



Research article

Ammonium and potassium removal from swine liquid manure using clinoptilolite, chabazite and faujasite zeolites



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ABSTRACT

This study concerns cationic exchanges performed in order to remove ammonium and potassium cations from manure by using various zeolites: clinoptilolite, chabazite and NaX faujasite. First, the effect of temperature (25 °C and 40 °C) on the exchange rate between zeolites and an ammonium chloride solution was investigated. Then, cationic exchanges were performed on these three zeolites using on one side a mixed ammonium and potassium chloride solution reproducing the chemical composition of a swine manure and on the other side the corresponding liquid manure. No significant difference was observed on the exchange rate and the trapping of ammonium cations by changing the temperature (25 or 40 °C). Clinoptilolite showed a good selectivity towards ammonium cations using model (NH₄Cl, and mixed NH₄Cl/KCl) solutions but is less efficient with the liquid manure. Chabazite and faujasite were found more efficient than clinoptilolite for trapping ammonium cations. However, NaX faujasite enables trapping 3 times more ammonium cations than chabazite from manure (60 and 20 mg/g, respectively). Moreover, chabazite allowed to trap the same amount of potassium cations than NaX faujasite (33 and 35 mg/g, respectively).

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1. Introduction

Liquid manures produced by livestock are rich in nitrogen, phosphorus and potassium (Levasseur, 1998; Tiquia, 2003), which are chemical elements necessary for plant growth. Traditionally, farmers used manure as fertilizer. However, the strong development of farming activity has increased the amount of manure to be spread, so regulation for slurry has been hardened over the years (Burton, 2011). Indeed, the excess fertilizer is not environmentally friendly, as it could cause eutrophication of cultures, then the infiltration of nitrogen and phosphorus compounds can lead to the pollution of underground waters. Several nitrogen removal processes exist such as nitrification/denitrification, ammonia stripping, chemical treatment or ion-exchange (De la Torre-Velasco et al., 2013; Estim and Mustafa, 2014; Jorgensen et al., 1976; Sarioglu, 2005).

Zeolites, which are aluminosilicates with a negatively charged microporous inorganic crystallized framework, compensated by cations located in the porosity, are the most important inorganic

cation exchangers (Rozić et al., 2000). They exhibit a high ion-exchange capacity, a high selectivity and a good compatibility with the environment.

For instance, clinoptilolite (HEU-type structure) is one of the most abundant natural zeolite used throughout the world. Many researchers have investigated ammonium removal from aqueous solutions by clinoptilolite zeolite due to its high trapping capacity and selectivity for this cation (Huang et al., 2010; Ji et al., 2007; Jorgensen et al., 1976; Karadag et al., 2006; Saltali et al., 2007; Vassileva and Voikova, 2009). Moreover, chemical pre-treatments of natural clinoptilolite (e.g. acids, bases, ionic solutions) were developed to improve its ion-exchange capacity (Jha and Hayashi, 2009; Ji et al., 2007; Klieve and Semmens, 1980; Vassileva and Voikova, 2009).

Chabazite (CHA-type structure), another natural zeolite, is very interesting for ion-exchange, due to its higher exchange capacity than clinoptilolite. However, less work has been conducted on the capture of ammonium cations by the chabazite due to its lower selectivity for this cation compared to potassium (Barrer et al., 1969; Lahav and Green, 1998). However, opposite result could also be found in the literature (Torracca et al., 1998), with the following selectivity for the chabazite zeolite NH₄⁺ > K⁺.

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Faujasite (FAU-type structure) is of particular interest for the removal of ions because it displays a large amount of compensation cations (low Si/Al molar ratio) and a three dimensional porous network with a large and accessible pore volume (Baerlocher et al., 2007). Barrer et al. (1956) were the first to highlight the ion exchange properties of faujasite. Thereafter, numerous researchers have investigated the exchange properties of Y zeolites (FAU-type zeolites with Si/Al molar ratio >1.5) and X zeolites (FAU-type zeolites with molar ratio $1 < \text{Si/Al} < 1.5$) (Almeida et al., 2012; Martins et al., 2007; Romero et al., 2005; Sherry, 1966; Theng et al., 1968; Wang et al., 2008; Zheng et al., 2008), and on the exchange mechanism (Jeffroy et al., 2011; Ostroski et al., 2011; Wang and Sun, 2013).

The main goal of this work is to study the cation exchange of ammonium and potassium from a swine liquid manure on zeolites. For this, three different zeolites were used, two natural ones: clinoptilolite and chabazite, and a synthetic one having a high cation-exchange capacity (CEC): NaX faujasite. Exchanges were also performed on model solutions containing only ammonium cations or a mixture of ammonium and potassium cations. The different samples were fully characterized before and after exchange by X-Ray Diffraction (XRD), X-Ray Fluorescence spectrometry (XRF), Atomic Absorption Spectrophotometry (AAS), N_2 physisorption and Thermogravimetric and Differential Thermal Analyses (TGA/DTA).

2. Material and methods

2.1. Zeolite samples

Two natural zeolites, clinoptilolite (named in this study “HEU ZC”) and chabazite (named in this study “CHA S”), were provided by two companies, Zeochem Diffusion and SOMEZ, respectively. The third selected zeolite (zeolite 13X, named “FAU 13X”) was purchased from Fluka. Samples were used without further purification.

2.2. Manure sample

The liquid fraction of manure used for ion exchanges with zeolites was provided by Biowatt company in Bréhan, France. It was collected after an anaerobia digestion process in a digester of a biogas plant.

The composition of the liquid fraction of manure was characterized by the Institute of Ground and Environment of Oldenburg, Germany. After drying, the liquid fraction of manure has a solid content close to 6 wt%, in the form of 4 wt% of organic matter and 2 wt% of mineral matter. The mineral composition (in wt%), performed by inductively coupled plasma optical emission spectrometry (ICP-OES) is the following: 0.36% K_2O ; 0.21% CaO ; 0.09% MgO ; 0.38% P_2O_5 ; 0.05% S; with some traces of copper and zinc. A total nitrogen content of 1 wt% was found by the Kjeldahl method, and flow analysis and spectrometric detection give a rate of 0.77 wt% of ammonium cation.

2.3. Exchange procedures

The experimental exchange equilibrium data were obtained in batch experiments. In all cases, 3 exchange batch experiments were done with a liquid/solid ratio of 20 mL/g. A portion of 40 mL of the exchange solution and a zeolite mass of 2 g were mixed during 15 min at 25 °C or 40 °C in a 50 mL glass beaker. The exchange time (15 min) was determined from a preliminary study and the temperature range (25–40 °C) corresponds to the natural temperature of the swine manure. After that, a Büchner filtration followed by several washings with demineralized water were performed. Three quarters of the retentate were again put in contact with a fresh

30 mL exchange solution during 15 min. After filtration and washing steps, two-thirds of retentate were again mixed with a fresh 20 mL exchange solution during 15 min. Retentates, not engaged in the next steps, were analyzed by X-ray fluorescence spectrometry, and filtrates characterized by atomic absorption spectrophotometry (AAS).

Under similar conditions, exchanges were performed with the three zeolites from a liquid pig manure previously filtered through a 2 microns membrane.

Model solutions were prepared by dissolving NH_4Cl (99.5 wt%, Sigma–Aldrich) and KCl (99 wt%, Prolabo) salts in demineralized water with ion concentration simulating the swine manure composition: an aqueous NH_4Cl solution with an ammonium concentration of 0.77 wt% (0.43 M) (labeled S1 solution) and a mixed $\text{NH}_4\text{Cl}/\text{KCl}$ aqueous solution with ammonium and potassium concentrations of 0.77 wt% (0.43 M) and 0.30 wt% (0.08 M), respectively (labeled S2 solution).

2.4. Characterization methods

X-ray diffraction pattern of the raw zeolites was recorded using a PANalytical MPD X'Pert Pro diffractometer operating with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm) in the 2θ degrees range 3–50 and equipped with an X'Celerator real-time multiple strip detector.

N_2 adsorption/desorption manometry was performed at 77 K on a Micromeritics ASAP 2420 apparatus, after activation of the samples at 350 °C for 15 h under vacuum. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t -plot methods, respectively.

Elemental analysis of the sample was performed by wavelength dispersive X-ray fluorescence spectrometry (XRF) using a PHILIPS MagiX apparatus. For this analysis, the zeolite powder was pelletized under a pressure of 4 tons for 2 min with a hydraulic press.

TG and DTA analyses were performed on a Setaram Labsys TG-DTA thermo analyser with a 10 °C min^{-1} heating rate, between 25 °C and 800 °C, under air.

A Varian A.A 240 FS atomic absorption spectrometer was used to determine the Na, K and Ca concentrations in the permeates. As a radiation source, hollow cathode lamps of Na, K and Ca were used. The corresponding wavelengths and applied electric currents were: $\lambda_{\text{Na}} = 589.6$ nm and $I_{\text{Na}} = 5.0$ mA, $\lambda_{\text{K}} = 766.5$ nm and $I_{\text{K}} = 5.0$ mA, $\lambda_{\text{Ca}} = 422.7$ nm and $I_{\text{Ca}} = 10$ mA. An air-acetylene flame, with flow rates of 13.5 and 2.0 L/min, respectively, is used for the sodium and potassium analyses and a nitrous oxide-acetylene mixture (11.0 and 7.9 L/min, respectively) for the calcium one.

CHN Elemental Analysis were performed by an external laboratory, the Molecular Chemistry Pole of Welience, Dijon, France.

3. Results and discussion

3.1. Zeolite characterization

The HEU ZC zeolite sample used in this study is a clinoptilolite-rich tuff from Beli Plast mine in Bulgaria. The HEU-type structure (monoclinic symmetry) displays a two dimensional channel system with 10 and 8-membered ring (MR) openings running along the [001], [001] and [100] directions and pore apertures close to $3.1 \times 7.5 \text{ \AA}^2$, $4.6 \times 3.6 \text{ \AA}^2$ and $4.7 \times 2.8 \text{ \AA}^2$, respectively (Baerlocher et al., 2007).

According to the powder X-ray diffraction pattern (not reported), the material contains beside clinoptilolite, small amounts of cristobalite and still much lower amounts of muscovite. The following overall chemical composition (wt%): 77.3% SiO_2 ; 12.9% Al_2O_3 ; 0.8 MgO ; 0.6% Na_2O ; 3.6% K_2O ; 3.4% CaO ; 1.4% Fe_2O_3 was determined from XRF analysis. The idealized chemical formula

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