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Ammonium removal from landfill leachate by Clinoptilolite adsorption followed by bioregeneration

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ABSTRACT

This paper reports on the application of a new process for ammonium nitrogen removal from landfill leachate using a reactor filled with zeolite. The process consisted of ammonium nitrogen adsorption from raw leachate followed by zeolite regeneration via nitrification. Zeolite initial adsorptive capacity was first evaluated. Afterwards, biological regeneration was carried out using zeolite containing adsorbed ammonium in the presence of nitrifying bacteria suspension and sodium bicarbonate. The adsorptive capacity (q) was reduced by only 4.55% after regeneration from $q = 10.80 \pm 2.14$ mg NH_4^+-N/g zeo to 10.32 ± 0.74 mg NH_4^+-N/g zeo. Regeneration by nitrification occurred in 72 h and the main product was nitrite.

1. Introduction

Among the environmental issues that challenge the sustainable development of humanity for the near future, solid waste management is on the spotlight. Population growth, coupled to changes in solid waste characteristics and amount produced per capita, is a matter for global concern, with available resources and energy on the brink of exhaustion. Although reduction, reuse and recycling are priorities for minimizing solid waste disposal, landfilling is still a reality that needs to be addressed in many countries. Even in developed countries such as the US, where efforts have been successful to reduce the amount of municipal solid waste disposed in landfills, this alternative remain as the final destination for 54% of the total waste generated [1,2]. In this regard, landfill leachate is a consequent and direct impact that must be treated and properly discharged.

Landfill leachate is a heterogeneous mixture consisting of refractory organic compounds, heavy metals, inorganic contaminants, humic and fulvic acids, and high nitrogen concentrations [3]. Organics are biodegraded anaerobically in landfills and, since there is no degradation pathway for ammonium in anaerobic systems [4], this results in accumulation of this compound and increased toxicity [5]. Due to its composition, specifically regarding high ammonium concentrations and refractory organic matter, this wastewater is suitable to be treated by anammox after partial nitrification (PN) [6]. However, variations in ammonium concentrations due to seasonal factors may result in shock loads that affect PN process.

Depending on the wastewater characteristics and emission standards, the development of new technologies or process adaptations might be necessary. Landfill leachate treatment normally involves biological and/or physical-chemical processes to achieve the strict and increasingly restrictive quality standards for discharging treated leachate into water bodies [7]. Industrial wastewaters and landfill leachate usually require a pre-treatment step to adapt their composition to biological processes and to enhance removal efficiencies.

The presence of high and variable ammonium concentration is considered one of the main problems for the application of biological process to treat landfill leachate. In this context, the use of zeolite adsorption process can be applied to control ammonium shock loads [8]. Zeolite adsorption is also considered a promising alternative for nitrogen removal from anaerobically pretreated wastewater and nitrate recovery with further regeneration, including the opportunity for soil fertilizer production [9]. Clinoptilolite, a natural zeolite with high affinity for ammonium, can be used as ion exchanger. Previous studies have shown that the

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Table 1
Landfill leachate characteristics in the experiment.

Parameter	Values	Parameter	Values
pH	8.2–8.36	Fe	4.452 mg/L
COD	4,353.9 mg/L	Zn	0.672 mg/L
Ammonium	2,292 mg NH_4^+ –N/L	Pb	0.52 mg/L
Nitrite and Nitrate	nd	Cd	0.128 mg/L
Sulfate	119.9 mg/L	Ni	0.650 mg/L
Phosphate	51.18 mg/L	Mn	0.128 mg/L
Total alkalinity	10,665 mg $CaCO_3$/L	Cu	0.036 mg/L
		Cr	0.658 mg/L

nd – not detected.

natural Clinoptilolite and other zeolites can be effective in removing ammonium from wastewater [10–12].

AIYUK et al. [13] designed a compact low-cost system to remove carbon and nitrogen from sewage. The authors proposed the biological regeneration of the zeolite and the use of nitrified effluent generated for irrigation in agriculture. The biologically regenerated zeolite showed 94.8% of its initial ammonium adsorptive capacity. There are also other studies on ammonium removal from wastewater using zeolites [14–16].

Zeolites adsorption might be an effective option for ammonium removal from leachates, as well as to prevent shock loads. Zeolites are generally cheap and do not need any processing prior to use as other materials like activated carbon do [17]. Besides the ability to control shock loads, the use of zeolite for ion exchange allows also the operation over a wide range of temperature and pH [16].

Ammonium adsorption on zeolite and its biological regeneration by nitrification may minimize the impacts due to seasonal variation of ammonium concentrations [18]. During zeolite regeneration, ammonium oxidizing bacteria (AOB) are not subjected to ammonium shock loadings. Therefore, the aim of this study was to evaluate ammonium adsorption in zeolites and its regeneration by nitrification.

2. Materials and methods

2.1. Leachate and zeolite characterization

Landfill leachate was collected from a municipal landfill in the city of São Carlos, Brazil. This landfill was operated for approximately 15 years, and was recently shut down. Table 1 shows the characterization of the leachate.

Table 2 presents the chemical composition of the Clinoptilolite used for ammonium adsorption. The described Clinoptilolite is a zeolite found in Cuba.

2.2. Batch tests

The batch tests were performed in borosilicate 200 mL bottles filled with 150 mL of leachate and zeolite. Tests were carried out in four phases: i) Three particle size (0.4–1 mm, 1–3 mm and 3–8 mm) of Clinoptilolite were tested in 24 h assays with leachate 25% diluted to choose the best zeolite particle size; ii) Contact time tests using leachate ranging from 25% leachate diluted with tap water to raw leachate; iii) The zeolite concentration test was also tested using raw leachate; and iv) effect of pH on ammonium adsorption of raw leachate dosing 30 g zeo/L (Table 3). Tests of phases ii and iii were used to data fitting using isotherms model as below.

Batch tests to verify the adsorptive capacity of zeolite were performed in triplicate at 150 rpm and at 25° C. No leachate pretreatment was conducted prior to testing and pH was not adjusted, except in the pH test. The zeolite was washed in distilled water and dried out at 100° C during 24 h prior to isotherm adsorption tests.

Table 2
Chemical composition of Clinoptilolite.

Component	%
SiO_2	68.0
Al_2O_3	12.0
Na_2O	2.67
K_2O	1.40
MgO	0.80
CaO	0.98
FeO_3	1.11
TiO_2	0.37
P_2O_5	0.03
Loss of ignition	12.64

Source: Celta Brasil Inc.

2.3. Data fitting

The ammonium removal capacity (q) represents the mass of ammonium removed per mass of zeolite at time t (Eq. (1)) [19,20]. The q values were determined by isotherm curves and experimentally by average capacity in each test as described in Table 3. The experimental data were fitted using the Langmuir model (LM) and the Freundlich model (FM) and the equilibrium curves were obtained (Eqs. (2) and (3), respectively).

$$q_t = \frac{(C_0 - C_t)\cdot V}{W_{zeo}} \quad (1)$$

Where C_0 and C_t are the initial ammonium concentration and after time t (mg NH_4^+-N/L), respectively, V is volume of the solution (L), and W_{zeo} is the mass of the dry zeolite (g).

$$q_e = \frac{q_{max} * K * C_f}{1 + K * C_f} \quad (2)$$

Where q_e is the amount adsorbed, C_f is the equilibrium concentration of adsorbate, q_{max} is the amount of adsorbate per unit mass of zeolite corresponding to complete monolayer coverage, and K is the Langmuir constant related to binding energy.

$$q_e = K_f * C_f^{\frac{1}{n}} \quad (3)$$

Where K_f and 1/n are constants and C_f is the equilibrium concentration of adsorbate.

2.4. Zeolite regeneration by nitrification

At the end of the batch experiments, the zeolite with adsorbed ammonium was subjected to regeneration by nitrification. The regeneration was carried out at 30 °C in triplicate 2 L aerated flasks containing 12 g of zeolite, 1.620 mL of 1 g $NaHCO_3$/L solution (regenerant liquid) and 180 mL of enriched nitrifying biomass suspension (10% v/v). The medium used to enrich nitrifying biomass contained (per L of water): 1 g $NaHCO_3$, 297 mg NH_4Cl, 300 mg $MgSO_4$. $7H_2O$, 180 mg $CaCl_2 \cdot 2H_2O$, 27 mg KH_2PO_4 and 1 mL of metal solution presented in Table 4. The regenerated zeolite was reused in a new adsorption test using raw leachate (30 g zeo/L) and new values of q were obtained. The overview of the experiment is presented in Fig. 1. The dissolved oxygen (DO) was kept between 4.1 and 5 mg/L in the aerated flasks to promote both ammonium and nitrite oxidation without limitation.

2.5. Analytical methods

The concentrations of NH_4^+-N, NO_2^--N and NO_3^--N were measured from filtered samples (0.20 μm) using a Dionex© Ion Chromatograph ICS 5000 [21]. Due to the color of the raw leachate, ammonium nitrogen (NH_4^+-N) determinations in the adsorption