- Ammonium assists orthophosphate removal from high-strength wastewaters by natural zeolite
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   (D.-J. Lee).
- 13
- 14 Abstract

Nutrients discharge correlates to eutrophication of receiving waters. Phosphorus (P) and nitrogen 15 (N), if recovered from wastewaters, can be applied to land as essential nutrients for plant growth. 16 This study used natural zeolite in batch and continuous tests to simultaneously remove P and N from 17 orthophosphate and ammonium-nitrogen laden wastewaters at pH 3-11.In P only tests, pH>9 is 18 favorable to P removal. When ammonium was also present, P removal was significantly enhanced. 19 Ammonium was first adsorbed onto the zeolite via ion exchange to release  $Ca^{2+}$  ions from the zeolite 20 lattice. This ion exchange reaction was independent of the presence of P. Then the released  $Ca^{2+}$  ions 21 precipitated the dissolved phosphate, which was greatly dependent on the concentration of 22 ammonium. Zeolite column could effectively remove P and N from fermentation liquor with minimal 23 adsorption of volatile fatty acids. Implications to practice of zeolite treatment were discussed. 24

25 Keywords Ammonium; Phosphate; Simultaneous removal; Mechanism; Natural zeolite;
26 Fermentation liquor

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#### 28 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.

11 This study for the first time applied natural zeolite only to simultaneously remove 12 orthophosphate and ammonium-nitrogen from high-strength synthetic wastewater and fermentation 13 effluent. Batch and column tests were adopted to confirm the feasibility of using natural zeolite as a 14 pretreatment unit for making fermentation liquor applicable to subsequent processes such as the 15 BNR process. Experimental conditions with sufficient N and P removals were identified. Based on 16 experimental findings, the mechanisms of phosphorus removal by zeolite with the assistance of 17 ammonium were disclosed.

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# 19 2. Materials and methods

#### 20 **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 12h, 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 1 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>.

The feed solutions (N-P mixtures) were prepared by mixing and diluting 4000 mg-N l<sup>-1</sup> of 2 ammonium chloride (NH<sub>4</sub>Cl) and 1000 mg-P  $l^{-1}$  of sodium di-hydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) stock 3 solutions at prescribed ratio. The pH of feed solution was adjusted by adding 0.5 M of sodium 4 hydroxide (NaOH) or hydrochloric acid (HCl). All chemicals were of analytical grade. Wastewater 5 was collected from the effluent of the laboratory fermentation reactor of swine manure at pH 9.3 and 6 35 °C. The fermentation effluent had 1.11% of total solids (TS), 63.1 mg  $l^{-1}$  of orthophosphate 7 phosphorus (PO<sub>4</sub><sup>-</sup>-P), 1252 mg l<sup>-1</sup> of ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N), 5470 mg l<sup>-1</sup> of volatile fatty 8 acids (VFAs) and 2804 mg-CaCO<sub>3</sub> l<sup>-1</sup> of total alkalinity. 9

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# 11 2.2. Batch experiments

The batch experiments in 250 ml conical flasks were conducted to consider the effects of pH, 12 ammonium and phosphate concentrations on adsorption/removal performances. The flasks with 100 13 ml solution and 10 g natural zeolite were capped and shaken horizontally at 150 rpm and 25 °C for 14 24 h in a thermostatic shaker (HZQ-X3000, China). Table S1 lists the experimental conditions. The 15 suspension was filtered via 0.45 µm filter and the filtrate was analyzed. After tests, the zeolites and 16 precipitate at the flask bottom were collected and washed by deionized water and then freeze-dried 17 (SCIENTZ-12N, China) for 24h. All the above procedures were repeated at least in triplicates with 18 the mean values being reported. 19

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# 21 **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 ( $20\pm1$  °C). The column was filled with 300g 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 10mlmin<sup>-1</sup>, giving 20 min of contact time. Table S1 lists the other experimental
 conditions. Effluent from the column was collected and filtered via 0.45 μm filter for analysis.

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#### 4 2.4. Analytical methods

Determination of TS, NH<sub>4</sub>-N, PO<sub>4</sub>-P and total alkalinity (titrated to pH 4.3) in filtrate were in 5 accordance with the Standard Methods [22]. pH of suspension was measured using a pH meter 6 (Multi 340i-WTW, Germany). Concentrations of Ca<sup>2+</sup> and K<sup>+</sup> were measured using atomic 7 absorption spectroscopy (Hitachi-Z 5000, Japan). The concentrations of VFAs (C<sub>2</sub> to C<sub>5</sub>) were 8 determined using a gas chromatography (7890A, Agilent, USA) fitted with HP-FFAP (30 m×0.25 9 mm×0.25 mm) capillary column and FID detection. The surface morphology and chemical 10 compositions of zeolite and collected precipitates were analyzed by the same methods used in Lin et 11 al. [16]. 12

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 (mg g<sup>-1</sup>),  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of nitrogen or phosphorus (mg l<sup>-1</sup>), respectively, V is the feed solution volume (l) and M is the mass of zeolite used (g).

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# 19 **3. Results**

# 20 **3.1. Batch tests**

In P-only tests, 100 mg-P l<sup>-1</sup> was effectively removed at pH 8–11, reaching 60.2% removal (0.607 mg g<sup>-1</sup>) at pH 11 (**Fig. 1**). 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 mgl<sup>-1</sup> 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 mg-P  $l^{-1}$  and 0–2000 mg-N  $l^{-1}$  or 1000 mg-N  $l^{-1}$ 8 and  $0-1000 \text{ mg-P l}^{-1}$  (Fig. 2). With initial 100 mg-P l<sup>-1</sup>, the P removal was increased from 43.8% to 9 98.9% as N was increased to 200 mg  $l^{-1}$  (**Fig. 2a**). With up to 200 mg-N  $l^{-1}$ , all dosed ammonium was 10 removed by the zeolite. As the N concentration was further increased, the P removal rate was 11 remained at around 100%, but the N removal rate was declined, reaching 48% at 2000 mg-N l<sup>-1</sup> (Fig. 12 **2a**).With 1000 mg-N  $l^{-1}$ , the removal of dosed 20–400 mg-P  $l^{-1}$  was complete; however, the P 13 removal rate declined at >600 mg-P  $l^{-1}$  (Fig. 2b). The P removal was 54.2% when using the mixture 14 of 1000 mg-N  $l^{-1}$  + 1000 mg-P  $l^{-1}$  (Fig. 2b). In all the tests in Fig. 2b, the N removal rate was kept 15 around 70% regardless of the P concentration. 16

As noted in the above tests, the tested zeolite removed limited quantities of dosed P, reaching 0.607 mg g<sup>-1</sup> 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 °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 hr. (**Fig 3(a)**). Both kinetic data of N and P removals well fitted the 1 intra-particle diffusion model with three-linear regions (Fig. 3(b)) [4,24] using

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

where  $k_d$  is the coefficient of intra-particle diffusion (mg g<sup>-1</sup>·min<sup>-1/2</sup>). Multi-linear plots indicated that 3 three steps took place in N and P removal processes: firstly,  $NH_4^+$  and  $PO_4^{3-}$  diffused from the 4 solution to the external surface of adsorbent; the second step was gradual adsorption stage on the 5 6 external and internal surface of zeolite, which was followed by the final equilibrium stage. The 7 best-fit results were given in **Table 2**. The  $k_{d2}$  and  $k_{d3}$  values for P were both much lower than those for N, suggesting that adsorption phase of P was very poor in the present zeolite [24], and  $PO_4^{3-}$ 8 removal occurred most probably in the external boundary layer film of liquor surrounding the zeolite 9 particles. 10

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#### 12 **3.2.** Column tests

The zeolite column was used to treat the synthetic wastewater with 1163 mg-N  $1^{-1}$  and 70 mg-P 14  $1^{-1}$  at pH 9.30. At the initial 80 min, both N and P were completely removed. Breakthrough occurred 15 at 100 min. Effluent N concentration reached 50% of the influent at 160 min, while the P 16 concentration was increased slowly, reaching 20 mg-P  $1^{-1}$  at 360 min (**Fig. 4a**). Since the contact time 17 was only 20 min, a worse performance for continuous tests was expected compared with the batch 18 tests lasting for 24 h.

The result by using the zeolite column to treat real wastewater at 20 min of contact time was shown in **Fig. 4b**. With feeding solution of 63.1 mg-P  $\Gamma^1$ , 1252 mg-N  $\Gamma^1$ , 2000 mg-CaCO<sub>3</sub>  $\Gamma^1$ , and 5470 mg-VFA  $\Gamma^1$ , in the first 60 min of column test, all N and >90% of P were removed with unchanged VFA and TA levels. Breakthrough of N and P occurred since 80 min. Meanwhile, the TA level was gradually increased. At 360 min, the TA in effluent was increased from 2000 mg to 2800 mg  $\Gamma^1$ . The tested zeolite had no adsorption on the VFAs in the suspensions.

#### 1 **4.** Discussion

#### 2 4.1. Removal mechanisms

Soluble inorganic P can be present in four different chemical forms:  $H_3PO_4$  at pH<2;  $H_2PO_4^-$  at PH 3-6.5;  $HPO_4^{2-}$  at pH 7.5-12;  $PO_4^{3-}$  at pH>12 [25]. As listed in **Table 1**, different zeolites can have very different P removal capacities, likely due to distinct dominant mechanisms. The increased removal rates of P at high pH in **Fig. 1** suggested that neither anion exchange nor electrostatic attraction control the present P removal since excess OH<sup>-</sup> at pH 11 did not compete with  $HPO_4^{2-}$  from adsorption sites [26].

9 The SEM images revealed that after wastewater treatment the surface of zeolite was converted from flat and smooth to irregular and rough, with precipitate forming on the surface (Figs. S2 in the 10 Supplementary Materials). The EDS results revealed that the precipitate had a composition of O 11 (55.8%), Ca (25.5%), P (15.3%), Mg (2.73%), Na (0.67%) and K (0.02%), indicating the precipitate 12 is calcium phosphate precipitate, correlating with the chemical precipitation works reported by Kãv 13 et al.[27]. Based on the previous EDS analysis [16], Ca is the secondary primary cation component 14 (next to Al) in the crystal framework of natural zeolite amounting for 2.09% of total atoms weight, 15 which could be replaced by Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> in the solution easily [12,28]. Just as shown in Table 3, at 16 initial pH 4.0 condition the co-presence of ammonium promoted 530.7 mg  $l^{-1}$  of more Ca<sup>2+</sup> to release, 17 while at initial pH 9.0 condition, concentrations of both  $Ca^{2+}$  and  $PO_4^{3-}$  decreased significantly. That 18 was probably because at alkaline condition,  $Ca^{2+}$ , OH<sup>-</sup> and PO<sub>4</sub><sup>3-</sup> (in the form of HPO<sub>4</sub><sup>2-</sup>) could react 19 chemically to form hydroxyapatite (HAP) which has the highest thermodynamic stability among 20 various calcium phosphate precipitates [29]. The following mechanisms were supposed to occur in 21 the present N-P-zeolite system: 22

23 Zeolite-Ca<sup>2+</sup> + 2Na<sup>+</sup> 
$$\rightarrow$$
 Ze-2Na<sup>+</sup> + Ca<sup>2+</sup> (2)

24 Zeolite-Ca<sup>2</sup> + 2NH<sub>4</sub><sup>+</sup> 
$$\rightarrow$$
 Ze-2NH<sub>4</sub><sup>+</sup> + Ca<sup>2+</sup> (3)

$$25 \qquad 5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5OH(PO_4)_3 \downarrow + 3H_2O \tag{4}$$

Restated, the Ca<sup>2+</sup> on zeolite was exchanged with sodium and ammonium ions in the studied system. Reactions (2) and (3) are independent of the concentration of phosphorus (**Fig. 2b**). Phosphorus was removed by precipitation with the freed Ca<sup>2+</sup>. In the P-only tests, limited quantities of Ca<sup>2+</sup> were released by the Na<sup>+</sup>, so limited quantities of phosphorus was removed (**Fig. 2a**). The reaction eq. (4) can occur at pH>7, and will be at favorable rate only at pH>9 [30], which interprets that the excess removal of P at pH>9 (**Fig. 2**) is a kinetics-controlled rather than a thermodynamics-controlled process.

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# 9 4.2. Implications to practice

10 Comparing the results from column tests with synthetic wastewater and fermentation effluent, 11 the studied zeolite removed 15.6% and 39.4% less ammonium and phosphate, respectively. This 12 occurrence should be attributable to the role of competing ions on adsorption sites for N removal and 13 on precipitation species for P removal.

Based on the stoichiometric relationship in Eqs. (3) and (4), to remove 1 mole of P needs 3.3 14 moles of N. At pH 9.3 about 700 mg l<sup>-1</sup> of ammonium ion (=50 mmol l<sup>-1</sup>) were removed by 10 g of 15 the studied zeolite (Fig. 2a), while the  $Ca^{2+}$  concentrations in the suspensions were noted at 462 mg 16  $1^{-1}$ . Hence, at pH 9.3 if assuming 25 mmol  $1^{-1}$  of Ca<sup>2+</sup> was released accompanied with the adsorption 17 of 50 mmol  $l^{-1}$  ammonium ions, considering the corresponding removal of P to be 78.1mg  $l^{-1}$ (=2.52 18 mmol  $l^{-1}$ ), yielding a molar ratio of (NH<sub>4</sub><sup>+</sup> assumption)/(P removal)=(20/1), about six times to that by 19 stoichiometry (3/3/1). The Ca<sup>2+</sup> ions can form precipitates with carbonate and other anions, which 20 account for the excess ammonium adsorption noted in these tests. 21

As  $K^+$  is preferred than  $NH_4^+$  in ion exchange for natural zeolite[31], the 797 mg l<sup>-1</sup> of K in the fermentation liquor should significantly inhibit ammonium adsorption by zeolite. On the other hand, alkalinity was produced in fermentation [32], with the formed  $CO_3^{2-}$  being a strong competitor to phosphate for precipitation[30].Therefore, the N+P wastewaters with few competing cations such as 1  $K^+$  or Na<sup>+</sup> for ion exchange reaction and competing anions such as CO<sub>3</sub><sup>2-</sup> for precipitation reaction 2 can reach simultaneous N and P removal by zeolite treatment. When N+P feed has high levels of K<sup>+</sup> 3 or Na<sup>+</sup>, high P removal should be achieved with poor N removal performance. With N+P feed of 4 high levels of CO<sub>3</sub><sup>2-</sup>, P removal would be suppressed. Manipulation of the removal performances of 5 N, P and other ions can be easily made by adjusting the dose amount of zeolite.

6 The studied zeolite did not adsorb VFA, so the produced effluent with low concentrations of N 7 and P can be utilized as supplemented carbon sources for BNR treatment process [5,33]. The 8 adsorbed zeolite and precipitate are enriched in N and P hence can be used as agricultural fertilizers. 9 The zeolite treatment is environmental friendly and cost effective for simultaneous removal of N and 10 P from wastewaters.

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#### 12 **5.** Conclusions

This study applied natural zeolite for simultaneous removal of P and N from wastewaters. At pH 9.3, recoveries of P and N were high. A two-step mechanism was proposed to interpret the experimental data: ammonium was adsorbed to zeolite by releasing  $Ca^{2+}$  ion to solution, then the released  $Ca^{2+}$  ions formed precipitate with phosphate for removal. To reach high levels of simultaneous removal of P and N, an N/P ratio >3.3 was proposed as the criterion. Fermentation liquor after zeolite treatment can provide carbon sources to BNR process and the used zeolite can be used as green fertilizer.

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#### 21 **REFERNECES**

- [1] Q.W. Min, Y.L. Jiao. Effects of agricultural non-point source pollution on eutrophication of
   water body and its control measure. *Acta Ecologica Sinica*, 3 (2002) 001.
- [2] A. Hedström. Ion exchange of ammonium in zeolites: a literature review. *Journal of Environmental Engineering*, 127 (2001) 673–681.

- [3] D. Karadag, Y. Koc, M. Turan, B. Armagan. Removal of ammonium ion from aqueous solution
   using natural Turkish clinoptilolite. *Journal of Hazardous Materials*, 136 (2006) 604–609.
- [4] R. Moser-Engeler, K.M. Udert, D. Wild, H. Siegrist. Products from primary sludge fermentation
  and their suitability for nutrient removal. *Water Science and Technology*, 38 (1998) 265–273.
- 5 [5]Y. Chen, S. Jiang, H. Yuan, Q. Zhou, G. Gu. Hydrolysis and acidification of waste activated
  6 sludge at different pHs. *Water Research*, 41 (2007) 683–689.
- [6] X.R. Kang, G.M. Zhang, L. Chen, W.Y. Dong, W.D. Tian. Effect of Initial pH adjustment on
   hydrolysis and acidification of sludge by ultrasonic pretreatment. *Industrial & Engineering Chemistry Research*, 50 (2011) 12372–12378.
- [7] L. Lin, C. Wan, X. Liu, D.J. Lee, Z. Lei, Y. Zhang, J.H. Tay. Effect of initial pH on mesophilic
   hydrolysis and acidification of swine manure. *Bioresource Technology*, 136 (2013) 302–308.
- [8] A. Terada, K. Hibiya, J. Nagai, S. Tsuneda, A. Hirata. Nitrogen removal characteristics and
   biofilm analysis of a membrane-aerated biofilm reactor applicable to high-strength nitrogenous
   wastewater treatment. *Journal of Bioscience and Bioengineering*, 95 (2003) 170–178.
- 15 [9] G.V. Tsitsishvili, T.G. Andronikashvili, G.N. Kirov, L.D. Filizova. Natural zeolites. Ellis
  16 Horwood New York, 1992.
- [10] J.W. Choe, J.H. Kim, T.H. Chung. Effect of competing cation on ammonium ion exchange:
   Characteristics of zeolite in a bi-solute system. *Journal of Environmental Science and Health Part A- Toxic/Hazardous Substances & Environmental Engineering*, 34 (1999) 1553–1567.
- [11] H.M. Huang, X.M. Xiao, B. Yan, L.P. Yang. Ammonium removal from aqueous solutions by
   using natural Chinese (Chende) zeolite as adsorbent. *Journal of Hazardous Materials*, 175
   (2010) 247–252.
- [12] V.J. Inglezakis. The concept of "capacity" in zeolite ion-exchange systems. *Journal of Colloid and Interface Science*, 281 (2005) 68–79.
- 25 [13] M. Sprynskyy, M. Lebedynets, R. Zbytniewski, J. Namiesnik, B. Buszewski. Ammonium

1	removal from aqueous solution by natural zeolite, Transcarpathian mordenite, kinetics,
2	equilibrium and column tests. Separation and Purification Technology, 46 (2005) 155–160.
3	[14] Y.F. Wang, F. Lin, W.Q. Pang. Ammonium exchange in aqueous solution using Chinese natural
4	clinoptilolite and modified zeolite. Journal of Hazardous Materials, 142 (2007) 160-164.
5	[15] G. Markou, D. Vandamme, K. Muylaert. Using natural zeolite for ammonia adsorption from
6	wastewater and as nitrogen releaser for the cultivation of Arthrospira platensis. Bioresource
7	Technology, 155 (2014)373–378.
8	[16] L. Lin, Z. Lei, L.Wang, X. Liu, Y. Zhang, C. Wan, DJ. Lee, J.H. Tay. Adsorption mechanisms
9	of high-levels of ammonium onto natural and NaCl-modified zeolites. Separation and
10	Purification Technology, 103 (2013) 15–20.
11	[17] T.H. Dao. Competitive anion sorption effects on dairy wastewater dissolved phosphorus
12	extraction with zeolite-based sorbents. Journal of Food Agriculture and Environment, 1 (2003)
13	263–269.
14	[18] N.S. Dionisiou, T. Matsi, N.D. Misopolinos. Phosphorus Adsorption-Desorption on a
15	Surfactant-Modified Natural Zeolite: A Laboratory Study. Water, Air, & Soil Pollution, 224
16	(2013) 1–10.
17	[19] C. Jiang, L. Jia, Y. He, B. Zhang, G. Kirumba, J. Xie. Adsorptive removal of phosphorus from
18	aqueous solution using sponge iron and zeolite. Journal of Colloid and Interface Science, 402
19	(2013) 246–252.
20	[20] D. Wu, B. Zhang, C. Li, Z. Zhang, H. Kong. Simultaneous removal of ammonium and
21	phosphate by zeolite synthesized from fly ash as influenced by salt treatment. Journal of
22	Colloid and Interface Science, 304 (2006) 300-306.
23	[21] N. Karapınar. Application of natural zeolite for phosphorus and ammonium removal from
24	aqueous solutions. Journal of Hazardous Materials, 170 (2009) 1186-1191.
25	[22] APHA. Standard Methods for the Examination of Water and Wastewater. American Public

- 1 Health Association: Washington, DC, 2005.
- [23] Q. Du, S.J. Liu, Z.H. Cao, Y.Q. Wang. Ammonia removal from aqueous solution using natural
   Chinese clinoptilolite.*Separation and Purification Technology*, 44 (2005) 229–234.
- [24] M.S. Onyango, D. Kuchar, M. Kubota, H. Matsuda. Adsorptive removal of phosphate ions from
  aqueous solution using synthetic zeolite. *Industrial &Engineering Chemistry Research*, 46
  (2007) 894–900.
- 7 [25] S.L. Tisdale, W.L. Nelson, J.D. Beaton. Soil fertility and fertilizers. Collier Macmillan
  8 Publishers, 1985.
- 9 [26] K. Chen, K. Zhao, H. Zhang, Q. Sun, Z. Wu, Y. Zhou, Y. Zhong, F. Ke. Phosphorus removal
  10 from aqueous solutions using a synthesized adsorbent prepared from mineralized refuse and
  sewage sludge. *Environmental Technology*, 34 (2013) 1–8.
- [27] M. Kõv, M. Liira, U. Mander, R. Mõtlep, C. Vohla, K. Kirsimäe. Phosphorus removal using
   Ca-rich hydrated oil shale ash as filter material-the effect of different phosphorus loadings and
   wastewater compositions. *Water Research*, 44 (2010) 5232–5239.
- [28] Y. Watanabe, H. Yamada, H. Kokusen, J. Tanaka, Y. Moriyoshi, Y. Komatsu. Ion exchange
   behavior of natural zeolites in distilled water, hydrochloric acid, and ammonium chloride
   solution. *Separation Science and Technology*, 38 (2003) 1519–1532.
- [29] M. Van Kemenade, P.L. De Bruyn. A kinetic study of precipitation from supersaturated calcium
   phosphate solutions. *Journal of Colloid and Interface Science*, 118 (1987) 564–585.
- [30] M.B. Vanotti, A.A. Szogi, P.G. Hunt. Extraction of soluble phosphorus from swine wastewater.
   *Transactions of the ASAE*, 46 (2003) 1665–1674.
- [31] L.L. Ames. The cation sieve properties of clinoptilolite. *American Mineralogist*, 45 (1960)
   689–700.
- [32] S.G. Sommer, S. Husted. The chemical buffer system in raw and digested animal slurry. *The Journal of Agricultural Science*, 124 (1995) 45–53.

1	[33] X. Chen, K. Wendell, J. Zhu, J. Li, X. Yu, Z. Zhang. Synthesis of nano-zeolite from coal fly ash
2	and its potential for nutrient sequestration from anaerobically digested swine wastewater.
3	Bioresource Technology, 110 (2012) 79–85.
4	[34] S. Meng, Y. Li, T. Zhang, J. Chen, P. Xu, C. Song, L. Fan, L. Qiu. Influences of environmental

- 5 factors on lanthanum/aluminum-modified zeolite adsorbent (La/Al-ZA) for phosphorus
- 6 adsorption from wastewater. *Water, Air, & Soil Pollution*, 224 (2013) 1–8.

# 1 FIGURE CAPTIONS

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

Figure 2(a). Effects of initial ammonium concentration on ammonium and phosphate removal rates by the natural zeolite at initial  $100 \text{ mg-P l}^{-1}$  condition.

9 Figure 2(b). Effects of initial phosphate concentration on ammonium and phosphate removal rates by
 10 the natural zeolite at initial 1000 mg-N l<sup>-1</sup> condition.

Figure 3(a). Effects of contact time on ammonium and phosphate concentration by the natural zeolite
at initial 1000 mg-N l<sup>-1</sup> and 100 mg-P l<sup>-1</sup> condition.

Figure 3(b). Kinetic plots of intra-particle diffusion model for ammonium and phosphate removals
by the natural zeolite at initial 1000 mg-N l<sup>-1</sup> and 100 mg-P l<sup>-1</sup> condition.

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Figure 4(a). Breakthrough of ammonium and phosphate removals by the natural zeolite in columntests treating N-P mix.

Figure 4(b). Breakthrough of ammonium, phosphate, total alkalinity and VFAs removals by the natural zeolite in column tests treating the fermentation liquor.

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Material	$q_t(\mathrm{mgg}^{-1})$	pН	Effect	Removal mechanism proposed		
HDTA-Br modified zeolite	0.194	4.2, 10.4	pH increased, removal increased	Anion exchange & electrostatic attraction	[18]	
Zeolite	0.71	3.0-10.0	pH increased, removal decreased	Electrostatic attraction	[26]	
HUD synthetic zeolite	79.40	2.5 - 10.0	pH increased, removal decreased	Chemical interaction & electrostatic	[24]	
				attraction		
La/Al-modified zeolite	2.43	2.0 - 12.0	Favorable range: 4.0-8.0	Electrostatic attraction	[34]	
Synthesized zeolite-Al	54.17	5.71	NA	Chemical interaction & ligand exchange.	[20]	
Synthesized zeolite-Ca	30.46	6.78	NA	Chemical interaction	[20]	
Zeolite	0.30	NA	NA	Electrostatic attraction or	[19]	
				anion-exchange.		

Table 1. Zeolites used as the adsorbents for phosphate removal.

Adsorption stage	Parameters	NH <sub>4</sub> -N	PO <sub>4</sub> -P
Einst stopp	<i>k</i> <sub><i>d</i>1</sub>	1.331	0.144
riist stage	$R^2$	0.903	0.990
Second stage	$k_{d2}$	0.496	0.034
Second stage	$R^2$	0.968	0.949
Third stage	k <sub>d3</sub>	0.023	$7.217 \times 10^{-5}$
	$\mathbf{R}^2$	0.877	0.640

Table 2. Kinetic parameters for ammonium and phosphate removal using the natural zeolite.

Table 3. Concentrations of ions in batch experiments before and after zeolite adsorption.

Solution type	Initial pH	Before/after	Ion concentration (mg $l^{-1}$ )					
		adsorption	$NH_4^+-N$	$PO_4^{3-}-P$	Ca <sup>2+</sup>	$Na^+$	$Mg^{2+}$	$\mathbf{K}^+$
Р	4.0	before	0	101	0	90.0	0	0
		after	0	94.4	65.3	43.6	1.3	3.1
	9.0	before	0	102	0	123	0	0
		after	0	59.8	2.3	11.2	0.3	0.2
N-P mixture	4.0	before	990	102	0	75.4	0	0
		after	285	92.6	597	545	7.1	58.6
	9.0	before	981	102	0	234	0	0
		after	281	14.5	462	662	7.3	64.5



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



Figure 2(a). Effects of initial ammonium concentration on ammonium and phosphate removal rates by the natural zeolite at initial 100 mg-P  $l^{-1}$  condition.



Figure 2(b). Effects of initial phosphate concentration on ammonium and phosphate removal rates by the natural zeolite at initial 1000 mg-N  $l^{-1}$  condition.



Figure 3(a). Effects of contact time on ammonium and phosphate concentration by the natural zeolite at initial 1000 mg-N  $l^{-1}$  and 100 mg-P  $l^{-1}$  condition.



Figure 3(b). Kinetic plots of intra-particle diffusion model for ammonium and phosphate removals by the natural zeolite at initial 1000 mg-N  $I^{-1}$  and 100 mg-P  $I^{-1}$  condition.



Figure 4(a). Breakthrough of ammonium and phosphate removals by the natural zeolite in column tests treating N-P mix.



Figure 4(b). Breakthrough of ammonium, phosphate, total alkalinity and VFAs removals by the natural zeolite in column tests treating the fermentation liquor.

# SUPPLEMENTARY MATERIALS

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

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Figure S1.Adsorption isotherm (mg g<sup>-1</sup> versus mg  $l^{-1}$ ) of ammonium ions onto zeolite surface (25°C).



Figure S2.SEM images of the natural zeolite before adsorption (a), zeolites after treating the N-P feed solution (b), the precipitate formed in feed solution after zeolite treatment (c), and zeolites after treating the fermentation liquor (d).

	Factor	Operational conditions						
		Influent type	Initial	Initial	pН	Temperature(°C)	Time(h)	
			$NH_4-N(mgl^{-1})$	$PO_4$ - $P(mgl^{-1})$	•		. ,	
Batch	pН	P solution*	0	100	3.0-11.0	25	24	
		N-P mixed solution <sup>b</sup>	1000	100	3.0-11.0	25	24	
	N-P	N-P mixed	0-2000	100	9.3	25	24	
	interaction	solution						
		N-P mixed	1000	0-1000	9.3	25	24	
		solution						
	Contact	N-P mixed	1000	100	9.3	25	0-24	
	time	solution						
Column	Feed	N-P mixed	1163	70.4	9.3	20	6	
		solution						
		Fermentation	1252	63.1	9.3	20	6	
		liquor						

Table S1. Testing conditions for the batch and continuous experiments.

\* Through diluting 1000 mg-P l<sup>-1</sup> of sodium di-hydrogen phosphate (NaH<sub>2</sub>PO<sub>4</sub>) stock solutions with deionized water