

Electrochemical oxidation of landfill leachates at pilot scale: evaluation of energy needs

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ABSTRACT

Two of the main drawbacks to be overcome before full scale implementation of boron-doped diamond electro-oxidation were addressed in this work; its energy consumption and hazard of formation of chlorinated organics. This was framed within a study in which the technical and economic feasibility of BDD electro-oxidation of landfill leachate was evaluated at pilot scale. On one hand, its technical feasibility was assessed based on COD and NH_4^+ removal, allowing the selection of the operation conditions that provide optimal energy efficiency, and special attention was paid to the risk of formation of undesired by-products such as nitrite, nitrate ions and trihalomethanes. On the other hand, treatment costs were estimated based on energy consumption required to reach the disposal limits to natural watercourses established by legislation. The results were compared with those of other commonly used AOPs. Under the operating conditions studied, the concentration of COD decreased below the disposal limit (160 mg L^{-1}) and ammonia concentration reached values as low as 30 mg L^{-1} . The energy consumption needed was estimated at 54 kWh/m^3 and the formation of chlorination by-products appeared to be low as the maximum total trihalomethane concentration detected was $432 \text{ } \mu\text{g/L}$.

Key words | electrochemical oxidation, landfill leachate, specific energy consumption, trihalomethanes

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INTRODUCTION

Enforcement of stringent environmental laws has driven researchers to develop various alternative processes such as electrochemical oxidation, wet oxidation, ozonation and fenton oxidation for the efficient treatment of various kinds of low biodegradable wastewaters. In particular, electro-oxidation by means of boron-doped diamond anodes (BDD) has proved to be an efficient alternative (Polcaro *et al.* 2009). Boron-doped diamond is an electrode material with outstanding properties such as high chemical inertness, dimensional stability and wide working potential window. Upon anodic polarization, the decomposition of water molecules can lead to the appearance of hydroxyl radicals which mediate the oxidation processes in the vicinity of the electrode surface.

Oxidation of model substances such as phenol, oxalic acid, and dyes has been extensively studied although nowadays, attention is shifting towards the treatment of real wastes. Most of these studies have been performed on a laboratory scale where BDD electro-oxidation has proved to be an alternative for the removal of non-biodegradable and/or toxic organic pollutants and ammonia nitrogen (Cabeza *et al.* 2007; Polcaro *et al.* 2009). These encouraging results have prompted researchers to implement this technology at pilot scale (Rüdiger *et al.* 2007; Serikawa *et al.* 2009). In particular, in a previous study performed by this research group, a pilot plant with a total anode area of 1 m^2 was used to treat landfill leachate (Anglada *et al.* 2009). Several runs were performed to check the performance of

doi: 10.2166/wst.2010.130

the system and the different phenomena that occur during the electro-oxidation process of landfill leachate at pilot scale were elucidated. The pilot scale implementation of electrochemical oxidation proved that it is a technically feasible technology able to oxidize COD completely and almost all ammonia under appropriate conditions.

Nevertheless, its economical feasibility, mainly in terms of minimization of the energy demand, is required to extend the pilot scale results to industrial applications. Cañizares *et al.* (2009) recently compared conductive diamond electrochemical oxidation (CDEO) of several pollutants at lab scale with two commonly used AOPs (ozonation and Fenton oxidation) in terms of performance and treatment costs. It was observed that the performance of CDEO is usually better than that of the other AOPs and that it can compete satisfactorily in terms of operation and investment costs with Fenton oxidation.

Another pending issue is the risk of formation of chlorination by-products. It should be kept in mind that although the presence of chloride in the landfill leachate improves the oxidation of ammonia due to enhanced indirect chlorine/hypochlorite production efficiency, it also increases the hazard of formation of chlorinated organics.

Thus, the aim of this study was to evaluate the energy consumption during the electrochemical oxidation of landfill leachate at a BDD pilot plant and to evaluate the applicability of this technology by comparing its operation results and treatment costs with those obtained with conventional biological treatment and a commonly used AOP. The effect of current density was studied and the formation of chlorinated by-products during the electrochemical process was evaluated.

METHODS

Landfill leachate

The landfill leachate used in this study was collected from March 2008 to June 2008 from the municipal landfill site of Meruelo in Cantabria, Spain. The raw leachate was initially treated *on-site* by a biological process of activated sludge to reduce biodegradable organic compounds and ammonia. The physicochemical characteristics of the

Table 1 | Characterization of the biologically pre-treated leachate used as feed in this work

Parameter	Range	Average
pH	8.05–8.23	8.16
Conductivity (mS/cm)	8.7–10.7	9.4
Total organic carbon, TOC (mg/L)	300–390	340
Chemical oxygen demand, COD (mgO ₂ /L)	770–970	860
[NH ₄ ⁺] (mg/L)	630–900	780
Anion concentrations		
Chloride (mg/L)	1,470–1740	1630
Nitrite (mg/L)	10–250	95
Nitrate (mg/L)	5–1730	1110
Sulphate (mg/L)	80–120	98

biologically pre-treated leachate are shown in Table 1. As can be seen, the biological process proved to be inefficient. The generated effluent, with an average concentration of COD (860 mg/L) and ammonium (780 mg/L) is above the disposal limits. Also, the landfill leachate presents a high value of the electrical conductivity, due to the high concentration of chloride anions, permitting the application of electrochemical oxidation without the addition of more electrolytes.

Electrochemical system

The electrochemical system used in the laboratory is comprised of a circular boron-doped diamond anode and a stainless steel cathode with a surface area of 70 cm² each and an inter-electrode gap of 5 mm. The feed is circulated from a reservoir to the cell and back in a closed loop, using a recirculation flowrate of 11 L/min. Other experimental details can be found in a previous work (Cabeza *et al.* 2007).

The elements of the pilot plant can be grouped in three sectors: the feeding system, the electro-oxidation unit, and the power supply, instrumentation, and control unit. The feeding system includes a tank of 750 L and three pumps that feed the electrolyte to be treated into three parallel fluid lines. At the bottom of the tank there is a refrigeration coil that is used with rain water. As the fluid leaves the tank it is distributed in three treatment lines disposed in parallel. Each line consists of five sets,

containing each set ten DiaCells (anode-cathode pair, electrode gap 1 mm). The electrode materials are the same as those used in the laboratory but in this case the total anode surface is 1.05 m². Electric power is supplied by three power rectifiers with a maximum output of 750 A, 16 V. The pilot plant includes also conductivity, temperature, pH and ORP probes which give online measurements and a ventilation system. It is operated by means of a PLC. A schematic diagram of the experimental system can be found in a previous work (Urtiaga *et al.* 2009).

Procedure

The experiments were performed under the galvanostatic state in discontinuous mode. A volume of 250 L of biologically pretreated leachate was treated in each experiment. In all cases, the leachate was previously ultrafiltrated in a *ZeeWeed 10* hollow-fiber membrane module (nominal pore size = 0.04 μm, nominal surface area = 0.93 m²), to avoid eventual plugging or short-circuit of the electrode compartments. The flow rate was adjusted to 300 L/min per line (6 L/min/cell). The influence of the current density was studied in the range 300 A/m² to 1,200 A/m². Thus, the experiments were carried out at a current density higher than the limiting current density calculated for the initial COD concentration. Each experiment was performed at least twice and the results presented in this work are the average values.

The same procedure was followed at laboratory scale but in this case the feed volume was 1 L and the recirculation flow rate was adjusted to 11 L/min/cell.

Analytical determinations

Chemical oxygen demand (COD) was determined by closed reflux and colorimetric method (*Spectroquant NOVA 400, Merck*) following the analytical procedure 5220D from Standard Methods (Standard Method 1998). Ammonium nitrogen concentration was obtained by distillation and titration according to the Standard Method 4500 (Standard Method 1998). The concentration of trihalomethanes was determined by headspace injection followed by gas chromatography with an electron capture detector (ECD).

RESULTS AND DISCUSSION

Effect of current density

As expected, current density exerted a great influence on the performance of electro-oxidation (Anglada *et al.* 2009). On one hand, an increase in current density brought about a reduction in the electrolysis time needed to reach the discharge limits for NH₄⁺ (15 mg/L) and COD (160 mg/L). On the other hand, this was usually counteracted by a higher electrical charge ($Q = It/v$) and thus by a lower efficiency. For instance, the specific electrical charge required to reduce the concentration of COD from an average initial value of 860 mg/L to 160 mg/L, increased from 8.8 kAh/m³ to 15.1 kAh/m³ when current density was increased from 300 A/m² to 1,200 A/m². This was accompanied by a decrease in treatment time from 7 to 3 hours, respectively. Nevertheless, the concentration of COD was reduced below 160 mg/L for all applied current densities and ammonia concentrations as low as 30 mg/L were reached.

Concerning the formation of oxidation by-products, the concentration of nitrate ions increased during the process due to partial oxidation of ammonia. For instance, at a current density of 300 A/m², the concentration of N-NO₃⁻ increased from 18.3 mgN/L to 37.9 mgN/L after 8 hours of treatment. In contrast, nitrite ions were eliminated completely at all the applied current densities. Regarding other aspects of the operation, the pH of the solution remained at an almost constant value of 8.2 throughout the electro-oxidation process when a current density of 300 Am⁻² was applied. However, a drop in the pH value from 8.2 to approximately 3 was observed at higher current densities. Thus, by working at a current density of 300 Am⁻², the pH value of the effluent remains within the disposal limits to natural watercourses (pH: 5.5–9.5) and does not have to be adjusted at the end of the treatment. Nevertheless, it should be noted that no corrosion problems were detected during the operation of the plant and that although operation at low pH values (pH < 3) is not advisable as it reduces the efficiency of ammonia oxidation due to the lost of “active chlorine” in the form of gaseous chlorine (Anglada *et al.* 2009), the process is able to handle leachate with a wide range of pH. This is in agreement with the results obtained

by Serikawa *et al.* (2009) who reported that boron-doped diamond electro-oxidation can be applied to wastewaters with a wide range of pH values (0–14).

The operational cost in electrochemical oxidation is due to energy consumption. Energy consumption (W , kWh m⁻³) is directly proportional to specific electrical charge passed (Q , KAh m⁻³) and to cell potential (V , V) as shown in Equation (1).

$$W = QV \quad (1)$$

In Figure 1, the variation of the cell potential with the specific electrical charge passed is shown. In all cases, the cell potential was almost constant during the electrochemical treatment. This indicates that there was no corrosion or formation of passivating layers on the anode surface during the treatment. Cell voltage increased from an average value of 6.1 V to 8.8 V when the applied current density increased from 300 A/m² to 1,200 A/m².

The energy consumption needed to reduce the concentration of COD below 160 mg/L and to reach an arbitrarily NH₄⁺ removal percentage of 70% is given in Figure 2. Additionally, the results were compared with those obtained in the laboratory. In Figure 2 slight discrepancies between the results obtained at laboratory and pilot scale for NH₄⁺ data were observed. These could be due to fluctuations in the characteristics of the raw leachate, which

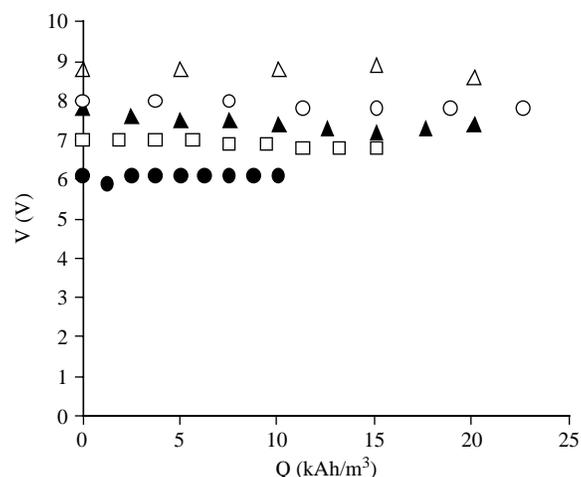


Figure 1 | Variation of cell potential with the specific electrical charge passed in the electrochemical oxidation of biological treated leachate at different current densities: ● 300 A/m²; □ 450 A/m²; ▲ 600 A/m²; ○ 900 A/m²; △ 1,200 A/m².

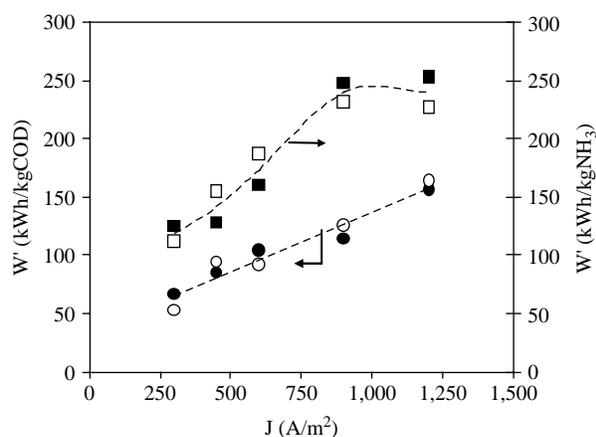


Figure 2 | Influence of current density on specific energy consumption at laboratory (full symbols) and pilot scale (empty symbols). The data were calculated for a reduction in COD concentration below 160 mg/L and for a reduction in the concentration of NH₄⁺ of 70%.

are known to affect the oxidation kinetics of ammonia (Anglada *et al.* 2009); at lab scale the average initial concentrations were COD₀ = 1,370 mg/L, [NH₄⁺]₀ = 950 mg/L and [Cl⁻] = 2,042 mg/L. Taking this into account, it can be said that good agreement between the results obtained at laboratory and pilot scale was obtained and the lowest energy consumption was reached by far for a current density value of 300 A/m². For example, an increase in current density from 300 A/m² to 600 A/m² resulted in an increase of the specific energy consumption needed to reduce the concentration of COD to 160 mg/L from 53 to 94 kWh/kg COD. Similar results in terms of energy consumption have been reported for other electrode materials. Wang *et al.* (2001) reported that the energy consumed during electrochemical oxidation with Ti/SnO₂ anode of landfill leachate at laboratory scale was 80 kWh/kg COD, and 55 kWh/kg COD when the leachate had been previously treated by a UASB. Chiang *et al.* (2001) used coagulation and carbon adsorption as pre-treatments for electro-oxidation of an old leachate. In both cases, electrochemical oxidation by means of a PbO₂/Ti anode gave a total COD removal of approximately 89% and an energy consumption of 43 kWh/kg COD. Deployment of membrane bioreactor prior to electro-oxidation by means of Ti/Pt has also been observed to decrease energy consumption to around 60–70 kWh/kg COD (Aloui *et al.* 2009; Feki *et al.* 2009)

Operation cost

In this study, the operation costs were estimated for an applied current density of 300 A/m^2 which is the current density for which the lowest energy consumption was obtained. Although a longer treatment time was needed when a current density of 300 A/m^2 was applied, it was still much lower than the hydraulic retention time (>5 days) of conventional biological treatment of landfill leachate (Alvarez-Vazquez *et al.* 2004). In Figure 3 the energy consumption required to oxidize COD and NH_4^+ during the electrochemical oxidation of landfill leachate at 300 A m^{-2} is shown. The specific energy consumption needed to reach the disposal limits for COD and NH_4^+ were 54 kWh/m^3 and 93 kWh/m^3 , respectively. The latter was estimated from the linear fitting of the NH_4^+ concentration *vs* energy consumption data.

Prices of electricity are highly dependent on the particular country. If the present unitary electricity cost for industrial use in Spain, which is around $\text{€}0.10 \text{ (kWh h}^{-1}\text{)}$ (Cañizares *et al.* 2009), is considered then the energy cost for landfill leachate treatment by electrochemical oxidation would be $\text{€}9.3 \text{ m}^{-3}$. Nevertheless, it should be kept in mind that energy cost is highly dependent on the desired extent of treatment; i.e. if the main purpose of applying electrochemical oxidation is only to reduce the concentration of COD below the discharge limit, then

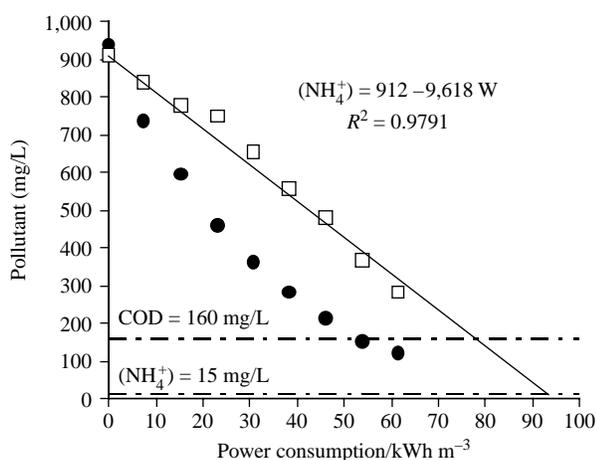


Figure 3 | Energy consumption versus ● COD and □ NH_4^+ concentration, during electrochemical oxidation of landfill leachate at 300 A/m^2 . Solid line represents linear fitting of the NH_4^+ experimental results. Dotted lines represent discharge limits for COD and NH_4^+ .

the energy cost would be $\text{€}5.4 \text{ m}^{-3}$. This price is much higher than that of conventional biological treatment processes (Duggan 2005). However, CDEO presents the advantages that it is able to oxidize bio-recalcitrant compounds and that no sludge is generated during the process. Also, the process can be restarted-up quickly after an operation problem in contrast to biological processes which usually require long acclimatizing periods so that in case of accidental lost of microorganisms, the time necessary to restart-up the process is excessively long (Alvarez-Vazquez *et al.* 2004).

If compared with other advanced oxidation processes, BDD electro-oxidation is found to be able to compete satisfactorily both in terms of treatment efficiency and operation costs. Primo *et al.* (2008) investigated the treatment of the landfill leachate object of this study by several advanced oxidation processes, namely photo-Fenton, Fenton-like, Fenton and $\text{UV/H}_2\text{O}_2$. COD removals that ranged between 30% and 85% were obtained and removal efficiencies were found to decrease in the order: photo-Fenton $>$ Fenton-like $>$ Fenton $>$ $\text{UV/H}_2\text{O}_2$ $>$ UV. However, none of these processes were capable of solving the ammonia environmental problem. In particular, Fenton and photo-Fenton treatment yielded 78% and 85% COD reduction and the operation cost was estimated at $\text{€}9 \text{ m}^{-3}$ and $\text{€}15 \text{ m}^{-3}$, respectively (Primo 2008). Englehardt *et al.* (2006) also compared electrochemical oxidation with other AOPs (Fenton, O_3 , UV, $\text{UV} + \text{O}_3$, and $\text{O}_3 + \text{H}_2\text{O}_2$) and found that electro-oxidation and Fenton treatment are attractive technologies in terms of COD reduction and operating cost.

Trihalomethane analysis results

The electrochemical oxidation of organic compounds in the presence of chloride can lead to the formation of chlorinated organic compounds as by-products. Since halogenated compounds are an important issue in wastewater regulations, it is important to monitor their formation during water treatment processes. In this study the concentration of THMs was measured during the electrochemical treatment of landfill leachate at an applied current density of 300 A/m^2 . This is the current density for which the lowest operational costs were obtained. Figure 4 shows

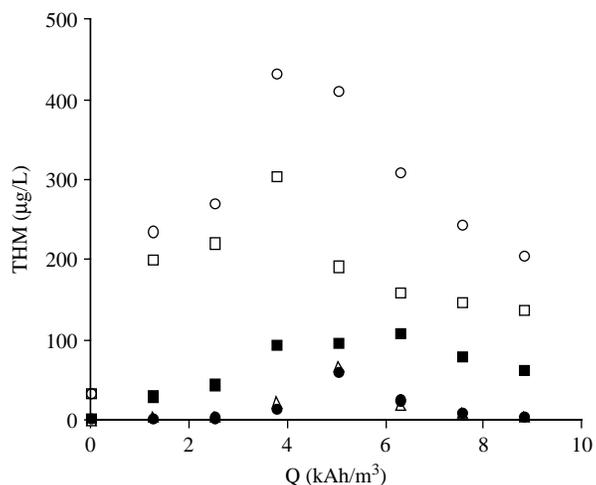


Figure 4 | □ CHCl₃, ■ BrCHCl₂, △ Br₂CHCl, ● Br₃CH and ○ total THM concentration profiles.

the evolution of the concentration of the four THMs (CHCl₃, BrCHCl₂, Br₂CHCl and Br₃CH) during the electrochemical treatment. In all cases, the concentration of THM increased reaching a maximum and then it decreased at a much slower rate. Similarly, Shao *et al.* (2006) observed that indirect electrochemical oxidation of landfill leachate by electro-generated active chlorine resulted in the formation of chlorinated by-products (AOX), but these could be eliminated by prolonged electrolysis.

In addition, THMs with higher chloride content were formed in higher concentrations due to the lower bromide to chloride ion content in the waste water. The maximum concentration detected for each compound was: 300 µg/L of CHCl₃; 108 µg/L of BrCHCl₂; 66 µg/L of Br₂CHCl and 59 µg/L of Br₃CH. Moreover, the higher the chloride content, the faster the THM compound appeared and the longer it took to disappear after its concentration had reached a peak. This is in agreement with the results obtained by Cominellis & Nerini (1995) who observed that chloroform was the main final organochlorinated compound during the oxidation of phenol in the presence of NaCl. Xie *et al.* (2006) studied the formation of chlorination by-products during the electrochemical denitrification of the sludge centrate liquor of digested wastewater sludge with an NH₄⁺, COD and Cl⁻ content of around 640 mg/L, 220 mg/L and 5,278 mg/L, respectively. The formation of these by-products appeared to be minimal with a total THM concentration of 300 µg/L or lower. In the present study,

the maximum and final total trihalomethane concentration detected was 432 µg/L and 210 µg/L, respectively, and are similar to the values reported by Xie *et al.* (2006).

CONCLUSIONS

In the present study the technical and economical feasibility of electrochemical oxidation, by means of boron-doped diamond anodes, for landfill leachate treatment was evaluated. Conductive diamond electrochemical oxidation proved to be a technically feasible technology for COD elimination which can compete in terms of operation results and treatment costs with Fenton oxidation. Moreover, under appropriate conditions, electro-oxidation can eliminate COD completely and almost all ammonia. Within the studied range of current densities (300–1,200 A/m²), the lowest energy consumption was obtained at 300 A/m². At this current density, the operation cost of electrochemical oxidation was around €5.4 m⁻³ and €9.3 m⁻³ to reduce the concentration of COD to 160 mg/L and that of NH₄ to 15 mg/L, respectively. The concentration of N-NO₃⁻ increased from 18.3 mgN/L to 37.9 mgN/L and the formation of chlorination by-products appeared to be low as the maximum total THM concentration detected was 432 µg/L.

ACKNOWLEDGEMENTS

Financial support from projects CTM2006-00317, INGENIO-CONSOLIDER TRAGUA and 062/SGTB/2007/3.1 and MARE, S.A. is gratefully acknowledged. A. Anglada also thanks the Spanish Ministry of Science and Innovation for a predoctoral research grant.

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