



# Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite



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## ABSTRACT

Nutrients discharge correlates to eutrophication of receiving waters. Phosphorus (P) and nitrogen (N), if recovered from wastewaters, can be applied to land as essential nutrients for plant growth. This study used natural zeolite in batch and continuous tests to simultaneously remove P and N from orthophosphate and ammonium-nitrogen laden wastewaters at pH 3–11. In P only tests, pH > 9 is favorable to P removal. When ammonium was also present, P removal was significantly enhanced. Ammonium was first adsorbed onto the zeolite via ion exchange to release Ca<sup>2+</sup> ions from the zeolite lattice. This ion exchange reaction was independent of the presence of P. Then the released Ca<sup>2+</sup> ions precipitated the dissolved phosphate, which was greatly dependent on the concentration of ammonium. Zeolite column could effectively remove P and N from fermentation liquor with minimal adsorption of volatile fatty acids. Implications to practice of zeolite treatment were discussed.

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## 1. Introduction

Excess discharge of nitrogen (N) and phosphorus (P) to receiving waters yields occurrence of water body eutrophication [1]. Biological nutrient removal (BNR) process is effective to remove nitrogen and phosphorus [2], but it requires expensive supplemented carbon source [3]. Volatile fatty acids (VFAs) produced by anaerobic fermentation of organic wastes are suitable carbon sources for the BNR process [4]. However, the accompanied high levels of nitrogen (NH<sub>4</sub><sup>+</sup>-N > 400 mg l<sup>-1</sup>) and phosphorus (PO<sub>4</sub><sup>-</sup>-P > 100 mg l<sup>-1</sup>) in the fermentation liquor have to be effectively removed [5–7]. Cost-effective and simple practice with end products recyclable to land use is welcome to remove N and P in fermentation effluents [8].

Zeolite is an aluminosilicate mineral that can be used as ammonium adsorbent at the release of Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup> and/or Mg<sup>2+</sup> from the crystal framework [9–15]. For instance, Lin et al. [16] noted the release of Ca<sup>2+</sup> ions from their zeolite during ammonium adsorption. Zeolite was also applied for phosphorus removal based on the mechanisms of anion exchange and electrostatic attraction [17–19]. Few studies focused on simultaneous removal of N and

P by zeolite [20]. Karapınar [21] applied the natural zeolite and dosed calcium ions to remove N and P in separated processes.

This study for the first time applied natural zeolite only to simultaneously remove orthophosphate and ammonium-nitrogen from high-strength synthetic wastewater and fermentation effluent. Batch and column tests were adopted to confirm the feasibility of using natural zeolite as a pretreatment unit for making fermentation liquor applicable to subsequent processes such as the BNR process. Experimental conditions with sufficient N and P removals were identified. Based on experimental findings, the mechanisms of phosphorus removal by zeolite with the assistance of ammonium were disclosed.

## 2. Materials and methods

### 2.1. Materials

The zeolite used in this study was obtained from Shenshi Mine located in Jinyun, Zhejiang Province, China without modification. After crushing, size sieving to 0.8–1.43 mm, washing with deionized water and air-drying at 105 ± 1 °C for 12 h, the prepared zeolite was used in the experiments. The chemical and physical characteristics of the zeolite were reported in Lin et al. [16]. In brief, the natural zeolite has main mineral species of clinoptilolite-Na, heulandite and quartz, with surface area of 14.33 m<sup>2</sup> g<sup>-1</sup> and an ion exchange capacity (IEC) of 0.92 meq g<sup>-1</sup>.

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The feed solutions (N–P mixtures) were prepared by mixing and diluting  $4000 \text{ mg-N l}^{-1}$  of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and  $1000 \text{ mg-P l}^{-1}$  of sodium di-hydrogen phosphate ( $\text{NaH}_2\text{PO}_4$ ) stock solutions at prescribed ratio. The pH of feed solution was adjusted by adding  $0.5 \text{ M}$  of sodium hydroxide ( $\text{NaOH}$ ) or hydrochloric acid ( $\text{HCl}$ ). All chemicals were of analytical grade. Wastewater was collected from the effluent of the laboratory fermentation reactor of swine manure at pH 9.3 and  $35^\circ\text{C}$ . The fermentation effluent had 1.11% of total solids (TS),  $63.1 \text{ mg l}^{-1}$  of orthophosphate phosphorus ( $\text{PO}_4\text{-P}$ ),  $1252 \text{ mg l}^{-1}$  of ammonium nitrogen ( $\text{NH}_4\text{-N}$ ),  $5470 \text{ mg l}^{-1}$  of volatile fatty acids (VFAs) and  $2804 \text{ mg-CaCO}_3 \text{ l}^{-1}$  of total alkalinity.

## 2.2. Batch experiments

The batch experiments in 250 ml conical flasks were conducted to consider the effects of pH, ammonium and phosphate concentrations on adsorption/removal performances. The flasks with 100 ml solution and 10 g natural zeolite were capped and shaken horizontally at 150 rpm and  $25^\circ\text{C}$  for 24 h in a thermostatic shaker (HZQ-X3000, China). Table S1 lists the experimental conditions. The suspension was filtered via  $0.45 \mu\text{m}$  filter and the filtrate was analyzed. After tests, the zeolites and precipitate at the flask bottom were collected and washed by deionized water and then freeze-dried (SCIENTZ-12N, China) for 24 h. All the above procedures were repeated at least in triplicates with the mean values being reported.

## 2.3. Column experiments

The fixed-bed column experiments were carried out in vertical upflow columns (made of Plexiglas) with 1 m height and 60 mm internal diameter at room temperature ( $20 \pm 1^\circ\text{C}$ ). The column was filled with 300 g of the natural zeolite at 23 cm depth. The influent with desired pH were pumped into the column bottom using the metering pump (MasterFlex L/S, Cole Parmer, USA) at a constant flow rate of  $10 \text{ ml min}^{-1}$ , giving 20 min of contact time. Table S1 lists the other experimental conditions. Effluent from the column was collected and filtered via  $0.45 \mu\text{m}$  filter for analysis.

## 2.4. Analytical methods

Determination of TS,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  and total alkalinity (titrated to pH 4.3) in filtrate were in accordance with the Standard Methods [22]. pH of suspension was measured using a pH meter (Multi 340i-WTW, Germany). Concentrations of  $\text{Ca}^{2+}$  and  $\text{K}^+$  were measured using atomic absorption spectroscopy (Hitachi-Z 5000, Japan). The concentrations of VFAs ( $\text{C}_2$  to  $\text{C}_5$ ) were determined using a gas chromatography (7890A, Agilent, USA) fitted with HP-FFAP ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm}$ ) capillary column and FID detection. The surface morphology and chemical compositions of zeolite and collected precipitates were analyzed by the same methods used in Lin et al. [16].

The removal performance was evaluated by the amount of ammonium or phosphate removed by per unit mass of zeolite, which could be calculated according to  $q = V(C_0 - C_e)/M$ , where  $q$  is the removal capacity ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of nitrogen or phosphorus ( $\text{mg l}^{-1}$ ), respectively,  $V$  is the feed solution volume (l) and  $M$  is the mass of zeolite used (g).

## 3. Results

### 3.1. Batch tests

In P-only tests,  $100 \text{ mg-P l}^{-1}$  was effectively removed at pH 8–11, reaching 60.2% removal ( $0.607 \text{ mg g}^{-1}$ ) at pH 11 (Fig. 1).

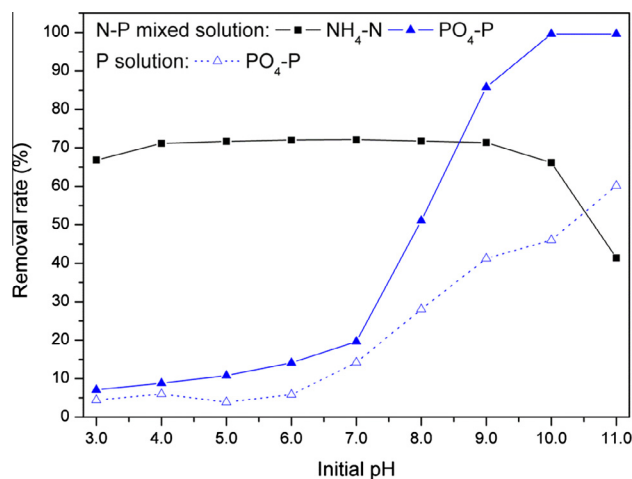


Fig. 1. Effects of pH on ammonium and phosphate removal rates by the natural zeolite in P-only and N–P mix, respectively.

Conversely, P removal at pH < 7 was low. Similar or contradictory results about the pH-dependent phosphorus removal by zeolites were listed in Table 1. Different chemical compositions of zeolites may be responsible to the noted difference in pH dependence. In N–P mixtures, the ammonium adsorption capacity onto the tested zeolite used was declined with increasing pH at alkaline condition, especially at pH > 9. This observation correlates with the findings by Lin et al. [16]. The P removal was improved in the presence of ammonium, particularly significant at pH 9–11 (Fig. 1). Restated, the P removal rate at pH 9, 10 and 11 was increased from 41.2%, 46.0% and 60.2% to 85.8%, 99.7% and 100%, respectively in the presence of  $1000 \text{ mg l}^{-1}$  ammonium. White precipitates were noted to form during the test. Hence, as Fig. 1 shows, pH > 9.0 had adverse effects on ammonium removal but enhanced phosphate removal. At pH 9.3, high removals of both P and N were achieved.

Further tests at pH 9.3 were conducted with  $100 \text{ mg-P l}^{-1}$  and  $0\text{--}2000 \text{ mg-N l}^{-1}$  or  $1000 \text{ mg-N l}^{-1}$  and  $0\text{--}1000 \text{ mg-P l}^{-1}$  (Fig. 2). With initial  $100 \text{ mg-P l}^{-1}$ , the P removal was increased from 43.8% to 98.9% as N was increased to  $200 \text{ mg l}^{-1}$  (Fig. 2a). With up to  $200 \text{ mg-N l}^{-1}$ , all dosed ammonium was removed by the zeolite. As the N concentration was further increased, the P removal rate was remained at around 100%, but the N removal rate was declined, reaching 48% at  $2000 \text{ mg-N l}^{-1}$  (Fig. 2a). With  $1000 \text{ mg-N l}^{-1}$ , the removal of dosed  $20\text{--}400 \text{ mg-P l}^{-1}$  was complete; however, the P removal rate declined at  $>600 \text{ mg-P l}^{-1}$  (Fig. 2b). The P removal was 54.2% when using the mixture of  $1000 \text{ mg-N l}^{-1} + 1000 \text{ mg-P l}^{-1}$  (Fig. 2b). In all the tests in Fig. 2b, the N removal rate was kept around 70% regardless of the P concentration.

As noted in the above tests, the tested zeolite removed limited quantities of dosed P, reaching  $0.607 \text{ mg g}^{-1}$  at pH 11. At pH 9.3, the N removal depended only on N concentration rather than on P concentration. The adsorption isotherm at  $25^\circ\text{C}$  resembled a Langmuir curve with an abrupt increase in adsorption quantity at low N concentration regime (Fig. S1). Conversely, the P removal was significantly affected by the N concentration.

Ammonium removal by zeolite was proposed as monolayer molecular adsorption with zeolite [13,23]. Rate-limiting step for P removal with zeolite was claimed as the electron exchange between phosphorus and the zeolite surface [19]. In the N–P mixture both ammonium and phosphate were mostly removed in 3 h. (Fig. 3a). Both kinetic data of N and P removals well fitted the intraparticle diffusion model with three-linear regions (Fig. 3b) [4,24] using

$$q_t = k_d t^{1/2} + C \quad (1)$$

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