Short communication

Nitrate removal from electro-oxidized landfill leachate by ion exchange

Oscar Primo, María J. Rivero, Ana M. Urtiaga, Inmaculada Ortiz *

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

A B S T R A C T

Treatment of landfill leachates by electrochemical oxidation led to the complete removal of chemical oxygen demand and ammonium nitrogen. However, as result of the ammonium oxidation, the partial formation of nitrate ions was observed. Ion exchange technology was investigated as a polishing step in the treatment of landfill leachates. Removal of nitrate from aqueous solutions was studied using two selective anion exchangers: *Purolite A 520E* and *Purolite A 300*, under a fixed bed configuration. The following aspects of the ion exchange system were experimentally analyzed: (i) the influence of the presence of other competitive anions in solution, sulfate and chloride, during the loading step, (ii) the breakthrough point and resin saturation as a function of chloride concentration in the feed stream and, (iii) the efficiency of the regeneration step working with NaCl solutions at several concentrations. After a comparison of the experimental results, it was concluded that the resin *Purolite A 300* showed a better behavior. Experimental analysis of the equilibrium isotherms made it possible to determine the equilibrium constant ($K = 3.21$) and the maximum capacity ($q_{max} = 183$ mg g^{-1}), important parameters in the design of the treatment process.

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1. Introduction

Leachate generation is one of the most serious environmental problems related to waste disposal in landfill. Advanced oxidation processes (AOPs) have been widely studied for landfill leachate treatment in the past decade [1]. Traditional AOPs, such as Fenton or photo-Fenton processes, have proved to be efficient for non-biodegradable organic compound removal, but are ineffective for ammonium removal [2].

Recently, there has been an increasing interest in the use of electrochemical oxidation processes for the treatment of polluted wastewaters. This technology is considered to be a promising alternative, because of its easy operation and effectiveness for the destruction of pollutants, especially refractory organic compounds. Electrochemical oxidation has been successfully applied to the removal of organic constituents, ammonia nitrogen and color from landfill leachates [3]. During the electro-oxidation, pollutants can be oxidized either directly or indirectly. At the anode, some compounds can be directly oxidized. Additionally, oxidation reactions may occur in the bulk solution by means of the oxidant species electrolytically generated. It is proposed that ammonium degradation takes place mainly due to the indirect oxidation process in the presence of chloride ions. However, ammonium oxidation can lead to the formation of nitrate ions [4,5].

Nitrate contamination has become an environmental and health problem all over the world due to its harmful effects. Nitrates are extremely soluble in water and can move easily through soil into the drinking water supply [6]. Moreover, excess of nitrate contributes to eutrophication. To protect consumers from adverse effects associated with the high nitrate concentration in drinking waters, consumption should be limited and standards have been established [7]. According to WHO, drinking water must contain no more than 50 mg L^{-1} of nitrate and European Community recommends levels of 25 mg L^{-1} [8,9], so nitrate is a pollutant under regulation and, therefore, it is necessary to reduce its concentration prior to discharge.

Several methods for nitrate removal from water have been applied such as ion exchange, biological denitrification, reverse osmosis and electrodialysis [10–12]. The ion exchange process seems to be one of the most suitable processes to remove nitrate because of its simplicity, effectiveness, selectivity, recovery and relatively low cost [13]. Some ions such as sulfate could compete with nitrate for the exchange sites. Therefore, it is important to study this process in the presence of competing anions. Besides, the use of selective resins for nitrate ion could be beneficial. The application of ion exchange to eliminate nitrate ions in surface and groundwaters has been published in the literature [6,8,14,15].

The aim of the present work was to study the efficiency of ion exchange in the application to nitrate removal from electro-oxidized landfill leachates to complete the treatment. Two anion exchange resins, *Purolite A 520 E* and *Purolite A 300*, for nitrate removal from aqueous solutions that contained also sul-

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* Corresponding author. Tel.: +34 942201585; fax: +34 942201591.
E-mail address: ortizi@unican.es (I. Ortiz).

Table 1
Physico-chemical properties of the resins

Property	Purolite A 520E	Purolite A 300
Skeleton	Macroporous styrene – divinylbenzene	Polystyrene cross-linked with divinylbenzene
Functional groups	Quaternary ammonium	$R(CH_3)_2(C_2H_4OH)N^+$
Physical aspect	Opaque cream spherical beads	Clear spherical beads
Granulometry (mm)	0.3–1.2	0.3–1.2
Ionic form	Cl^-	Cl^-
Moisture retention (%)	50–56	40–45
Limit of temperature (°C)	100	77
Limits of pH	0–14	No limitations
Shipping weight ($g\,L^{-1}$)	680	705
Total exchange capacity ($meq\,g^{-1}$)	2.8	3.5–3.7
Total nitrate removal capacity ($mg\,g^{-1}$)	174	223

fate and chloride ions were investigated. The performance of resin columns was studied using different experimental conditions. A model and parameters that describe the equilibrium data were determined.

2. Experimental

2.1. Resin characteristics

Two anion exchange resins were tested for nitrate removal from an aqueous solution: (i) a macroporous strong base nitrate selective anion exchange resin *Purolite A 520E*, specially designed for the removal of nitrates from water for potable processes and (ii) a strong base non-selective gel anion exchange resin *Purolite A 300*, used in all types of demineralization processes. The resins were kindly provided by the Spanish delegation of *Purolite Int. Ltd.* The physical properties and specifications of the anion exchangers reported by the suppliers are given in Table 1.

2.2. Nitrate solutions

Ion exchange experiments were carried out using synthetic solutions as a feed stream. Model solutions with nitrate, sulfate and chloride were prepared by dissolving the appropriate amounts of $NaNO_3$, Na_2SO_4 and $NaCl$, respectively, in deionized water. The concentrations of each ion in the experiments are shown in Tables 2 and 3. Inorganic chemicals were supplied by *Panreac Química S.A.* as analytical grade reagents. The feed stream reproduced the concentration of the three main anions detected in the final effluent obtained after the treatment of landfill leachate by electro-oxidation [4,16].

2.3. Sorption–elution experiments

Equilibrium as well as dynamic results were obtained with a column test at room temperature using a glass column with an internal diameter of 3.28 cm and 15 cm in length.

Feed solution was pumped down-flow to the column filled with the ion exchange resin (47 g *Purolite A 520E* or 30 g *Purolite A 300*) using a *Watson-Marlow 313S* peristaltic pump. The feed flow was $0.23\,L\,h^{-1}$ in all experiments (flow velocity = $7.5 \times 10^{-5}\,m\,s^{-1}$). The breakthrough curves were obtained by analysis of successive samples of the effluent collected at regular time intervals. The elution of the retained anions from the resin was performed at $0.47\,L\,h^{-1}$ (flow velocity = $1.5 \times 10^{-4}\,m\,s^{-1}$) up-flow with a sodium chloride (NaCl) solution at different concentrations. Regeneration curves were obtained by measuring outlet nitrate and sulfate concentrations versus time. Finally, the resin was washed up-flow by deionized water at $0.47\,L\,h^{-1}$, before starting a new cycle.

2.4. Analytical determinations

The analyses of nitrate, sulfate and chloride ions were carried out using a *Dionex* ion chromatograph (model *DX120*) equipped with an autosampler and a conductivity cell detector. The separation was achieved using an *IonPac AS9-HC* column (4 mm × 250 mm) and an *IonPac AG9-HC* guard column (4 mm × 50 mm). Sodium carbonate 9.0 mM was used as mobile phase with a flow rate of 1 mL min^{-1}.

Table 2
Experimental conditions and results of column tests for nitrate removal

	Resin					
	47 g Purolite A 520E			30 g Purolite A 300		
Experiment	1	2	3	4	5	6
Chloride ($g\,L^{-1}$)	1.0	2.5	5.0	1.0	2.5	5.0
Nitrate ($g\,L^{-1}$)				1.0		
Sulfate ($g\,L^{-1}$)				0.2		
Breakthrough						
Capacity ($mg\,g^{-1}$)	74.8	58.8	36.8	80.6	68.6	39.9
BV	41.4	32.2	20.7	42.3	33.8	22.0
Saturation						
Capacity ($mg\,g^{-1}$)	83.3	65.4	47.4	95.1	81.5	51.7
BV	50.6	41.4	35.65	60.9	59.2	45.7
%Column utilization efficiency	77.3	74.2	66.7	73.0	59.1	62.3
Regeneration						
Regenerant (%NaCl)	6	8	4	6	8	4
Efficiency (%)	100	99	92	94	96	96
BV		10			15	

Table 3
Experimental conditions and results of nitrate and sulfate removal for equilibrium experiments using *Purolite A300* resin

Conditions and results					
Experiment	9	5		8	7
Nitrate (g L^{-1})	0.25	1.0		2.5	4.0
Chloride (g L^{-1})			2.5		
Sulfate (g L^{-1})			0.2		
Breakthrough nitrate					
Capacity (mg g^{-1})	24.0	68.6		75.0	67.7
BV	55.8	33.8		15.2	8.5
Saturation					
Nitrate					
Capacity (mg g^{-1})	28.3	81.5		110.0	138.1
BV	96.4	59.2		42.3	27.1
%Column utilization efficiency	56.6	59.1		52.1	64.3
Sulfate					
Capacity (mg g^{-1})	21.8	14.5		11.8	8.2
Regeneration					
Regenerant (%NaCl)			8		
Nitrate					
Efficiency (%)	100	100		96	97
BV			15		
Sulfate					
Efficiency (%)	100	87		90	93
BV			5		

The system operated at room temperature and the injection volume was 25 µL.

3. Results and discussion

3.1. Fixed bed column resin experiments

3.1.1. Loading step: effect of chloride concentration

The effect of chloride concentration in the capacity of nitrate removal of the two anion exchangers was tested. The influence of Cl$^-$ ions must be determined because this parameter affects in a great extent to the electro-oxidation results. It is a design variable for the previous treatment, therefore its concentration will probably change in real process. The breakthrough curves obtained as result of the experiments 1–6 (Table 2) are given in Fig. 1.

Resin saturation with nitrate ions happened faster when the Cl$^-$ concentration increased. The breakthrough and total capacity values obtained are summarized in Table 2. Breakthrough capacity was calculated after having fixed the breakthrough point at a concentration of 20 mg N-NO$_3^-$ L^{-1} (equivalent to 88.6 mg NO$_3^-$ L^{-1}). This value, that it is used as a guide, corresponds to the discharge limit into surface waters regulated in Spanish legislation in the Royal Decree 849/86. The current Spanish legislation (Royal Decree 606/2003) stipulates that limits will be established on the basis of the quality of the receiving environment. Saturation was assumed to have been reached when the concentration in the outlet stream of the column was $C/C_0 = 0.98$.

A higher capacity of *Purolite A 300* resin versus *Purolite A 520E* was observed. The highest saturation point of nitrate removal for *Purolite A 300* resin was obtained after 61 BV had flowed through the column with a total capacity of 95.1 mg NO$_3^-$ g^{-1} resin. The column utilization efficiency was about 73%. This parameter is defined as the ratio between the total amount of solute retained by the resin and the total amount passed through the column until saturation. Using *Purolite A 520E* resin, the highest exchange capacity was reached after 51 bed volumes (BV) had flowed through with a total capacity of 83.3 mg NO$_3^-$ g^{-1} resin. In these conditions, the column utilization efficiency was about 77%. In both cases, maximum capacity was achieved for the lowest chloride concentration in the feed stream.

A reduction in sulfate ion concentration in the effluent was only obtained working with *Purolite A 300* resin. The total capacity to remove sulfate ions using this resin was less than 24 mg SO$_4^{2-}$ g^{-1}. This data confirmed a better affinity of the anion exchanger for nitrate than sulfate ions.

A linear relationship that allows the prediction of the chloride concentration influence on the nitrate resin's capacity was empirically obtained for *Purolite A 520E* (Eq. (1)) and *Purolite A 300* (Eq. (2)):

$$q_e(\text{mg NO}_3^- \text{ g}^{-1}) = 90.25 - 0.0088\, C_{\text{Cl}^-}(\text{mg L}^{-1}) \quad r^2 = 0.98 \quad (1)$$

$$q_e(\text{mg NO}_3^- \text{ g}^{-1}) = 107.13 - 0.0109\, C_{\text{Cl}^-}(\text{mg L}^{-1}) \quad r^2 = 0.99 \quad (2)$$

Although the resin's capacity without Cl$^-$ ions was higher for resin *Purolite A 300*, the negative slope of the linear equation was slight higher. Therefore, the influence of Cl$^-$ for both resins' capacity should be considered. Due to the empirical character of Eqs. (1) and (2), the validity of both correlations should be limited to the experimental range of the operation conditions employed in this work.

3.1.2. Regeneration: effect of NaCl concentration

The adequate regeneration of the exhausted resin is essential from the economic point of view. Nitrate loaded onto the resin was eluted using NaCl solutions. The concentration of regenerant ranged from 4 to 8% (Table 2) and its effect on the efficiency of the regeneration step was studied.

The regeneration curves working with *Purolite A 520E* resin are illustrated in Fig. 1. In all experiments, the resin was completely regenerated after 10 BV of NaCl had flowed for 120 min. The nitrate concentration in the eluate reached values up to 5.1 g L^{-1}. The efficiency of the regeneration ranged from 92% to 100% (Table 2). When the resin adsorbed the higher amount of nitrate, NaCl with a concentration of 6% was used and regeneration was complete. A higher concentration of regenerant did not seem to increase the efficiency and lower concentration seemed to be insufficient.
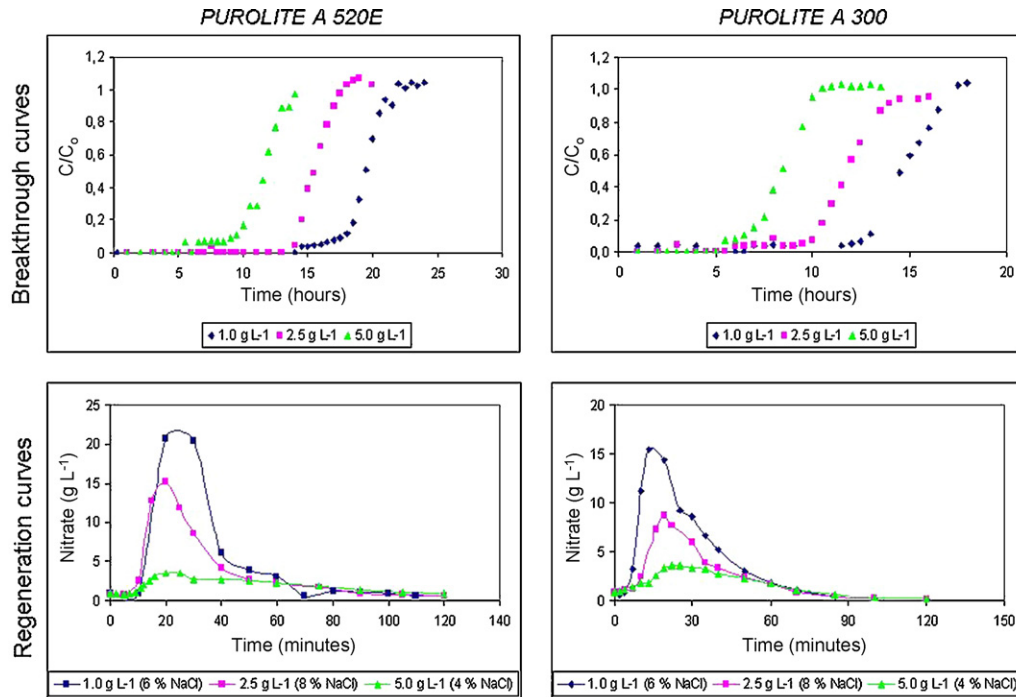
Fig. 1. Breakthrough curves and regeneration curves for experiments using: (a) *Purolite A 520E* resin (experiments 1–3) and (b) *Purolite A 300* (experiments 4–6). Loading step for several Cl⁻ concentrations (NO_3^- = 1.0 g L⁻¹, SO_4^{2-} = 0.2 g L⁻¹) and regeneration for several NaCl concentrations.

Purolite A 300 resin was completely regenerated with 15 BV of NaCl in 120 min of operation. The concentration of the regenerant scarcely affected the regeneration efficiency. The regeneration curves of nitrate are shown in Fig. 1. The nitrate concentration in the eluate reached values up to 4.5 g NO_3^- L⁻¹ and 1.68 g SO_4^{2-} L⁻¹. These concentrations corresponded to a concentration factor of 4.5 and 8.5 times, respectively, with regard to the feed stream concentrations.

The regeneration was slightly better working with *Purolite A 520E* resin because less regenerant solution and consequently less time were required and higher concentrations in the eluent were achieved.

3.2. Equilibrium studies

Purolite A 300 resin was selected to carry out the equilibrium studies because this resin had the highest capacity to remove nitrate ions. The regeneration was performed using 8% NaCl because this concentration guaranteed a complete and faster elution of the exhausted resin irrespective of the retained amount. The nitrate concentration ranged from 0.25 to 4.0 g L⁻¹ and the feed stream contained 2.5 g Cl⁻ L⁻¹ and 0.2 g SO_4^{2-} L⁻¹ (Table 3). Total capacity of the resin to remove nitrate and sulfate was calculated in each experiment and the values are shown in Table 3. When the nitrate concentration decreased, the capacity for sulfate removal increased because they were competing to be adsorbed on the resin. For the regeneration step, the total elution of sulfate ions was faster than nitrate elution, 5 and 15 BV of NaCl 8% being consumed respectively.

Equilibrium between resin and nitrate ion can be represented by the following chemical reaction:

$$R–Cl^- + NO_3^- \leftrightarrows Cl^- + R–NO_3^-$$
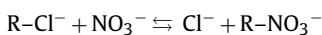
In this expression, R–Cl⁻ and R–NO₃⁻ represent points of the resin occupied by chloride and nitrate ions respectively, and NO_3^- and Cl⁻ represent the concentrations in the liquid phase.

The equilibrium constant for the ion exchange of nitrate ions can be expressed as (Eq. (3)):

$$K = \frac{[Cl^-][R–NO_3^-]}{[R–Cl^-][NO_3^-]} \tag{3}$$

Some authors consider that this is a non-ideal systems, therefore, the activity coefficients of all components both in the solution and in the solid phase, are different to unity. However, the complexity of the determination of the activity coefficients in the solid phase makes the equations difficult to apply. A simplified model based on the mass action law is the first approach widely used [14,17].

After defining the parameter F (Eq. (4)) and applying a mass balance for the resin (Eq. (5)), Eq. (3) is rewritten, leading to Eq. (6):

$$F = \frac{[Cl^-]}{[NO_3^-]} \tag{4}$$

$$q_{total} = [R–NO_3^-] + [R–Cl^-] = q_{NO_3^-} + q_{Cl^-} \tag{5}$$

$$F = K \left(\frac{q_{total}}{q_{NO_3^-}} - 1 \right) \tag{6}$$

The fitting of the experimental data to Eq. (6) by a linear regression allowed us to determine the parameters K and q_{total} from the slope and the intercept of a plot F vs. $1/q_{NO_3^-}$. The values of K and q_{total} were 3.21 and 182.70 mg g⁻¹ respectively, with a coefficient $r^2 = 0.99$. *Microsoft Office Excel 2003* was used to calculate these parameters. Beltrán de Heredia et al. [14] calculated a value of the equilibrium constant equal to 2.58 and a total capacity of 105 mg g⁻¹ for the ion exchange of nitrate ions by Amberlite IRN-78 resin.

The fitting of this model to the experimental data was evaluated by means of the standard deviation (σ) which is described by Eq. (7):

$$\sigma = \sqrt{\frac{\sum ((q_{e,exp} - q_{e,cal})/q_{e,exp})^2}{N - 1}}, \tag{7}$$

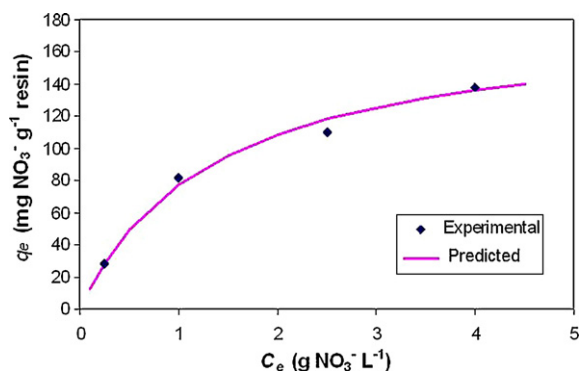**Fig. 2.** Fitting of equilibrium model and experimental data on *Purolite A 300* resin ($SO_4^{2-} = 0.2\,g\,L^{-1}$, $Cl^- = 2.5\,g\,L^{-1}$).

where $q_{e,exp}$ and $q_{e,cal}$ are the experimental and calculated capacity values, and N is the number of data available. The best fitting of the model with the experimental data was recorded for the higher r^2 values and the lower average σ value. Fig. 2 shows the comparison between experimental and simulated data using the equilibrium model with the calculated parameters. The results indicated that the model predictions described reasonably well the values of capacity to remove nitrate ions using *Purolite A 300 resin*, with an average deviation (σ) of 5.18%.

Knowledge of the equilibrium constant value (K) is useful to predict behavior and to design the ion exchange system. For instance, it is able to predict the composition of one phase that is in equilibrium with the other phase of known composition (Eq. (8)):

$$q_{NO_3^-} = \frac{Kq_{total}}{(K+F)},\tag{8}$$

where K and q_{total} are constant in a given ion exchange system, and if the feed stream composition is known (F), $q_{NO_3^-}$ in the equilibrium can be calculated, in the range of experimental variables studied in this work.

4. Conclusions

A laboratory study was conducted to compare the behavior of selective *Purolite A 520E* resin and *Purolite A 300* resin in the removal of nitrate from aqueous solutions. Electro-oxidized landfill leachates were used as feed phase. The composition showed high nitrate concentration due to the ammonium oxidation as well as to other anions like sulfate and chloride.

The efficiency of nitrate removal of both resins was compared. The capacity to retain nitrate ions was higher for *Purolite A 300* resin. Furthermore, this resin can remove other anions like sulfate from the aqueous solution due to its non-selective character. The initial

chloride concentration had a linear effect on the retention capacity. Both resins could be completely regenerated using a NaCl solution of 4–8 wt%.

For the *Purolite A 300* resin useful data for the design of the process were obtained. Equilibrium data were fitted to the chemical equilibrium model. An equilibrium constant (K) of 3.21 was obtained. The value of the maximum capacity to remove nitrate was equal to 183 mg NO_3^- g^{-1}.

Acknowledgments

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