



Simultaneous phosphate and ammonium removal from aqueous solution by a hydrated aluminum oxide modified natural zeolite



Diana Guaya^{a,b,*}, César Valderrama^a, Adriana Farran^a, Chabaco Armijos^b, José Luis Cortina^{a,c}

^a Department of Chemical Engineering, Universitat Politècnica de Catalunya-Barcelona Tech (UPC), Barcelona, Spain

^b Department of Chemistry, Universidad Técnica Particular de Loja, Loja, Ecuador

^c Water Technology Center CETaqua, Barcelona, Spain

HIGHLIGHTS

- Hydrated aluminum oxide modified zeolite was evaluated for the simultaneous phosphate and ammonium removal.
- Maximum adsorption capacities of 7.0 mg-P/g and 30 mg-N/g were obtained for modified zeolite.
- The phosphate and ammonium uptake was well described by Langmuir model.
- The pseudo second order kinetic model provided a good description for the phosphate and ammonium removal.
- The existence of competing ions did not affect the phosphate and ammonium adsorption.

ARTICLE INFO

Article history:

Received 6 January 2015

Received in revised form 1 March 2015

Accepted 2 March 2015

Available online 9 March 2015

Keywords:

Clinoptilolite

Natural zeolite

Modification

Hydrated aluminum oxide

Adsorption

Kinetic

ABSTRACT

A natural zeolite (Z-N), rich in clinoptilolite, was modified (Z-Al) by incorporation of hydrated aluminum oxide (HAIO) for the simultaneous phosphate and ammonium removal. The incorporation of surface hydroxyl groups ($\cong\text{Al-OH}$) into the zeolite structure, as active groups for phosphate removal, was characterized by acid–base titrations ($\text{pH}_{\text{PZC}} = 4.5 \pm 0.2$). The phosphate sorption increases from 0.6 mg-P/g for Z-N up to 7.0 mg-P/g while only a slight decrease on the ammonium sorption capacity from 33 mg-N/g of Z-N to 30 mg-N/g for Z-Al was observed. The HAIO modified zeolite sorption capacity for both phosphate and ammonium was slightly reduced by common ions typically present in secondary waste water effluents. Column experiments revealed higher enrichment factor for ammonium (120) than for phosphate (50) using 1 M NaOH as elution solution. A reduction of zeolite phosphate capacity with regeneration cycles was observed.

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1. Introduction

Nitrogen and phosphorus are essential nutrients for all living forms. However, an excessive growth of algae and the consequently depletion of the dissolved oxygen is an effect of the nutrient overloading (phosphate and ammonium) in natural water bodies [1,2]. Therefore, it has become a great challenge addressed to the simultaneous removal of both species (phosphate and ammonium) to avoid the consequences of eutrophication processes. Natural and synthetic zeolites have been widely studied for ammonium removal due to its high cationic exchange property [1,3,4] and they have been postulated as promissory materials for its removal from waste waters [5–8]. Zeolites and their modified forms have been widely used as effective adsorbents for waste

water treatment according to their mechanical and thermal properties, capability of cation-exchange and significant worldwide occurrence. Additionally, the safety, easy operation and maintenance, low treatment costs, high selectivity and the release of non-toxic exchangeable cations (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) make zeolites an attractive alternative [3,9,10]. Zeolites are hydrated crystalline aluminum-silicate materials with a framework structure where micro- and mesopores located by water and typically alkaline cations [11]. However, they have been rarely used for phosphate sorption due to the constant negative charge on their surface [12]. In order to improve the ion exchange capacity of natural zeolites for anionic species the incorporation or impregnation of iron and aluminum oxides, are the most widespread and excellent candidates for phosphate removal [13–18]. Zeolites exhibit different properties which depend on the geological location and they deserve a detailed characterization [19,20]. This study describes the modification of a Slovakian natural zeolite (clinoptilolite) with Al (III) to enhance the formation of hydrated aluminum oxide

* Corresponding author at: Department of Chemical Engineering, Universitat Politècnica de Catalunya-Barcelona Tech (UPC), Barcelona, Spain.

E-mail address: deguaya@utpl.edu.ec (D. Guaya).

(HAIO) onto the zeolite structure. Utilization of hydrated aluminum oxide in treatment processes cause difficulties in separation due to their small sizes that could be overcome by its impregnation into zeolite porous particles. No previous studies have been found about the hydrated aluminum oxide modification of a natural clinoptilolite for the simultaneous removal of both nutrients. Therefore, the findings of the present work provide insight into the simultaneous phosphate and ammonium sorption potential of hydrated aluminum oxide supported on a clinoptilolite and its regeneration for re-use in sorption and desorption cycles as low cost materials for industrial and domestic waste water treatment applications. The objectives of this study are: (i) synthesize supported hydrated aluminum hydroxide zeolites, (ii) characterize the modified zeolite, (iii) study the influence of pH and ions concentration on zeolites removal capacity, (iv) determine the equilibrium and kinetic sorption parameters, (v) determine the sorption selectivity in front of common ions in waste waters effluents and, (vi) evaluate their performance (sorption and desorption) on column experiments.

2. Materials and methods

2.1. Impregnation of hydrated aluminum oxide onto a natural zeolite

A natural zeolite (Z-N) obtained from Zeocem Company, Slovakian Republic was used. Samples were washed with deionized water and dried in an oven at 80 °C for 24 h. Particles below 200 µm mesh were used for batch experiments and particles between 800 and 1200 µm mesh were used for column experiments. Z-N was modified to the aluminum form by using an adaptation of the method reported by Jiménez-Cedillo et al. [14]. Thirty grams of natural zeolite were treated with 250 mL of NaCl (0.1 M) two consecutive times under reflux conditions for 4 h. Then, the zeolite in the sodium form (Z-Na) was washed with ~1500 mL of deionized water until no chloride was detected by the AgNO₃ test. Thirty grams of sodium zeolite (Z-Na) were treated two consecutive times with 250 mL of AlCl₃ (0.1 M) under reflux for 4 h. The aluminum zeolite (Z-Al) was washed using ~1500 mL of deionized water until no chloride was detected by the AgNO₃ test. Finally, it was dried in an oven at 80 °C for 24 h.

2.2. Physicochemical characterization of the zeolites

Z-N, Z-Na and Z-Al were characterized by X-ray diffraction (XRD) using a powder X-ray Diffractometer (D8 Advance A25 Bruker). Samples morphology and chemical composition were analyzed by a Field Emission Scanning Electron Microscope (FSEM) (JEOL JSM-7001F) coupled to an Energy Dispersive Spectroscopy system (Oxford Instruments X-Max). Samples composition reported are the average of at least four analyses for each sample. Infrared absorption spectra were recorded with a Fourier Transform FTIR 4100 Jasco spectrometer in the range of 4000–550 cm⁻¹ range. The specific surface area of Z-N and Z-Al was determined by the nitrogen gas sorption method on an automatic sorption analyzer (Micrometrics). The essays were replicated four times for each sample and the average data are reported. The point of zero charge (PZC) of Z-N and Z-Al was determined by the pH drift method [21,22]. An amount 0.1 g of zeolite was equilibrated in 25 mL of deionized water and 0.01 and 0.05 M NaCl solutions (pH from 2 to 11) for 24 h at 200 rpm and 21 ± 1 °C. The final pH was measured in a Crison GLP21 potentiometer, and the PZC was determined as the pH at which the addition of the sample did not induce a shift in the pH ($\Delta\text{pH} = \text{pH}_f - \text{pH}_i = 0$). The CIP method, common intersection point of potentiometric titration curves obtained at three ionic strengths was also used [23–25]. An

amount of 0.1 g of zeolite was equilibrated with 25 mL of solution at three different ionic strengths (0.01, 0.05 and 0.1 M NaCl) during 24 h at 200 rpm and 21 ± 1 °C. After the equilibration the suspension was basified to pH 11 using 0.1 M NaOH. The suspension was titrated until pH ≈ 3, with 0.01 M HCl using an automatic titrator (Mettler Toledo). The net surface charge is correlated with PZC from the titration data for the adsorbed amounts of [H⁺] and [OH⁻] ions. Therefore, titration curves of different ionic strength would intersect at pH = pH_{PZC}. The surface charge was calculated from the Eq. (1) [26].

$$b = C_b - C_a + [\text{H}^+] - [\text{OH}^-] \quad (1)$$

where b (mol/g) is the net hydroxide ions consumed, C_b and C_a (mol/L) are the base and acid concentrations, respectively and [H⁺] and [OH⁻] denote the protons and hydroxide concentration calculated from the measured solution pH for a given mass of zeolite (g) and a given volume of volume of solution (L). All measurements were performed in triplicate and the average value was reported.

2.3. Equilibrium and kinetic batch sorption studies

Batch equilibrium sorption experiments were carried out using standard batch methodology described elsewhere [8]. Given volumes (25 mL) of phosphate (P) and ammonium (N) aqueous solutions were shaken overnight with weighed amounts of dry samples (particle size < 200 µm) in polyethylene tubes using a continuous rotary mixer. Three different types of experiments were conducted:

- (i) Sorption capacity as function of phosphate and ammonium concentration: 0.25 g of Z-N and Z-Al samples were added to solutions in the concentration range: 1–2000 mg-P/L and 10–5000 mg-N/L, without pH adjustment.
- (ii) Sorption capacity as function of equilibrium pH: 0.1 g of Z-Al sample was equilibrated in solutions containing 25 mg-P/L and 25 mg-N/L. The pH was adjusted from 2 to 11 (using 0.1 M HCl/NaOH).
- (iii) Sorption capacity as function of phosphate and ammonium concentration in the presence of individual and mixtures of common competing ions present on waste water effluents: 0.1 g of Z-Al sample is added to 25 mg-P/L, 25 mg-N/L and individual competing ion (25 mg/L) solutions without pH adjustment. Also, the interference ions concentrations were fixed taking as reference the average annual composition of the stream from a tertiary treatment including a reverse osmosis step at the El Prat waste water treatment plant (Barcelona – Spain). The anions solution composition was: chloride (625 mg/L), bicarbonate (325 mg/L), sulfate (200 mg/L) and nitrate (30 mg/L) (prepared from the corresponding sodium salts). The cations solution composition was: sodium (260 mg/L), calcium (160 mg/L), magnesium (50 mg/L) and potassium (40 mg/L) (prepared from corresponding chloride salts). Then, 0.25 g of Z-Al sample was equilibrated in solutions ranging 1–2000 mg-P/L and 10–5000 mg-N/L and the mixture of competing ions.
- (iv) Batch kinetic sorption experiments were performed by addition of 0.1 g of Z-Al in solution containing 20 mg-N/L and 10 mg-P/L. Tubes were withdrawn sequentially at given times. All tests were performed by triplicate at 200 rpm and room temperature (21 ± 1 °C) and the average data are reported. Before to be analyzed samples were centrifuged for 10 min and filtered using cellulose nitrate membrane filters (45 µm). The total concentrations of phosphate and ammonium ions in the initial and remaining aqueous solution were determined.

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