyses always yielded COD values below the discharge limit ($\text{COD} < 160 \text{ mg L}^{-1}$); the COD removal rate increased with rising applied current, solution pH, and temperature, whereas it remained almost unaffected by the recirculation flow rate. These results indicate that the organic compounds were mainly removed by their indirect oxidation by the active chlorine generated from chlorides oxidation. The specific energy consumption necessary to reduce the organic load to below the disposal limit was 90 kWh m^{-3} .

Keywords Lead dioxide anode · Electrochemical oxidation · Landfill leachate

1 Introduction

Sanitary landfills are considered as the most cost effective and environmentally friendly method to address the disposal of municipal and industrial solid wastes. However, the production of leachates that can permeate the ground and pollute the stratum waters is usually a major drawback related to such method. Leachates are mainly generated by (i) precipitation and percolation through the wastes, (ii) decomposition processes occurring in the wastes, and (iii) water release from the wastes. They contain large amounts of organic pollutants, ammonia nitrogen, inorganic salts, and heavy metals, although their chemical composition is affected by several factors including seasonal precipitation, waste origin and, particularly, the age of the landfill. Thus, leachates from young landfills (i.e. <5 years old) contain a large amount of biodegradable organic matter such as volatile fatty acids and are characterised by a high COD (i.e. $>10000 \text{ mg L}^{-1}$) and BOD/COD ratio (>0.3); in contrast, old landfill leachates (i.e. >10 years old) contain biorefractory compounds such as humic and fulvic acids and are characterised by a low COD ($<4000 \text{ mg L}^{-1}$) and BOD/COD ratio (<0.1) [1].

The landfill leachates, especially those originated from old landfills, are only partially degraded during sewage treatment in activated sludge systems. Therefore, other technologies have been proposed for their handling and management [2, 3]. The most relevant physicochemical processes for the treatment of landfill leachates are the floatation [4], coagulation-flocculation [5], adsorption [6], wet air oxidation [7], membrane processes [8, 9], chemical oxidation using O_3 [10] and H_2O_2 [11], and the advanced oxidation processes (AOPs) that are based on the generation of hydroxyl radicals (i.e., Fenton's reagent, TiO_2 photocatalysis, $\text{O}_3/\text{H}_2\text{O}_2$, etc.) [12, 13]. However, according to a

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more stringent legislation on water quality and discharge introduced by many governments, conventional treatments are not always able to accomplish with the legal requirements and, consequently, other novel, more powerful methods have to be applied.

In this context, the electrochemical oxidation process, so-called ‘electrochemical incineration process’, is particularly appealing because the electrons provide a versatile, efficient, cost-effective, easily automatizable, clean technology [14, 15]. So far, the electrochemical oxidation treatment has been successfully applied for the oxidative decontamination of both synthetic and real effluents, including tannery and textile wastewaters [16–18], synthetic dyes [19–22] and pesticides [23–27], and landfill leachates [28, 29].

A wide variety of electrode materials such as dimensionally stable anodes (DSA) [30–33], platinum [34, 35], carbon-based anodes [36, 37], PbO_2 [30, 38], SnO_2 [38], and BDD [39–42] have been suggested for the electrochemical treatment of landfill leachate. In a pioneer paper [30], Chiang et al. compared the performance of various anode materials including graphite, lead dioxide-coated titanium (PbO_2/Ti), binary Ru–Ti oxide-coated titanium (DSA type), and ternary Sn–Pd–Ru oxide-coated titanium (SPR) for the electrochemical oxidation of a landfill leachate in the presence of different concentrations of chloride ions. In the presence of 2500–7500 mg L^{-1} of added Cl^- , both the COD and ammonium were removed due to the indirect electrolysis favoured by the in-situ electrogenerated chlorine. The COD removal efficiency decreased in the order $\text{SPR} > \text{DSA} > \text{PbO}_2 > \text{graphite}$ because of the higher chlorine/hypochlorite production efficiency of the SPR anode. A 92% COD removal and total ammonium removal were achieved after 240 min using the SPR at 0.15 A cm^{-2} when the additional chloride content was 7500 mg L^{-1} .

Other papers have reported that the use of three-dimensional carbon bed electrodes led to a mineralisation efficiency in the range 0.83–0.84 [36], whereas the use of Ti/RuO₂ anodes allowed a 90% decolourisation and 60% COD removal [33]. Even though these kinds of anodes exhibit low oxygen evolution overpotential, a high efficiency of the electrochemical process is observed due to the active chlorine-mediated oxidation process.

On the other hand, it has been demonstrated that the use of anodes with high oxygen evolution overpotential such as SnO_2 , PbO_2 , and BDD allows the removal of the organic load of the landfill leachate by both, direct and indirect oxidation, because these materials can electrogenerate highly reactive $\cdot\text{OH}$ by water discharge at their surface, thus increasing the overall current efficiency. For example, Urriaga and co-workers developed a pilot scale plant equipped with 1.05- m^2 BDD anodes for the oxidation of a

landfill leachate resulting from a biological pre-treatment [39–42]; the ammonium removal was almost complete and the COD was reduced from 1750 mg L^{-1} to below disposal limits (160 mg L^{-1}), with an energy consumption of ca. 35 kWh m^{-3} . But, despite providing high removal efficiency, the high cost of these anodes is still a major drawback that limits their widespread industrial application.

On the contrary, PbO_2 is an inexpensive material, which is relatively easy to prepare by anodic deposition in inorganic [43] and organic [44] acidic electrolytes; it shows low electrical resistivity, good chemical stability, and large surface area [44], thus being optimum for wide industrial applications such as the destruction of water organic pollutants. A comparative study between the PbO_2 and SnO_2 anodes was carried out by Cossu et al. for the treatment of a landfill leachate, obtaining an average current efficiency of ca. 30 and 10% for the COD and ammonium removal, respectively [38]. Although a similar activity was observed for both electrodes, SnO_2 anodes showed problems related to the service life, which limits their practical application [45].

Being PbO_2 an anode material with well-proven advantages, the aim of this work was to carry out the electrochemical treatment of a real landfill leachate by the anodic oxidation process using a PbO_2 anode in an electrolytic flow cell. Bulk electrolyses were performed at constant current to assess the influence of the main operation parameters, i.e., the current density, liquid flow rate, pH, and temperature on the COD decay and the current efficiency.

2 Experimental

2.1 Landfill leachate characteristics

The leachate was collected from an old municipal solid waste landfill located near the city of La Spezia (Italy). The samples were stored at 5 °C to keep the wastewater characteristics unaltered, and they were used without any pre-treatment. The main parameters (average values) of the wastewater were: pH = 8.20, 780 mg L^{-1} COD, BOD/COD <0.1, conductivity = 9.77 mS cm^{-1} , 1800 mg L^{-1} Cl^- .

2.2 Electrolytic systems

The bulk electrochemical oxidations were conducted in batch using an undivided electrolytic flow cell under galvanostatic conditions. For the treatment, the landfill leachate was kept in a thermostated glass reservoir of 0.35 L and it was recirculated through the electrolytic cell by means of a centrifugal pump working in the flow rate range 50–420 L h^{-1} . The cell contained a Ti grid coated with a PbO_2 layer (Ti/PbO_2) operating on both sides as the

anode, and two stainless steel (AISI 304) plates with only one side exposed to the solution as the cathodes. The dimensions of the electrodes were 6 cm × 5 cm and the interelectrode gap was 0.5 cm.

The deposit of lead dioxide was made by anodic deposition on a Ti substrate, using an aqueous solution containing 0.5 M Pb(NO₃)₂ and 0.05 M NaF, with 0.1 M HNO₃ as the electrolyte. The Ti grid was first sandblasted and chemically etched with concentrated HCl. The lead dioxide was galvanostatically deposited using a single compartment cell and working at a current density of 20 mA cm⁻² for 30 min [46]. In order to stabilise the electrode surface, a post-deposition treatment was applied to the PbO₂ films; the PbO₂ electrode potential was cycled between 0 and 1.8 V versus SCE in 0.5 M H₂SO₄ medium until successive voltammetric curves were found to be identical. The same PbO₂ electrode was used in all experiments because it did not undergo any significant corrosion during anodic polarisation; thus, the stabilisation step ensured that the release of lead ions was not a significant problem under the studied conditions.

2.3 Analytical procedures

During the experiments, bulk samples were withdrawn from the reservoir at regular intervals and conveniently analysed. The progressive oxidation of the landfill leachate was followed by the decay of the Chemical Oxygen Demand (COD), which was measured spectrophotometrically using a Dr Lange LASA50 system. The lowest detection limit of the instrument was 15 mg L⁻¹ COD. The concentration of active chlorine (i.e., chlorine, hypochlorous acid, and hypochlorite ion) was measured spectrophotometrically using a Dr Lange LASA50 system. The concentration of lead ion released into the effluent during the electrochemical degradation was measured using a Varian AA 240 FS atomic absorption spectrometer.

The current efficiency (C.E., in %) at a given time t for the electrochemical oxidation process was determined by using the following relationship [26]:

$$\text{C.E.} = \frac{(\text{COD}_0 - \text{COD}_t)M_{\text{O}_2}}{nIt} \cdot F \cdot V \cdot 100 \quad (1)$$

where (COD)₀ and (COD)_t are the chemical oxygen demands before the electrolysis and at time t (in g O₂ L⁻¹), respectively, I is the current (A), n is the number of electrons per mol of O₂, M_{O_2} is the molecular weight of O₂ (g mol⁻¹), and V is the volume of the treated solution (L).

The specific energy consumption (E_c , in kWh m⁻³) was obtained as follows:

$$E_c = \frac{U_{\text{cell}} \cdot I \cdot t}{V \cdot 3600} \quad (2)$$

where U_{cell} is the average cell voltage (V), I is the current (A), t is the electrolysis time (s), and V is the volume of the treated solution (L).

The absorbance of the solutions was measured on a Jasco V-630 spectrophotometer at different UV/Visible wavelengths using 1 cm path-length cells. The samples were conveniently diluted in some cases in order to satisfy the Lambert–Beer law.

3 Results and discussion

To determine the viability of the electrochemical treatment for the decontamination of the landfill leachate using a PbO₂ anode, the evolution of the UV/Visible spectra and the COD concentration was followed during the electrolyses, which were performed at 2 A, 420 L h⁻¹, and 25 °C. Figure 1 shows the spectra of the treated solution at different reaction times; note that these spectra showing high absorbance values resulted from the recalculation of the spectra corresponding to the diluted samples. These UV/Visible spectra for the raw landfill leachate show a peak and a pronounced shoulder in the UV region at about 220 and 274 nm, respectively, which are related to the presence of aromatic compounds, as well as a weak and broad absorption band in the visible region centered at about 470 nm (Fig. 1, inset) that is caused by the dark-brown colour of the effluent. Along the electrolysis, all the peaks decreased until disappearance, which means that the complete solution decolourisation and aromatics removal is achieved after about 8 h of electrolysis.

Figure 2 shows the time course of the normalised absorbance, i.e., the ratio between the absorbance at time t and the initial value, at wavelengths of 274 and 470 nm, as well as the evolution of the normalised COD during the

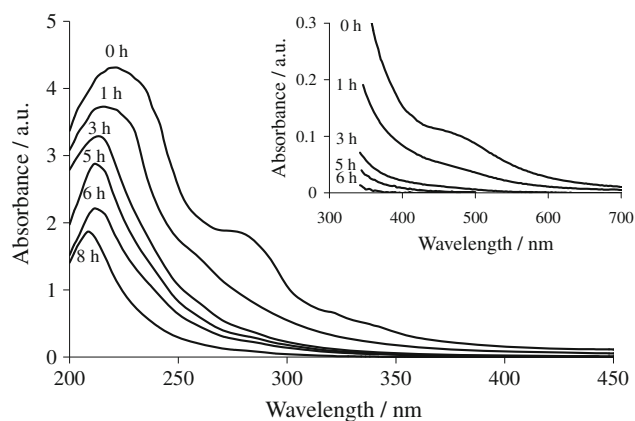


Fig. 1 UV/visible spectra of the raw landfill leachate solutions at different electrolysis times using the electrolytic flow cell with a PbO₂ anode. Conditions: $I = 2$ A; flow rate = 420 L h⁻¹; $T = 25$ °C

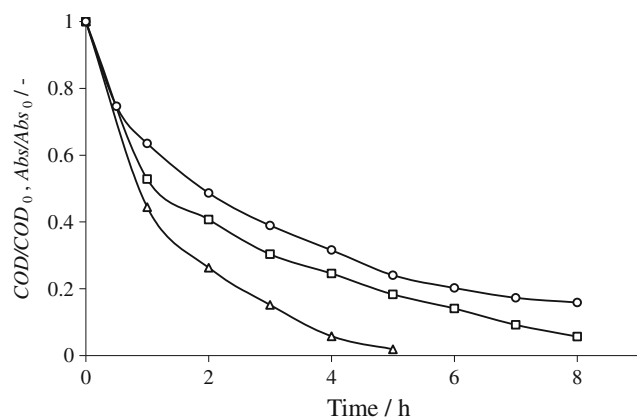


Fig. 2 Time evolution of the normalised absorbance at (□) 274 and (Δ) 470 nm and the (○) normalised COD during the electrolysis of the landfill leachate using a PbO_2 anode, using the same experimental conditions as in Fig. 1

electrolyses. As observed, the intensity of the band at 470 nm decreases more rapidly than that of the shoulder at 274 nm and the COD. This fact indicates that the first step in the oxidation process involves the removal of the colour (i.e., decrease of the band at 470 nm), which can be generally related to resonant structures or to the presence of aliphatic insaturations; then, the cleavage of the aromatic rings (i.e., removal of band at 274 nm) takes place, yielding aliphatic intermediates that are slowly but progressively mineralised to carbon dioxide.

As schematised in Fig. 3, the organic pollutants present in the landfill leachate can be oxidised by many reactions when a Ti/PbO_2 anode, which exhibits high overpotential for oxygen evolution, is used:

- (i) The direct electron transfer between the organic pollutants and the PbO_2 surface (Reaction 3):

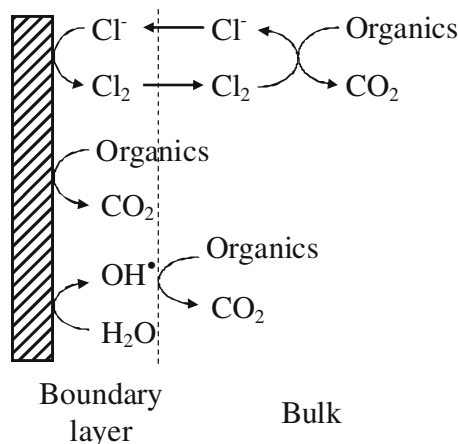
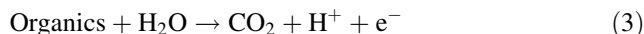
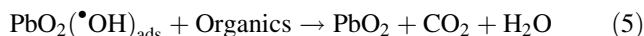
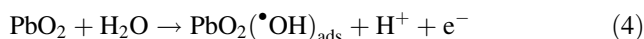


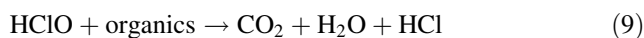
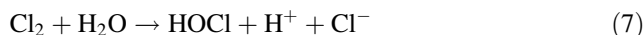
Fig. 3 Scheme showing the reactions and processes involved in the electrochemical oxidation of a landfill leachate using a PbO_2 anode



- (ii) The reaction with adsorbed hydroxyl radicals electrogenerated from water discharge (Reactions 4–5):



- (iii) The indirect oxidation with active chlorine (gaseous chlorine, hypochlorous acid or hypochlorite) electrogenerated from the oxidation of chloride ions present in the treated wastewater (Reactions 6–9):



In previous studies [24, 43], we have demonstrated that the direct oxidation of organics at a Ti/PbO_2 anode is theoretically possible within the region of electrolyte stability; but, the rate of such reaction shows a slow kinetics and during the electrolyses there is a decrease in the catalytic activity of the anode, which is commonly called ‘the poisoning effect’, due to the formation of a polymer layer/film that blocks the anode surface. The effective oxidation of the organic compounds, however, can be obtained at high anodic potentials in the region of electrolyte decomposition, thanks to the production of oxidising agents generated from the water itself, as for example the hydroxyl radicals (Reaction 4), or from species dissolved in the water, such as the chloride ions that are oxidised to active chlorine (Reactions 6–8). Thus, the contribution of the direct electron transfer to the oxidation of the organic components of the landfill leachate can be neglected.

In order to elucidate which oxidative reaction has a greater contribution to the COD and colour removal, and aiming at finding the best operation conditions, the anodic oxidation of the landfill leachate was performed under different applied current (0.5–3 A), liquid flow rate (50–420 L h^{-1}), pH (3.5–8.2), and temperatures (25–50 $^\circ\text{C}$) values.

It has been reported that when the main oxidants are the electrogenerated $\bullet\text{OH}$, the oxidation occurs at the anode surface and thus, working at high current, the process is controlled by the mass transport of the pollutants towards the electrode [23, 46]. Moreover, the reaction between the hydroxyl radicals and the organic molecules is very fast and its rate is only slightly affected by the solution pH [21] and temperature [47].

On the contrary, in chlorine-mediated electrolyses, the oxidation process occurs in the bulk of the solution, which

allows overcoming the mass transport limitations inherent to the previous $\bullet\text{OH}$ -mediated process; in this case, the oxidation process is controlled by the rate at which the charge passes in the cell [46, 48, 49]. Furthermore, the oxidation rate between the organics and the active chlorine increases with temperature [50], in agreement with the Arrhenius law, and it is also affected by the solution pH because the chlorine/hypochlorous acid equilibrium is pH-dependent [48, 51].

Figure 4 shows the trend of the COD with the electrolysis time (main) and with the specific charge passed (inset) during the treatment of the effluent at different applied current values, at flow rate = 420 L h⁻¹, pH = 8.2, and 25 °C. For the current in the range 1–3 A, the COD decreased to below the discharge limit (160 mg L⁻¹ COD) and, in particular, increasing the current resulted in a faster COD removal rate (i.e., dCOD/dt). Such enhancement of the oxidation power can be only associated with a greater production of active chlorine (Reactions 6–8) and/or hydroxyl radicals (Reaction 4). On the other hand, the applied current did not affect significantly the trend of the COD with the specific charge consumed during the treatment (Fig. 4, inset). This behaviour is characteristic of electrolysis operating under charge transfer control, such as the chlorine-mediated electrolyses or the $\bullet\text{OH}$ -mediated electrolyses that are performed applying a current value below the limiting one (I_L). In the latter two cases, all the current that is provided to the system is used to generate the oxidising species, which in turn are used specifically for the oxidation of the organic molecules. Consequently, the system reaches its highest efficiency because parallel parasitic reactions involving the destruction of $\bullet\text{OH}$ or Cl₂ are minimised.

Figure 5 depicts the influence of the recycle flow rate on the COD removal (main) and the current efficiency (inset)

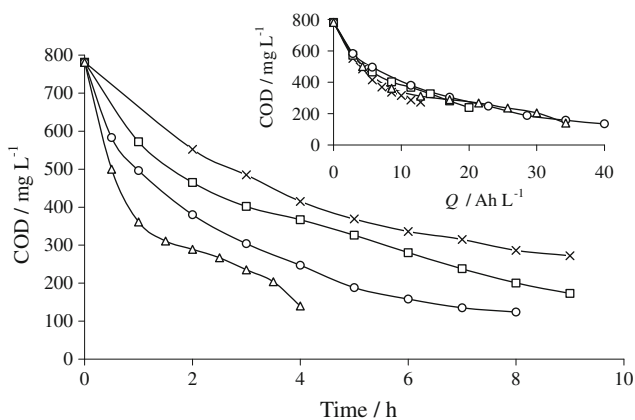


Fig. 4 Influence of the applied current on the evolution of the COD with the electrolysis time (main) and the specific charge (inset) during the electrolyses of the landfill leachate using the PbO₂ anode. Conditions: flow rate = 420 L h⁻¹; T = 25 °C; pH = 8.2; applied current (I): (x) 0.5; (□) 1; (○) 2; (Δ) 3 A

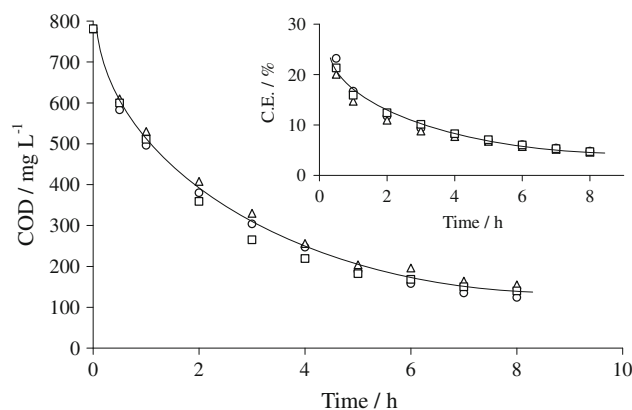


Fig. 5 Effect of the recycle flow rate on the time evolution of the COD (main) and the current efficiency (inset) during the electrolyses of the landfill leachate using the PbO₂ anode. Conditions: I = 2 A; T = 25 °C; pH = 8.2; flow rate: (Δ) 50, (○) 130, and (□) 420 L h⁻¹

with time during the electrolyses at 2 A. The flow rate was varied from 50 to 420 L h⁻¹, which corresponds to a mass-transfer coefficient in the cell in the range $(1.0\text{--}2.3) \times 10^{-5} \text{ m s}^{-1}$, measured with a ferri/ferrocyanide couple. No variation of the trend for the overall COD depletion and the current efficiency was observed at different liquid flow rates, which is clearly against the behaviour usually found for the $\bullet\text{OH}$ -mediated treatments [14]. This means that, under these conditions, the process is not controlled by the mass transport of the reactants from the bulk to the electrode surface. Consequently, the oxidation of organics mainly occurs in the bulk of the solution under the pre-eminent action of the chlorine-mediated process. In fact, the concentration of active chlorine in the solution was 0.45 mmol L⁻¹ at the end of the electrolyses.

The effect of the solution pH and the temperature on the COD removal is presented in Fig. 6. In the range pH

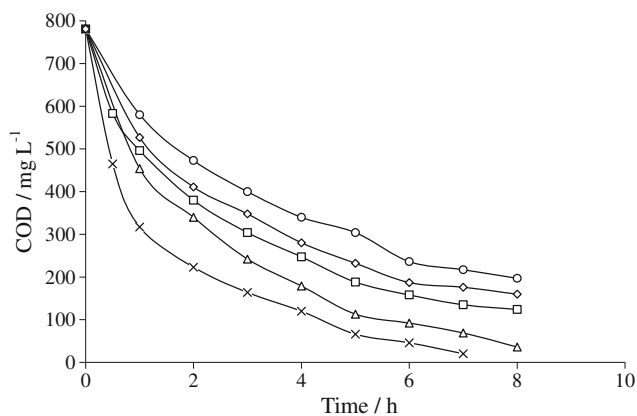


Fig. 6 Influence of the solution pH and the temperature on the evolution of COD with time during the electrolyses of the landfill leachate using the PbO₂ anode. Conditions: I = 2 A; flow rate = 420 L h⁻¹; T: (○, ◇, □) 25, (Δ) 40, (x) 50 °C; pH: (○) 3.5, (◇) 6, (□, Δ, x) 8.2

3.5–8.2, the oxidation rate increased when a higher solution pH was used. Again, these results confirm that the COD of the solution is mainly removed by the indirect oxidation process under the action of the active chlorine, because the alkaline pH prevents the loss of the chlorinated mediators, which is a common drawback related to: (i) evolving chlorine gas, which is a step that predominates when the pH reaches acidic values, and (ii) chlorate ion formation, which is produced at weakly acidic pH by reaction between hypochlorite and hypochlorous acid in the bulk of the solution. Such pH effect is similar to that also observed by other authors during the anodic mineralisation of organic compounds in chloride-containing media [48, 52]. Solution pH values higher than 8.2 were not tested in order to avoid the PbO₂ damage. The evolution of the COD at different temperatures is also presented in Fig. 6. Increasing temperature from 25 to 50 °C favours the organics oxidation; this can be explained by an increase of the rate of the chemical oxidation reaction between the organics and the electrogenerated active chlorine. In conclusion, the fastest COD removal was obtained at pH = 8.2 and at 50 °C, reaching the 160 mg L⁻¹ COD after only 3 h and yielding almost total decontamination at ca. 7 h.

From the standpoint of the industrial application of this electrochemical process for the treatment of landfill leachate, not only the electrolysis time but also the energy consumption is a key parameter to think about the economical viability of the system. Figure 7, reports the specific energy consumption (kWh m⁻³) as a function of the COD removal for the best experiment in Fig. 6 (i.e., optimum *T* and pH). The energy consumption trend exhibits a sharper increase at a higher COD removal; thus, 90 and 220 kWh m⁻³ are consumed to reach the discharge limit

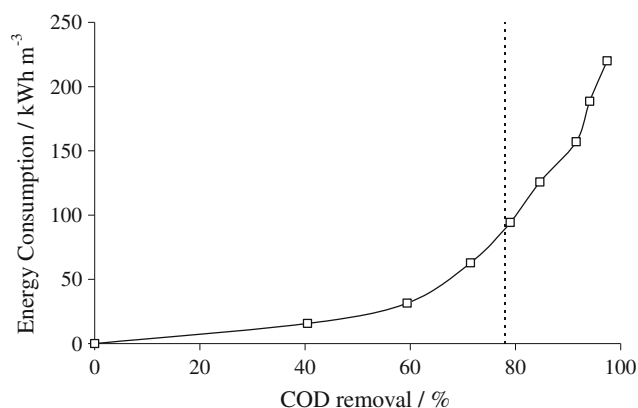


Fig. 7 Evolution of the energy consumption against the COD removal during the electrochemical treatment of the landfill leachate using the PbO₂ anode. Conditions: *I* = 2 A; flow rate = 420 L h⁻¹; *T* = 50 °C; pH = 8.2. The dotted line indicates the authorized discharge limit

(i.e., COD 160 mg L⁻¹ or ca. 80% COD removal) and the complete COD removal (not shown), respectively.

These values are significantly lower than those obtained by Nageswara Rao et al. using a three-dimensional carbon bed anode (i.e., 681 kWh m⁻³ for the complete COD removal) [36], but are still higher than those obtained by Urriaga et al. using the BDD anode (i.e., 35 kWh m⁻³ to reach a COD <160 mg L⁻¹) [42].

The main drawback of the PbO₂ electrodes is the possible leaching of lead ions during the electrolysis. Therefore, the concentration of lead ion was measured by atomic absorption spectrometry; lead ions were not detected in the landfill leachate after the electrolysis.

4 Conclusion

The electrochemical oxidation of a real landfill leachate has been investigated by anodic oxidation using an electrolytic flow cell with a PbO₂ anode under different experimental conditions to assess the influence of the applied current, recycle flow rate, pH, and temperature. The results revealed the following traits:

- The contribution of the indirect process mediated by the active chlorine electrogenerated from the chloride ions oxidation to the removal of the organic load of the effluent was greater than that of the •OH-mediated process.
- An increase in the applied current, solution pH, and temperature accelerated the COD removal and enhanced the current efficiency.
- The effect of the recycling flow rate on the mineralisation rate was not significant, revealing that the process was not under mass transport control.
- The specific energy consumption necessary to reduce the organic load to below the disposal limit (COD <160 mg L⁻¹) and to completely remove the COD were 90 and 220 kWh m⁻³, respectively.

Acknowledgments I.S. acknowledges the support from the members of the Laboratorio di Elettrochimica, Corrosione e Protezione dei Materiali Metallici of the Università degli Studi di Genova to draw up this paper.

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