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Abstract: The aim of this work is the definition of a clean process for the treatment of landfill leachates by integration of efficient technologies, namely electrooxidation and selective ion exchange, that reduce the initial concentration of the pollutants and allow re-use of the treated water. Treatment of the leachates by electrochemical oxidation using a boron doped diamond electrode led to complete removal of chemical oxygen demand and ammonium nitrogen. However, as a result of ammonium oxidation the partial formation of nitrate was observed. Ion exchange removal of nitrate was experimentally analyzed using the selective resin Purolite A520 E obtaining satisfactory results.

Keywords: Landfill leachate, electrochemical oxidation, ammonium removal, ion exchange, nitrate removal

INTRODUCTION

Leachates are defined as aqueous effluents generated as a consequence of rainwater percolation through wastes, chemical biological processes in wastes, and the inherent water content of wastes themselves. The combination

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of the previous factors result in hazardous aqueous wastes highly contaminated with various toxic pollutants i.e. organic compounds, ammonium, and heavy metals. Purification of landfill leachates is a difficult matter for which there is no general answer. The changing nature and composition of leachates depending on age, climatic conditions, etc., implies that universal treatments of wide application can not be proposed. In most cases, a single technology is not available in order to accomplish the stringent water quality outputs demanded nowadays by legislation. Moreover, in order to contribute to the sustainable development, the study of separation processes that permit water recycling, recovery, and reduction of waste levels is at present one of the greatest challenges to face.

Advanced oxidation processes (AOPs) for the treatment of old or biologically treated landfill leachates have been intensively studied in the past decade (1). AOPs oxidize the refractory organics to end-products such as carbon dioxide and water or to transform these organic substances into more easily biodegradable. Although traditional advanced oxidation processes have been demonstrated to be efficcient for the treatment of the non-biodegradable organic pollutants, they are ineffective for ammonium removal (2).

Since the 1970s, electrochemical oxidation has been succesfully applied to the treatment of textile waste waters (3), tannery waste waters (4, 5), coke-plant waste waters (6) and other waste waters containing cyanides (7) and phenol (8). Deng and Englehart (9) reviewed the state-of-the-art understanding of electrochemical oxidation of landfill leachate at both the laboratory and the pilot plant scale stressing on the removal of organic constituents, ammonia, nitrogen, and color. Electrochemical oxidation of landfill leachate under appropiate conditions can remove most COD, almost all ammonia (10–15), and removes color significantly.

During the electrochemical oxidation pollutants can be oxidized either directly or indirectly. At the anode, the electrode to which electrons travel, some pollutants (e.g., organic compounds) can be directly oxidized. Additionally, oxidation reactions may occur in the bulk solution by means of the oxidant generated by the electrodes. Ammonium degragation is proposed to take place mainly due to the indirect oxidation process. In the presence of chloride, chlorine is generated on the anode surface. This reaction is followed by diffusion of molecular chlorine to the bulk and the hydrolytic disproportionation to form hydrochlorous acid and hypochlorite ions (4). The anodic formation of chlorine is coupled to its homogeneous reaction with ammonium ions to form nitrogen (1).

$$2NH_4^+ + HClO \longrightarrow N_2 + 2H_2O + 6H^+ + 2Cl^- \tag{1}$$

However, previous works (3, 15) showed the formation of nitrate anion as a result of ammonium oxidation. Vlyssides et al. found that in an alkaline environment the ammonium nitrogen was removed and oxidized to nitrate while in acidic conditions it was transformed mainly to nitrogen gas. Cabeza et al. (15)

also observed that the ratio "*formed* $N\text{-}NO_3^-/$*removed* $N\text{-}NH_4^+$" decreased by increasing the initial chloride concentration of the leachate.

Nitrate is a pollutant under regulation, therefore it is necessary to have some treatment to reduce its concentration prior to discharge. Nitrate is a stable and highly soluble ion with low potential for coprecipitation or adsorption. These properties make it difficult for its removal using conventional technologies such us lime softening and filtration (16). Available methods for nitrate removal are ion exchange, biological denitrification, catalytic reduction, reverse osmosis, and electrodyalisis (17). The ion exchange process seems to be a suitable alternative because of its effectiveness, selectivity, recovery, and relatively low cost. Several nitrate selective resins have been developed. Nitrate specific resins have been proved to have affinity for the following ions in decreasing order; $NO_3^- > SO_4^{2-} > Cl^- > HCO_3^-$. The ion exchange process involves the contact between nitrate loaded water and a bed containing a strong anionic resin where nitrate ions are exchanged for chloride until the resin's exchange capacity is exhausted. The exhausted resin is regenerated using a concentrated solution of sodium chloride.

The aim of this work is the definition of a clean process for the treatment of landfill leachates. This process is based on the integration of an electro-oxidation step that oxidizes the organic matter and ammonium compounds completely followed by an ion exchange step in order to remove the nitric nitrogen formed during oxidation of ammonium nitrogen. Thus, the final water effluent could have suitable characteristics for its reuse.

METHODS

Leachate Characteristics

Leachates without any pretreatment were collected in July 2005 from the municipal landfill site of Meruelo (Cantabria, Spain). The physico-chemical characteristics are summarized in Table 1.

The low BOD_5/COD ratio indicated the difficulties involved in treating this type of aqueos solutions in a biological digestion process. Other major components present in the leachate were ammonium and chloride. The latter led to the formation of chlorine/hypoclorite during the electrochemical process. Moreover, the electrical conductivity suggests that the landfill leachate used in this study is quite a saline effluent, and consequently, it favours electrochemical oxidation treatment without addittion of further electrolytes.

Analytical Procedures

The leachates were characterized by means of the following methods:

The pH was measured with a Combo Gro'Check (Hanna Instruments) pH-meter and conductivity was measured with a Crison CM 35 conductivimeter.

Table 1. Landfill leachate characterisation

pH	8.35
Conductivity (mS cm^{-1})	12.77
Total suspended solids (mg L^{-1})	317
TOC (mg L^{-1})	2782
COD (mg L^{-1}) O_2	4434
BOD_5 (mg L^{-1}) O_2	640
BOD_5/COD	0.144
N-NH_4^+ (mg L^{-1})	1934
Fluoride (mg L^{-1})	16
Chloride (mg L^{-1})	3235
Nitrite (mg L^{-1})	0
Nitrate (mg L^{-1})	0
Phosphate (mg L^{-1})	55
Sulphate (mg L^{-1})	39
Chromium (mg L^{-1})	0.61
Lead (mg L^{-1})	0.01
Nickel (mg L^{-1})	0.19
Tin (mg L^{-1})	0.08
Iron (mg L^{-1})	4.56
Sodium (mg L^{-1})	2402.4
Potassium (mg L^{-1})	1475.6
Magnesium (mg L^{-1})	87.6
Calcium (mg L^{-1})	107.8
Manganese (mg L^{-1})	1.17
Silicon (mg L^{-1})	12.2
Zinc (mg L^{-1})	0.15
Color	Absorption Coefficient
λ 436 nm	249.2
λ 525 nm	116.3

Total suspended solids retained by a glass fiber and dried at 103–105°C were determined gravimetrically.

The chemical oxygen demand (COD) was determined by closed reflux and colorimetric method; ammonium nitrogen concentration was obtained by distillation (Buchi UK-355) and titration, both according to the Standard Methods for the Examination of Water and Wastewater (18). Biological oxygen demand (BOD5) was mesured by incubation during five days at 20°C. The total organic carbon (TOC) was determined by measuring the carbon dioxide formed from the complete oxidation of the sample, with a NDIR detector (TOC 1200 Euroglas). Ion chromatography (Dionex 120 IC with IonPac AS9-HC colum) was used to determine the inorganic anions concentration; whereas metals in leachates were mesured by induced coupled plasma (Perkin Elmer).

Finally, to evaluate the color, 436, 525, and 625 nm wavelengths were chosen. Measuremets were taken with a Merck Spectroquant NOVA 400 spectrophotometer.

Experimental

Electrochemical Oxidation

The electrochemical apparatus consisted of a single-compartment electrochemical cell available commercially (DiaCell 106). Boron doped diamond on silicon (BDD) was used as an anode and stainless steel (316 L) as a 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 electro-oxidation experiments was provided by a laboratory power supplier (Agilent 6654A) having the maximum output of 9A-60V. The leachate was stored in a glass tank and circulated through the electrolytic cell by a magnetic pump. Flow rate was adjusted to 11 L min^{-1} in order to facilite turbulence and to avoid a bad evacuation of gases. The experiments were carried out at a constant temperature of 20°C. In all cases the leachate was previously filtered to avoid the input of big particles or solid elements in the electrochemical compartments. 1000 mL of raw or diluted leachate was treated in each experiment.

The experimental set-up was operated in a batch recirculation mode at a constant current density, ranging from 150 to 900 A m^{-2}. Experiments were performed working with different initial concentrations of pollutants, employing raw leachate or diluted leachate. Experiments with the diluted leachate were carried out increasing the amount of chloride up to the concentration in the raw leachate by adding NaCl, in order to avoid the influence of this variable.

Ion Exchange

Strong base nitrate selective anion exchange resin Purolite A520 E was provided by Purolite Ibérica. This resin is a macroporous anionic resin that is specially designed for the removal of nitrates from drinking water. This resin has more affinity for nitrate ions than for other ions. Its physical properties reported by the suppliers are given in Table 2. The adsorption behavior of Purolite A 520E has been previously reported (17, 19).

In order to study the viability of the removal of nitrate ions, column tests were performed. Initially, synthetic waters containing nitrate, sulphate, and chloride anions were treated. Feed solutions were prepared with average values of anions in the range of the effluent coming from the electrochemically treated landfill leachate ($N\text{-}NO_3^- = 225\ mg\ L^{-1}$; $SO_4^{2-} = 200\ mg\ L^{-1}$; $Cl^- = 1000\ mg\ L^{-1}$). Column tests were carried out in a glass column with

Table 2. Physico-chemical properties of resin Purolite A 520 E

Skeleton	Macroporous styrene-divinylbenzene
Functional groups	Quaternary ammonium
Physical aspect	Opaque spherical beads, beige color
Particle size range	0.3–1.2 mm
Ionic form	Cl^-
Total exchange capacity (wet)	0.9 meq/mL min.
Total exchange capacity (dry)	2.8 meq/g min.
Moisture retention	50–56%
Max. temperature	100°C
pH	0–14
Real density	1.06

internal diameter of 3.28 cm. The column was packed with 47 g of dry resin. The aqueous solution was delivered down-flow to the column at a flow rate of 0.23 L h^{-1} using a peristaltic pump. The elution of nitrate from the resins was performed using 6% NaCl solution at 0.47 L h^{-1}.

RESULTS AND DISCUSSION

Electrochemical Oxidation

Landfill leachates collected from the landfill site of Meruelo (Cantabria, Spain) were treated by using an electrochemical oxidation process in a batch reactor under different conditions. Table 3 reports the operating conditions of the experiments carried out and the experimental results obtained after six hours of electro-oxidation. Final COD, N-NH_4^+, N-NO_3^-, Cl^- and SO_4^{-2} values are shown in the table. Concentrations of ammonium and nitrate ions are both expressed in grams of nitrogen to facilitate the comparison between the amount of removed N-NH_4^+ and the amount of formed N- NO_3^-. As an example the kinetics of all COD, N-NH_4^+ and N-NO_3 during experiment 5 are shown in Fig. 1.

As it is observed, COD and N-NH_4^+ can be completely removed after six hours by means of the electrochemical oxidation process under certain conditions of applied current density. The influence of the operating variables on the kinetics of N-NH_4^+ has been reported in a previous work (15). A more detailed kinetic analysis has been reported elsewhere (20). On the other side, as a result of ammonium oxidation, the formation of nitrate anions was observed. From the results it was concluded that half of the initial ammonium nitrogen was oxidized to NO_3^- anion. No presence of NO_2^- anion was observed at the end of the experiments.

The evolution of the concentration of chloride anions depended on the experimental conditions. Big differences in the removal of chloride after 6

Table 3. Operating conditions of the experiments. Comparison between the initial and final concentration of pollutants after 6 hours of electrochemical treatment

Exp	j A/m^2	COD mg/L Initial	COD mg/L Final	N-NH$_4^+$ mg/L Initial	N-NH$_4^+$ mg/L Final	Cl$^-$ mg/L Initial	Cl$^-$ mg/L Final	SO$_4^{2-}$ mg/L Final	N-NO$_3^-$ mg/L Final
1	900	3799	0	1707	0	2758	1137	110.9	897
2	600	3276	605	2020	1051	3032	2320	115.3	665
3	600	1728	26	1106	0	2157	622	76.6	449
4	300	1813	207	943	553	2064	1800	66.1	354
5	300	853	0	487	0	1792	571	38.1	211
6	150	773	108	487	238	1898	1768	35.8	193

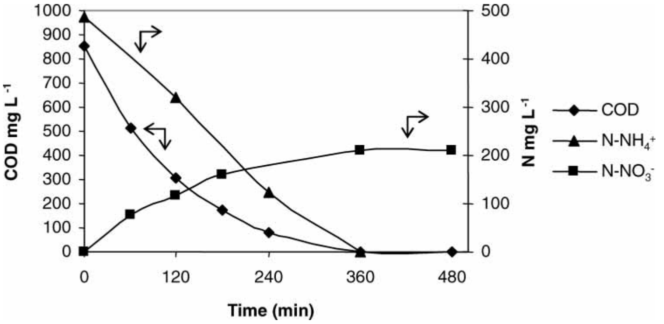

Figure 1. COD, N-NH_4^+, N-NO_3^- kinetics during electrochemical treatment of experiment 5 ($j = 300\ A\ m^{-2}$; $COD_0 = 853\ mg\ L^{-1}$, N-$NH_{4\cdot 0}^+ = 487\ mg\ L^{-1}$).

hours of electrochemical treatment are observed depending on the initial composition of the leachate and on the applied current density. It is observed that chloride removal is higher when working with high values of current density. In contrast, it is observed that the concentration of sulphate anion increases during electro-oxidation. It may be attributed to the oxidation of sulphide anion or of organic compounds containing sulphur. It is observed that the final value of the sulphate anion concentration depends on the initial concentration of pollutants but it does not depend on the applied current density.

Integrated Process: Electro-oxidation and Ion-Exchange

A literature survey revealed that several research projects were developed on denitrification of drinking water (21, 22), ground water (16) and fertilizer wastewater (23) using strong anionic exchange resins. In our case of study, nitrate formed in the electrooxidation process must be removed before the treated water could be re-used. The removal of nitrate anion from ground waters by ion-exchange in the presence of sulphate and chloride anions has been recently reported by Samatya et al. (17, 19). These authors studied the removal of nitrate by Purolite A 520 E resin. A remarkable influence of the competitive anions on the breakthrough point of nitrate was observed. The exchange of nitrate ions and resin ions was hindered by chloride and sulphate anions. Despite this selectivity tests results, it was considered that the uptake of nitrate from ground water was succesful.

Taking as reference the results of Samatya et al. (17), in this work a laboratory study was conducted in order to determine the viability of the combination of both electrochemical oxidation and ion-exchange technologies. A synthetic aqueous feed was prepared having similar average values of anionic concentration as the electrochemically treated landfill leachate

($N\text{-}NO_3^- = 225\ mg\ L^{-1}$; $SO_4^{2-} = 200\ mg\ L^{-1}$; $Cl^- = 1000\ mg\ L^{-1}$). The strong base nitrate selective Purolite A 520 E resin was selected. The breakthrough curve of the nitrate separation is shown in Fig. 2a, where experimental results are given as nitrogen and nitrate concentration. It is observed that the nitrate anion was effectively separated from chloride and sulphate contained in the analyzed wastewaters. The objective of the process is to reduce the concentration of nitrate-N below 10 mg L^{-1} that is the disposal limit established in the Spanish legislation. Thus, this value was selected as the breakthrough concentration. According to Fig. 2, the breakthrough point was obtained after flowing 50 bed volumes (BV), being the resin uptake at breakthough of 81.0 mg NO_3^-/g resin. The total capacity was evaluated as 87.8 mg NO_3^-/g resin, a value that is within the range reported by Samatya et al. (16) who found that the nitrate capacity varied with the amount of other anions present in the feed. The column utilization efficiency was aprox. 92%. A preliminary elution test is shown in Fig. 2b. The nitrate loaded onto the resin was eluted with 9.4 BV of 6% NaCl. Taking into account the availabitlity of sea water in the leachate treatment facility that is located close to the sea, future tests using sea water will be performed as recommended by the resin manufacturer.

Figure 3 presents a flow diagram of the proposed process. The left hand-side represents the electro-oxidation step of the landfill leachate, where the COD and ammonium removal is completely achieved. The right-hand side corresponds to the nitrate separation step using ion exchange. As a result a clean leachate with very low content of COD, ammonium, and nitrate is obtained.

CONCLUSIONS

Electrochemical oxidation has been demonstrated to be a succesful alternative for the treatment of landfill leachates. The total COD and ammonium removal

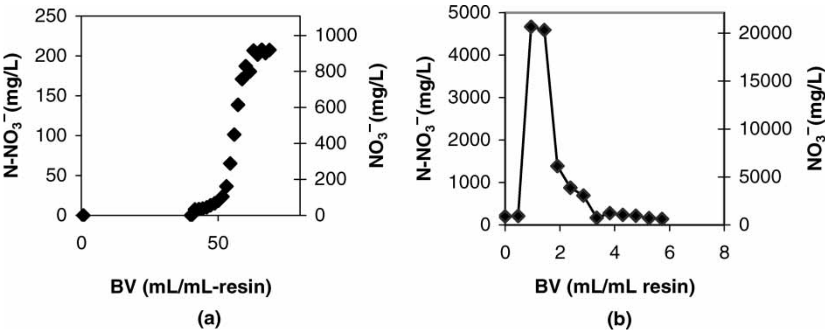

Figure 2. (a) Breakthrough curve of nitrate. (b) Elution curve of nitrate.

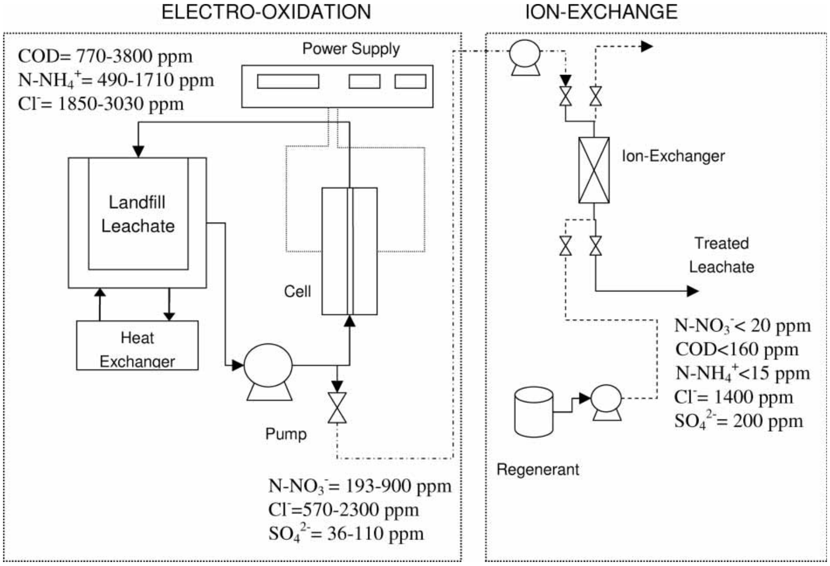

Figure 3. Diagram of the experimental system that combines electro-oxidation and ion exchange.

is achieved under certain operating conditions. However, half of the eliminated ammonium nitrogen is oxidized to nitrate. As the nitrate anion is a pollutant under regulation, further treatment is necessary to reduce its concentration.

The removal of nitrate from aqueous solutions containing other anionic species such us chloride and sulphate and from groundwaters by nitrate selective ion exchange-resins has led to promissing results. Moreover, a laboratory study was conducted to investigate the capacity of Purolite A 520 E ion-exchange resin for the removal of nitrate from inlet waters containing nitrate, sulphate, and chloride. The concentration of these anions was in the range of the electrochemically treated landfill leachate. 50 bed volumes (BV) of feed water were treated before the breakthrough point for nitrate concentration was reached, the resin uptake at this point being 81.0 mg NO_3^-/g resin.

Finally, it is proposed that the integration of both technologies is the definition of a clean process for the efficient treatment of landfill leachates, allowing for re-use of the treated water.

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