Ammonium removal from landfill leachate by anodic oxidation

Adelaida Cabeza, Ane Urtiaga *, María-José Rivero, Inmaculada Ortiz

Department of Chemical Engineering, University of Cantabria, Avda. de los Castros s/n. 39005 Santander, Spain

Available online 30 January 2007

Abstract

The feasibility of removing ammonium from landfill leachates by electrochemical oxidation was studied. Raw leachates and biologically/physico-chemically pretreated leachates from a municipal landfill site were treated. Boron doped diamond was used as anode and stainless steel as cathode, both electrodes with an area of 70 cm^2. The effects of the applied current density (15–90 mA cm^{-2}), the initial ammonium concentration (480–2000 mg L^{-1}), and the initial chloride concentration were experimentally studied. Total ammonium removal was obtained after 360 min of processing and almost half of the initial ammonium nitrogen was oxidized to nitrate. On the other hand, the concentration of chloride enhanced the rate of ammonium oxidation. In addition, the amount of N–NH$_4^+$ transformed into N–NO$_3^-$ decreased when additional chloride was provided.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Leachate treatment; Electrooxidation; Ammonium removal

1. Introduction

Leachates generated from municipal landfills can be considered complex effluents that often contain organic compounds, heavy metals, ammonium, chloride and many other soluble compounds. The composition and concentration of contaminants are influenced by the type of waste and the age of the landfill. A landfill leachate consists of a mixture of pollutants that has adverse effects on the environment.

In an effort to control the pollution caused by landfill leachates, many treatment processes have been studied. According to literature, the biological refractory nature of old landfill leachates involves the necessity of developing alternative methods other than biodegradation to effectively reduce the contaminant loading of these effluents. In most cases, a single technology is insufficient to achieve acceptable levels of pollution decrease and integrated bio-physico-chemical processes have to be developed. Rivas and Beltrán reviewed some of the most relevant works [1] on this topic. Among technologies other than bioprocesses, coagulation–floculation [2], adsorption on activated carbon, chemical oxidation and membrane processes [3] have been reported.

In the past decade, advanced oxidation processes for the treatment of old or biologically treated landfill leachates have been intensely studied to improve the removal of large recalcitrant organic molecules or to transform them into more easily biodegradable substances. In the review of Wang et al. [4] some oxidation processes such as the Fenton process, the photo-Fenton or oxidation processes using ozone, ozone with hydrogen peroxide, ozone with ultraviolet light and hydrogen peroxide with ultraviolet light were demonstrated to be effective for the post-treatment of the non-biodegradable organic pollutants, but they are ineffective for ammonium removal [5].

In recent years, the electrochemical oxidation process has been shown as a promising alternative for ammonium removal from different types of waste waters: tannery wastewaters [6–9], an effluent coming from the anaerobic digestion of a cattle manure [10], and domestic wastewater [11]. In these studies, different anodic materials such us Ti/Pt-Ir [6–8], Ti/RhO$_x$–TiO$_2$ [8], Ti/PdO-CO$_3$O$_4$ [8], TiO$_2$/TiRuO$_2$ [9], DSA$^®$ [10], and Ti/Pt [11], have been tested. In the case of landfill leachate, electrochemical degradation techniques using different types of anodes, i.e. TiO$_2$/RuO$_2$ [11,12], PbO$_2$/SnO$_2$ [14], Ti/Pt [15], SPR [16], and PbO$_2$/Ti [17], have also proved to be capable of removing the ammonium loading. In these studies the initial concentration of N–NH$_4^+$ ranged from 380 mg L^{-1} to 3000 mg L^{-1} and applied current densities ranged from 15 mA cm^{-2} [17], to 130 mA cm^{-2} [15]. The highest ammonium removal was obtained [15] by working with a Ti/Pt anode and a current density of 130 mA cm^{-2} and almost half of N–NH$_4^+$ content was removed after 2 h processing.

* Corresponding author. Tel.: +34 942201587; fax: +34 942201591.
*E-mail address:* urtiaga@unican.es (A. Urtiaga).

Fig. 1. Schematic diagram of the experimental apparatus.

Ammonium degradation takes place mainly due to the indirect oxidation process. The pollutant is destroyed in the bulk solution by the role of strong oxidants generated by the electrochemical reactions. In the presence of chloride, chlorine is generated on the anode surface,

$$2Cl^- \leftrightarrow Cl_{2\,(electrode)} + 2e^- \tag{1}$$

The rate of reaction (1) may be controlled by reaction kinetics or by mass transfer, depending on the applied current density, the chloride ion concentration and the hydrodynamic conditions. The anode reaction is followed by the diffusion of molecular chlorine to the bulk and the hydrolytic disproportionation to form hydrochlorous acid and hypochlorite ions depending on the pH [7]. The anodic formation of chlorine is coupled to its homogeneous reaction with ammonium ions,

$$2NH_4^+ + HClO \rightarrow N_2 + 2H_2O + 6H^+ + 2Cl^- \tag{2}$$
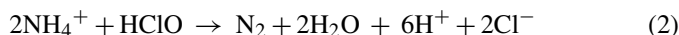
Previous studies [5,2–15] showed that the applied current density and the chloride concentration are relevant operation variables that influence the ammonium removal from landfill leachates. The results demonstrated that as the current density and the chloride concentration are increased, the ammonium removal efficiency is improved.

In the present work, electrochemical oxidation was studied in order to treat a leachate obtained from a municipal landfill site and a boron doped diamond (BDD) anode was used. This type of electrode shows a high chemical inertness and extended lifetime [18]. It also allows to directly produce hydroxyl radicals from water electrolysis owing to the high overpotential for oxygen production. This property leads to an excellent chemical oxygen demand (COD) removal efficiency. Due to the novelty of the BDD material, still few applications with real wastewaters are found in the literature [19]. Moreover, BDD is being used for water disinfection [20] due to the very efficient generation of free chlorine in the presence of chlorides. Hence, high ammonium removal efficiency is expected. Other anodic materials allowed high ammonium removal efficiencies; however, they were not so effective in the reduction of COD [11–17]. The aim of this study is to analyse the influence of the operation variables such as current density, chloride concentration and initial ammonium concentration on the electrooxidation of the ammonium contained in landfill leachates using a BDD anode.
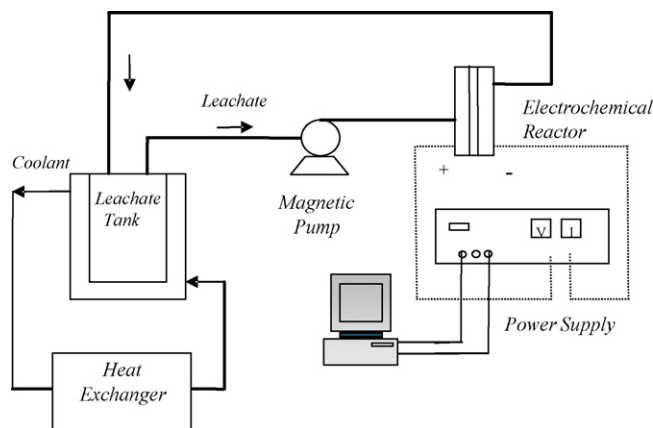
2. Experimental

The experiments were carried out in a single-compartment electrochemical cell. Boron doped diamond on silicon (BDD) was used as anode and stainless steel (316 L) as cathode. Both electrodes were circular with a surface area of 70 cm^2 each and an electrode gap of 5 mm. The electric power required during the electrolysis experiments was provided by a laboratory power supplier (Agilent 6654A) having the maximum output of 9 A, 60 V. The leachate was stored in a glass tank and circulated through the electrolytic cell by a magnetic pump. A refrigeration fluid was circulated through the cooling jacket to maintain the leachate at a temperature of 20 °C (Fig. 1).

Leachate used in this work was collected from the municipal landfill site of Meruelo (Cantabria, Spain). Experiments were carried out with raw leachates as well as with pretreated leachates. The physico-chemical characteristics of either two types of leachates are summarized in Table 1.

The pH was measured with a Combo Gro'Check pH-meter (Hanna Instruments) and the conductivity was measured with a Crison CM 35 conductivity meter. Total suspended solids (TSS) retained by a glass filter and dried at 103–105 °C were determined gravimetrically. Chemical oxygen demand (COD) was determined by the closed reflux and colorimetric method; ammo-

Table 1
Landfill leachates characterization

Parameter	Raw leachate	Pretreated leachate
pH	8.35	7.51
Conductivity (mS cm^{-1})	12.77	14.36
TSS (mg L^{-1})	317	1449
TOC (mg L^{-1})	2782	949
COD (mg L^{-1}) O$_2$	4434	1134
BOD$_5$ (mg L^{-1}) O$_2$	640	120
BOD$_5$/COD	0.14	0.11
N–NH$_4^+$ (mg L^{-1})	1934	859.4
Fluoride (mg L^{-1})	16	38.5
Chloride (mg L^{-1})	3235	1560
Nitrite (mg L^{-1})	–	–
Nitrate (mg L^{-1})	–	–
Phosphate (mg L^{-1})	55	–
Sulphate (mg L^{-1})	39	171.7

Table 2
Initial compositions and current densities used in the experiments

Type of leachate	Experiment	j (mA cm^{-2})	Dilution factor	COD (mg L^{-1})	N–NH$_4^+$ (mg L^{-1})	Cl$^-$ (mg L^{-1})
Raw leachate	1	90	1:1	3799	1707	2758
	2	60	1:1	3276	2020	3032
	3	60	1:2	1728	1106	2157
	4	30	1:2	1813	943	2064
	5	30	1:4	853	487	1792
	6	15	1:4	773	487	1898
Pretreatred leachate	7	30	1:1	1012	756	1420
	8	30	1:1	1019	738	3669
	9	30	1:1	1121	696	6350
	10	30	1:1	1056	732	8571

nium concentration was obtained by distillation and titration [21]. Biological oxygen demand (BOD) was measured by incubation during 5 days at 20 °C. Total organic carbon (TOC) was determined with an NDIR detector (TOC 1200 Euroglas). Ion chromatography (Dionex 120 IC with IonPac AS9-HC column) was used to obtain the concentrations of the inorganic anions.

Experiments carried out with raw leachates were conducted with variations in current density in the range $15\,\text{mA cm}^{-2} < j < 90\,\text{mA cm}^{-2}$. Also, the initial concentration of pollutants was changed by diluting the raw leachate in the ratios of 1/2 and 1/4. The anodic oxidation of the diluted leachate was carried out with addition of sodium chloride in order to obtain a chloride concentration similar to that found in the raw leachate.

On the other hand, experiments carried out with pretreated leachates were all conducted at a constant current density of $30\,\text{mA cm}^{-2}$. This value is close to the value of the limiting current density j_L that leads to obtain a high value of the instantaneous current efficiency for the COD removal [7] ($j_L = nFk_m$ [C], where j_L is the limiting current density, A m^{-2}; n the number of electrons involved in the reaction; F the Faraday constant, $F = 96485\,\text{C equiv.}^{-1}$; k_m is the mass transport coefficient, m s^{-1}; [C] the bulk COD, mol m^{-3}). In this set of experiments different amounts of NaCl (2500–7500 mg Cl$^-$) were added to the leachate in order to investigate the effect of the chloride concentration on the efficiency of the ammonium removal. Table 2 shows the operating conditions and initial concentrations of the two sets of experiments. Differences in the initial values of concentrations in the raw leachate are assigned to the natural variability of this type of complex waste.

3. Results and discussion

3.1. Raw leachate

The evolution of the concentration of N–NH$_4^+$ obtained in the experiments carried out with the original and diluted raw leachate is shown in Fig. 2. Total removal of ammonium is achieved after 360 min by working with (a) raw leachates at 90 mA cm^{-2}, (b) 1/2 diluted leachate at 60 mA cm^{-2} and (c) 1/4 diluted leachate at 30 mA cm^{-2}. Results are shown in Fig. 2(d) in dimensionless form referred to the initial ammonium concentration, NH$_4^+{}_0$ where the influence of the applied current density is observed by comparison of experiments with the same

initial concentration of ammonium (1–2; 3–4; 5–6). For a given value of ammonium concentration, as the applied current density increases the removal of ammonium takes place at a higher rate. In more detail, in Fig. 2(a) the raw leachate with an average initial ammonium concentration of 1864 mg L^{-1} is oxidized using two values of the applied current density, j, 90 and 60 mA cm^{-2}. At $j = 60\,\text{mA cm}^{-2}$, an initial delay zone characterized by low ammonium degradation kinetics is obtained. Later, ammonium degradation rates accelerates to be similar to that obtained at $j = 90\,\text{mA cm}^{-2}$. On the other hand, the influence of the initial concentration on the oxidation of ammonium is observed in Fig. 2(d) by comparing experiments carried out under the same applied current density (2–3 and 4–5). For instance, experiments 2 and 3 were performed working at the same applied current density, $j = 60\,\text{mA cm}^{-2}$, but using different initial ammonium concentration, NH$_4^+{}_0$, 2020 and 1106 mg L^{-1} respectively. As the initial concentration of ammonium increases the rate of oxidation decreases. This behaviour, as it will be discussed later, is assigned to the similar availability of secondary oxidants produced from chloride anions in both experiments.

As a result of the ammonium oxidation, the formation of nitrate was observed. The evolution of nitrates is shown in Fig. 3. The rate of nitrate formation depends on the value of the applied current density. Moreover, the nitrate concentration rises until it reaches a final value that depends on the initial concentration of ammonium. Nitrate formation finished, as observed in the plateau region found in experiments 1 and 3, when all the ammonium was removed. From the results it was observed that half of the initial ammonium nitrogen was found to be oxidized to nitrate anion.

3.2. Pretreated leachate

The experimental results given in Fig. 4 show the influence of the initial concentration of chloride on the electrochemical degradation of ammonium. The initial chloride concentration in the raw leachate was varied in the range $1420\,\text{mg L}^{-1} < \text{Cl}^- < 8570\,\text{mg L}^{-1}$, by addition of NaCl. These results demonstrate that as the chloride concentration increased the kinetics and the removal efficiency of ammonium were improved. The best ammonium removal efficiency obtained in this set of experiments was 95.8%, value that was obtained after 240 min of electrochemical treatment working at a current den-
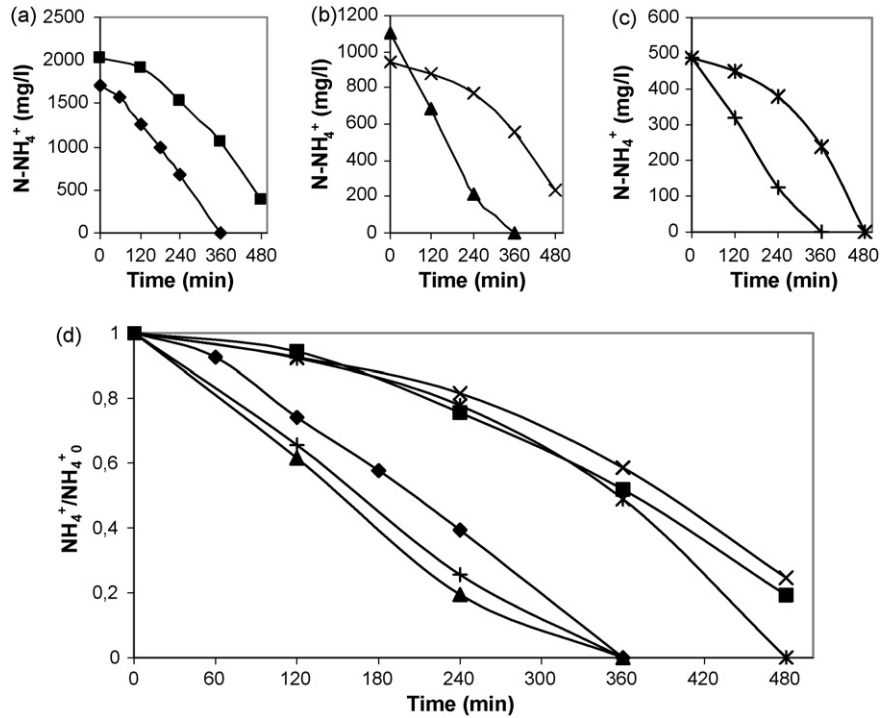
Fig. 2. (a–c) Evolution of N–NH$_4^+$concentration. (d) Evolution of dimensionless ammonium concentration [N–NH$_4^+$]/[N–NH$_4^{0+}$]. (♦) 1, raw leachate, $j = 90$ mA cm^{-2}; (■) 2, raw leachate, $j = 60$ mA cm^{-2}; (▲) 3, 1/2 diluted, $j = 60$ mA cm^{-2}; (×) 4, 1/2 diluted, $j = 30$ mA cm^{-2}; (+) 5, 1/4 diluted, $j = 30$ mA cm^{-2}, and (*) 6, 1/4 diluted, $j = 15$ mA cm^{-2}.
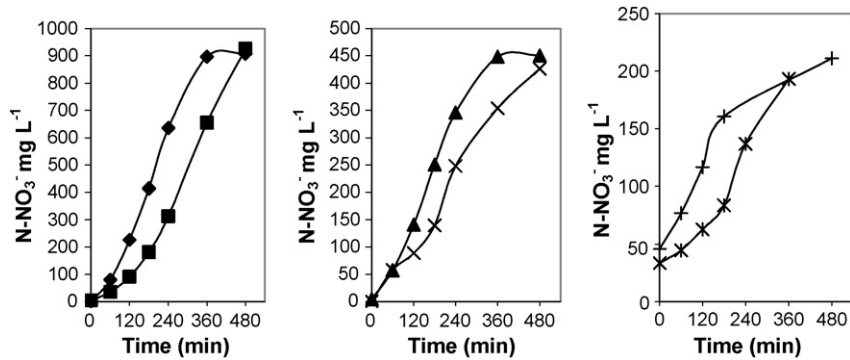

Fig. 3. Production of nitrate during the electrochemical leachate treatment. (♦) exp. 1, raw leachate, $j = 90$ mA cm^{-2}; (■) exp. 2, raw leachate, $j = 60$ mA cm^{-2}; (▲) exp. 3, 1/2 diluted, $j = 60$ mA cm^{-2}; (×) exp. 4, 1/2 diluted, $j = 30$ mA cm^{-2}, (+) exp. 5, 1/4 diluted, $j = 30$ mA cm^{-2}, (*) exp. 6, 1/4 diluted, $j = 15$ mA cm^{-2}.
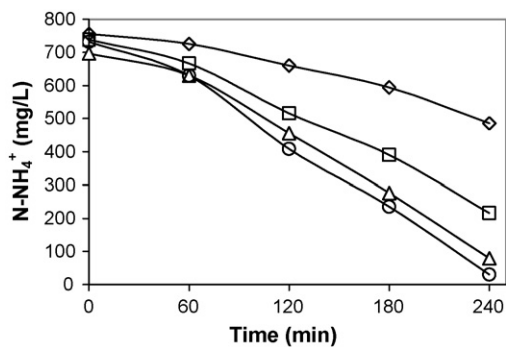

Fig. 4. Evolution with time of the ammonium concentration of the pretreated leachate during the electrochemical treatment. Influence of the chloride concentration. (◇) exp. 7, Cl$^-$, 1420 mg L^{-1}; (□) exp. 8, Cl$^-$, 3669 mg L^{-1}; (△) exp. 9, Cl$^-$, 6350 mg L^{-1}; (○) exp. 10, Cl$^-$, 8570 mg L^{-1}.

sity of 30 mA cm^{-2} and with an initial chloride concentration of 8570 mg L^{-1}. The evolution with time of the nitrate concentration was also determined (Fig. 5). In this case, the plateau region is not observed because the ammonium is not completely removed after 240 min of processing. However, by comparison of the results of experiments 4 and 10, both performed at the same value of current density, $j = 30$ mA cm^{-2}, and with a similar initial ammonium concentration, it is observed that the formation of nitrate seems to be reduced in experiment 10 with regard to experiment 4, effect that could be assigned to the higher chloride concentration of experiment 10.

According to the literature [13], ammonium removal takes place mainly by secondary oxidation through the in-site electrochemical production of hypochlorite using the chloride anions. So, as the chloride concentration increases a higher hypochorite
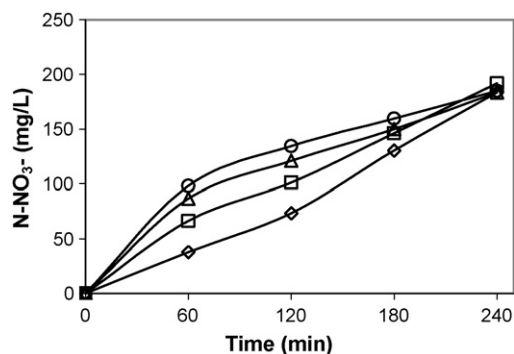
Fig. 5. Nitrate concentration. Effect of the chloride concentration ($\Diamond$) exp. 7, Cl$^-$, 1420 mg L^{-1}; ($\square$) exp. 8, Cl$^-$, 3669 mg L^{-1}; ($\triangle$) exp. 9, Cl$^-$, 6350 mg L^{-1}; ($\bigcirc$) exp. 10, Cl$^-$, 8570 mg L^{-1}.

availability and better kinetics of ammonium removal are obtained. These results about the influence of the chloride concentration are in agreement with data reported by Deng and Englehart [22].

4. Conclusions

The removal of ammonium from leachates obtained form an urban solid waste landfill using the electrochemical oxidation process is studied. A boron doped diamond electrode was employed. Experimental results show an excellent ammonium removal efficiency leading to treated leachates with a N–NH$_4^+$ concentration below the disposal limit (15 mg L^{-1}). Two types of leachates were employed, i.e., the raw leachate as obtained from the landfill, with an initial N–NH$_4^+$ concentration of 1900 mg L^{-1} and a leachate after biological and physico-chemical treatments, with an initial N–NH$_4^+$ concentration of 860 mg L^{-1}. When varying the initial ammonium concentration (by dilution of the raw leachate) in the range $480 < \text{N–NH}_4^+ < 2000$ mg L^{-1}, total ammonium removal was obtained in less than 360 min of processing working with values of the current density in the range 30–90 mA cm^{-2}. At the same time, almost half of the initial ammonium nitrogen was oxidized to nitrate. The influence of the chloride concentration was studied working with the pretreated leachate, by adding NaCl. It was observed that when additional Cl$^-$ was provided, the treatment efficiency increased. In addition to the improvement of the ammonium removal efficiency, the amount of N–NH$_4^+$ transformed into N–NO$_3^-$ decreased.

References

[1] F. Rivas, F. Beltrán, Study of different integrated physical-chemical + adsorption processes for landfill leachate remediation, Ind. Eng. Chem. Res. 44 (2005) 2871–2878.

[2] F. Rivas, F. Beltrán, Stabilized leachates: ozone activated carbon treatment and kinetics, Water Res. 37 (2003) 4823–4834.

[3] F. Rivas, F. Beltrán, Ozone promoted wet air oxidation of landfill leachates, Ind. Eng. Chem. Res. 44 (2005) 749–758.

[4] F. Wang, D.W. Smith, M. Gamal El-Din, Application of advanced oxidation methods for landfill leachate treatment—a review, J. Environ. Eng. Sci. 2 (2003) 413–427.

[5] P. Wang, I.W.C. Lau, Electrochemical oxidation of leachate pretreated in an upflow anaerobic sludge blanket reactor, Environ. Techn. 22 (2001) 373–381.

[6] L. Szpyrkowicz, J. Naunczyk, F. Zilio-Grandi, Electrochemical treatment of tannery wastewater using Ti/Pt and Ti/Pt/Ir electrodes, Water Res. (1995) 517–524.

[7] L. Szpyrkowicz, G. Kelsall, S.N. Kaul, M. De Faveri, S. Satyanarayan, Performance of electrochemical reactor for treatment of tannery wastewaters, Chem. Eng. Sci. 56 (2001) 1579–1586.

[8] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, Influence on the anode material on electrochemical oxidation for the treatment of tannery wastewater, Water Res. 39 (2005) 1601–1613.

[9] M. Panizza, G. Cerisola, Electrochemical oxidation as a final treatment of synthetic tannery wastewater, Environ. Sci. Technol. 38 (2004) 5470–5475.

[10] I. Ihara, K. Umetsu, K. Kanamura, T. Watanabe, Electrochemical oxidation of the effluent from anaerobic digestión of diary manure, Bioresour. Technol. (2005).

[11] A.G. Vlyssides, P.K. Karlis, Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes, J. Hazard. Mater. (2002) 215–226.

[12] P.B. Moraes, R. Bertazzoli, Electrodegradation of landfill leachate in a flow electrochemical reactor, Chemosphere 58 (2005) 41–46.

[13] L. Chiang, T. Wen, Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate, Water Res. 29 (1995) 671–678.

[14] L.C. Chiang, J.E. Chang, Electrochemical oxidation combined with physical-chemical pretreatment processes for the treatment of refractory landfill leachate, Environ. Eng. Sci. 18 (2001) 369–379.

[15] R. Cossu, A.M. Polcaro, Electrochemical treatment of landfill leachate: oxidation at Ti/PbO$_2$ and Ti/SnO$_2$ anodes, Environ. Sci. Technol. 32 (1998) 3570–3573.

[16] A.G. Vlyssides, P.K. Karlis, Treatment of leachate from a domestic solid waste sanitary landfill by an electrolysis system, Environ. Technol. 22 (2001) 1467–1476.

[17] L.C. Chiang, J.E. Chang, Electrochemical treatability of refractory pollutants in landfill leachate, Hazard. Waste Hazard. Mater. 12 (1995) 71–82.

[18] I. Tröster, M. Fryda, D. Herrmann, L. Schäfer, W. Häinni, A. Perret, M. Blaschke, A. Kraft, M. Stadelmann, Electrochemical advanced oxidation process for water treatment using Diachem electrodes, Diamond Relat. Mater. 11 (2002) 640–645.

[19] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with boron doped diamond electrodes: a new advanced oxidation process, J. Hazard. Mater. B103 (2003) 243–261.

[20] T. Furuta, H. Tanaka, Y. Nishiki, L. Pupunat, W. Haenni, Ph. Rychen, Legionella inactivation with diamond electrodes, Diamond Relat. Mater. 13 (2004) 2016–2019.

[21] A Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater, 17th ed., Washington, DC, 1989.

[22] Y. Deng, J.D. Englehardt, Electrochemical oxidation for landfill leachate treatment, Waste Management 27 (3) (2007) 380–388.