Removal of phosphate from aqueous solution using modified zeolite clays

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Abstract: Phosphate adsorption capabilities of different treated zeolite clays were assessed from aqueous solution. Natural zeolites were treated by thermal activation over 120–800 °C for 2 h, and by hydrochloric acid solution from 1%-9%, respectively. The mechanisms of phosphate adsorption of these modified products were also studied through adsorption isotherms and adsorption kinetics experiments. The acid activation increased the phosphate sorption capacity and the highest phosphate sorption capacity occurred at AZT9 (zeolite activated by 9% hydrochloric acid), while thermal activation did not have the same effect. AZT9 showed higher adsorption rate than natural zeolite (ZT). The phosphate adsorption isotherms of ZT, H400 and AZT9 are fitted well with Langmuir equation in terms of R2 values. It suggested that the adsorption of phosphate on zeolite was homogeneous multilayer adsorption. Based on R2 values, the kinetics of phosphate adsorption on these three zeolites can be satisfactorily described by pseudo-second-order kinetic equation. Results of this study suggested that acid modified zeolite could be potentially used as a promising adsorption media for phosphate removal.

1 Introduction
Zeolite is a kind of aluminosilicate with tetrahedral skeleton structure existing widely in nature. It’s chemical composition is \([\text{M}_2(\text{I}),\text{M}(\text{II})\text{OAl}_2\text{O}_3\text{Si}_2\text{·mH}_2\text{O}]\), \(\text{M}_2(\text{I})\) and \(\text{M}(\text{II})\) are monovalent and bivalence metal ions respectively, usually sodium, potassium, strontium, calcium, barium and so on. There are many holes and channels with uniform size inside the crystal lattice. The surface area is very large, reaching 400–800 m² g⁻¹. The zeolites also have great dispersion force and large static electricity, so it has good adsorption performance.

Xiao Juqiang et al. (2003) studied the adsorption of phosphorus by natural clinoptilolite from Gansu. The results showed that the adsorption equilibrium could be reached in 10 minutes. The removal rate of phosphorus is 83.7%. Meng Hong (2001) discussed adsorption effect of the activated zeolite, which had better adsorption effect in the pH range of 4–12, and adsorption capacity could be above 4 mg g⁻¹. The phosphorus removal rate of city sewage reached 84.8%, but the removal efficiency for poly phosphide was not ideal. Zhao Guiyu et al. (2007) used the natural clinoptilolite from Jinyun in Zhejiang province to remove phosphorus from sewage, and the adsorption reaction accorded with the Langmuir equation. At 25 °C, the maximum saturated adsorption capacity of zeolite with 0.3 μm for phosphorus was 101.01 mg kg⁻¹. Sun Jiashou (1997) applied modified zeolite on phosphorus wastewater and found that phosphate adsorption capacity could reach 24.57 mg g⁻¹, the removal rate of phosphorus is greater than 98%, the effluent phosphorus concentration could also be reduced to 0.46 mg L⁻¹. While further experiments showed that less adsorption capacities were tested for phosphoric acid and poly phosphoric acid.
Therefore, this study was designed to: (1) modify natural zeolite with different simple methods to form zeolite products, then (2) to evaluate the potentials of using the zeolite for phosphate removal from wastewater in batch adsorption experiments, and finally (3) to ascertain the practical applicability of the zeolite products for real wastewaters.

2 Materials and methods

2.1 Adsorbents

Natural zeolite clay (ZT) used was from Dantu County (China). The natural sample was manually ground and selected for particles < 160 μm. The bulk chemical analysis of the ZT was listed in Table 1.

Thermal activated zeolites were prepared by heating over a range of temperatures (120, 200, 300, 400, 500, 600, 700 and 800 °C) at a period of 2 h. They were labeled as H120, H200, etc.

Thirty grams of natural zeolite were dispersed into 250 mL of hydrochloric acid solution (volume fraction of 1%, 3% and 9%) at 70°C. After a mixing time of 2 h, the clay suspension was centrifuged after cooling, then the solid sediments was washed with distilled water until no Cl\(^{-}\) was tested by Ag\(\text{-NO}_3\) test solution. The products were dried at 105 °C, ground and stored in polyethylene bottles before use. These were labeled AZT1, AZT3 and AZT9.

| Chemical analysis (wt.%) | ZT  | H400 | AZT9 |
|--------------------------|-----|------|------|
| Al\(_2\)O\(_3\)         | 13.72 | 14.55 | 13.66 |
| Fe\(_2\)O\(_3\)         | 1.93  | 2.13  | 1.73  |
| CaO                      | 2.03  | 2.21  | 0.98  |
| MgO                      | 2.20  | 2.33  | 1.99  |
| MnO\(_2\)                | 0.037 | 0.039 | 0.03  |
| K\(_2\)O                 | 1.07  | 1.42  | 1.26  |
| Na\(_2\)O                | 1.20  | 1.66  | 1.42  |
| TiO\(_2\)                | 0.21  | 0.24  | 0.23  |
| P\(_2\)O\(_5\)          | 0.10  | 0.11  | 0.01  |
| SiO\(_2\)                | 65.92 | 67.57 | 68.68 |
| LOI\(^a\)                | 11.54 | 7.34  | 9.87  |

\(^a\) Loss on ignition at 950 °C

2.2 Batch adsorption experiments

2.2.1 Single point adsorption experiments. To evaluate the impact of heated zeolites on the phosphate adsorption capacity, natural and modified zeolite with different temperature were used. A defined volume of the phosphate stock solution, with concentrations of 10 mg P/L was added to 0.5 g of adsorbents. The mixture was stirred at 200 rpm in thermostatic shaker for a defined period, then the orthophosphate removal was calculated and the optimum material was selected. To evaluate the impact of acid activated zeolite on the phosphate adsorption capacity, natural and modified zeolite with different acid volume were used. A defined volume of the phosphate stock solution, with concentrations of 20 mg P/L was added to 0.5 g of adsorbents. The remaining steps were the same as described above.

2.2.2 Phosphate adsorption isotherms. Phosphate adsorption isotherms were carried out with different initial concentrations of phosphate and a fixed concentration of the adsorbents at room temperature (25 °C). 0.5 g of the sample was loaded in 100 mL conical flasks, and 50 mL of PO\(_4^{3-}\) solution was then added. Thirteen levels of initial phosphate concentrations (0, 3, 6, 10, 30, 50, 80, 100, 120, 140, 160, 180 and 200 mg P/L) were used. The flask was capped and stirred magnetically at 200 rpm for 24 h to ensure approximate equilibrium. After phosphate adsorption, the solution was filtered through a 0.22 μm membrane filter and then analyzed for PO\(_4^{3-}\). The quantity of adsorbed phosphate (adsorption capacity) was calculated from the decrease of the phosphate concentration in solution.
2.2.3 Phosphate adsorption kinetics. Phosphate adsorption kinetics was evaluated at room temperature (25 ℃) and at original pH value. The initial phosphate concentration was 10 mg P/L while the adsorbent quantity was 0.5 g. Reaction solutions were sampled at intervals between 0 and 24 h of adsorption.

2.2.4 pH effect on phosphate adsorption. The effect of pH on phosphate removal by H400 was examined in the pH region between 2 and 10. The tests were carried out at constant experimental conditions with an initial solution concentration 10 mg P/L and 0.5 g adsorbent. All the tests were carried out at constant retention time, fixed at 24 h.

2.2.5 Sample Analysis. XRD patterns of the prepared samples were acquired with a D/MAX2200 X-ray diffractometer using CuKα radiation (40 kV, 40 mA) and a Ni filter. All XRD patterns were obtained from 3.0º to 60.0º with a scan speed of 4.0 º/min. Chemical analyses of the adsorbents were determined by LiBO₂-ICP-AES method (Soil Science Society of China, 2002), using an induced coupled plasma atomic emission spectrophotometer (ICP-AES) (Thermo IRIS Advantage). The analysis of phosphate (as phosphorous) was done by the molybdenum-blue ascorbic acid method with a UV-Vis spectrophotometer (UV/VIS 721 model) (Soil Science Society of China, 2002).

3 Results and discussion

3.1 Phosphate adsorption capacity of activated zeolites

The phosphate adsorption capacities of eight thermal treated zeolites are given in Figure 1(a). The curves showed that zeolite heated at different temperature had different phosphate adsorption capacity. Compared with ZT, thermal treated samples did not behave better phosphate adsorption ability. When the heating temperature increases to 400 ℃, the adsorption capacity increases with temperature, and then the phosphate adsorption capacity no longer increases, even reduces. In order to clarify the phosphate adsorption mechanism, so H400 was still chosen as the next batch adsorption experimental material. Figure 1(b) showed the phosphate adsorption capacities of three acid treated zeolites, compared with natural sample. While the acid solution was set at 9%, the phosphate adsorption capacity reaches the maximum, followed by 3% and 1%. In comprehensive consideration of removal efficiency and economic costs, AZT9 was used as subsequent test material.

![Graph](image1.png)

(a) heated zeolites  
(b) acid activated zeolites

Fig. 1 Variation of the phosphate adsorption capacity of heated zeolites and acid activated zeolites

3.2 Maximum adsorption capacity

The isothermal adsorption data of ZT, H400 and AZT9 are summarized in Figure 2. According to Fig. 2, AZT9 had highest adsorption capacities than the H400 and AT, which were 1.18 mg/g, 0.44 mg/g and 0.39 mg/g, respectively, at the phosphate initial concentration of 200 mg/L. It is noted here that H400 had higher adsorption capacities than ZT when the initial phosphate concentration was above 10 mg/L. The adsorption data were fitted with the Langmuir isotherm:

$$q = q_m b C / (1+bC)$$
Where \( q \) (mg/g) and \( C \) (mg/L) are the equilibrium concentrations of an adsorbate on the zeolite and in the aqueous solution, respectively, \( b \) is adsorption isothermal constant (Table 2). The adsorption data agree with the Langmuir isotherm reasonably. With reference to phosphate adsorption tests, parameters such as size of adsorbate, retention time and phosphate concentration have varied, and these factors also influence the outcomes of experiments. And there are no researchers who have carried out the investigations exactly in the same way and data should not be compared (Westholm, 2006). Therefore, data on P adsorption capacity should only be compared when similar experimental conditions have been employed (Gan et al., 2011).

![Adsorption isotherms of natural zeolite (ZT), H400 and AZT9 plotted as equilibrium adsorbed amount (\( q \)) vs. equilibrium concentration (\( C_e \)) at 25 °C](image)

**Table 2** Estimated isotherm and kinetic model parameters for phosphate adsorption.

| \( T \) (25 °C) | Langmuir isotherm | Second-order equation |
|----------------|-------------------|-----------------------|
| \( q_m \) (mg/g) | \( b \)           | \( R^2 \)             | \( k_2 \) (g/(mg min)) | \( R^2 \)       |
| ZT             | 0.285             | 0.067                 | 0.974                  | 62.31            | 0.9977        |
| H400           | 0.503             | 0.044                 | 0.996                  | 49.69            | 0.9995        |
| AZT9           | 0.735             | 0.055                 | 0.977                  | 306.58           | 0.9999        |

3.3 *Phosphate adsorption kinetic results*

In Figure 3, the results of phosphate adsorption kinetic data for ZT, H400 and AZT9 at 25 °C are presented. The AZT9 had fast kinetics than AT and H400, the majority of phosphate adsorption on the AZT9 was completed in 0.5 h. Four typical kinetic equations were used for fitting the experimental data, while estimated parameters of pseudo second-order equation were listed based on \( R^2 \). All the adsorption system of phosphate/ZT, H400 and AZT9 obey the pseudo second-order kinetic model and thus supports the assumption behind the model that the adsorption is due to chemisorption (Demirbas, 2008).

3.4 *pH effect on phosphate adsorption*
The impact of pH on the phosphate adsorption on the H400 is shown in Figure 4. As seen from Figure 4, the pH value of the phosphate solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The phosphate adsorption tends to decrease with the increase of pH for the ZT, from 0.26 mg P/g at pH 3.0 to 0.02 mg P/g at pH 9.0. Similar trends were also observed for phosphate adsorption on fly ash (Agyei et al., 2002) and other adsorption materials. The low phosphate uptake in alkaline pH range can be attributed to the competition of hydroxide ions with phosphate ions for adsorption sites. The pH of the aqueous solution is an important variable that influences the adsorption of anions and cations at the solid-liquid interfaces.

![Fig. 3 Phosphate adsorption kinetic data for ZT, H400 and AZT9 (C₀=10 mg/L)](image)

![Fig. 4 Impact of pH on phosphate adsorption capacity of AT and H400 (C₀=200 mg/L)](image)

**4 Conclusions**
The performance characteristics were investigated to remove phosphate for heated zeolites and acid activated zeolites. It has been demonstrated that the natural zeolite has phosphate adsorption ability and can be used as a low cost adsorbent. Hydrochloric acid activation is an effective method to enhance the adsorption capacity of the natural clay, and is also an easily handling operation compared with other chemical activation.

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