Application of different activated attapulgites to purify phosphate contaminated wastewater

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Abstract: Phosphate adsorption capabilities of different activated attapulgites were investigated. The natural attapulgites 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 AAT3 (attapulgite activated by 3% hydrochloric acid), while thermal activation did not have the same effect. AAT3 showed higher adsorption rate than natural attapulgite (AT). The phosphate adsorption isotherms of AT, H400 and AAT3 are fitted well with Langmuir equation in terms of R² values. It suggested that the adsorption of phosphate on attapulgite was homogeneous multilayer adsorption. Based on R² values, the kinetics of phosphate adsorption on these three attapulgites can be satisfactorily described by pseudo-second-order kinetic equation. Results of this study suggested that acid modified attapulgite could be potentially used as a promising adsorption media for phosphate removal.

1 Introduction
With the expansion of the scope and the intensification of human activities, a large number of wastewater containing nitrogen and phosphorus was poured into the water body, resulting in excessive algae breeding, water quality deterioration and water eutrophication problem. Phosphorus is one of the key elements to cause eutrophication of water body [9]. In various methods of phosphorus removal in wastewater, biological method may change the composition of the waste water and it is not easy to realize. Application of chemical method is limited because of its high cost and large amount of sludge produced. Among these techniques, adsorption gradually attracted people's attention with its efficiency and simplicity [4]. In the study of the adsorption application in wastewater treatment, it is most important to develop a new high efficient adsorbent for the new process.

Attapulgite resource is abundant in China and the most abundant attapulgite deposits are located in the east of Anhui Province and the west of Jiangsu Province, China [8]. Attapulgite is a hydrated aluminum-magnesium silicate mineral with a fibrous morphology characterized by a high surface area, which make it a potentially attractive adsorbent [2]. Therefore, the objectives of this study are (1) to modify natural attapulgite with different simple methods to form attapulgite-derivatives, then (2) to evaluate the potentials of using the attapulgite for phosphate removal from wastewater in batch ad-
sorption experiments, and finally (3) to ascertain the practical applicability of the attapulgite products for real wastewaters.

2 Materials and Methods

2.1 Adsorbents
The natural attapulgite clay (AT) used was mined from the Longwang mountain at Xuyi County (China). The natural sample was manually ground and selected for particles < 160 μm. The bulk chemical analysis of the AT was listed in Table 1.

The heated attapulgite samples were prepared by thermal treatment at a period of 2 h over a range of heating temperatures (120, 200, 300, 400, 500, 600, 700 and 800 °C). These were labeled H120, H200, etc.

Thirty grams of natural attapulgite 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 AgNO₃ test solution. The products were dried at 105 °C, ground and stored in polyethylene bottles before use. These were labeled AAT1, AAT3 and AAT9.

| Chemical analysis | AT  | H400 | AAT3 |
|-------------------|-----|------|------|
| Al₂O₃             | 7.92| 8.50 | 7.97 |
| Fe₂O₃             | 4.07| 4.34 | 3.74 |
| CaO               | 0.57| 0.59 | 0.03 |
| MgO               | 11.27| 11.76| 8.81 |
| MnO₂              | 0.070| 0.076| 0.056|
| K₂O               | 0.84| 0.95 | 0.92 |
| Na₂O              | 0.00| 0.00 | 0.00 |
| TiO₂              | 0.51| 0.55 | 0.57 |
| P₂O₅              | 0.21| 0.22 | 0.03 |
| SiO₂              | 56.36| 60.44| 59.81|
| LOI               | 18.23| 12.11| 18.11|

* Loss on ignition at 950 °C

2.2 Batch adsorption experiments

2.2.1 Single point adsorption experiments
Artificial orthophosphate solutions were used throughout the adsorption tests. Initially, a stock solution of 1000 mg/L in orthophosphates was prepared by dissolving a certain amount of chemically pure K₂HPO₄·3H₂O in distilled water. An aliquot of the stock solution was mixed with a certain volume of water so that a phosphate solution was prepared at the desired experimental concentration.

To evaluate the impact of heated attapulgites on the phosphate adsorption capacity, natural and modified attapulgite 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 attapulgite on the phosphate adsorption capacity, natural and modified attapulgite 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 °C) and at original pH value. The initial phosphate concentration was 20 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 AT and 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 20 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 CuKa 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 LiBO$_2$-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 attapulgites
The phosphate adsorption capacities of eight thermal treated attapulgites are given in Figure 1(a). The curves showed that attapulgite heated at different temperature had different phosphate adsorption capacity. Compared with AT, thermal treated samples did not behave better phosphate adsorption ability. When the heating temperature increases to 400 °C, 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 attapulgites, compared with natural sample. While the acid solution was set at 3%, the phosphate adsorption capacity reaches the maximum, followed by 9% and 1%. In comprehensive consideration of removal efficiency and economic costs, AAT3 was used as subsequent test material.
3.2 Maximum adsorption capacity

The isothermal adsorption data of AT, H400 and AAT3 are summarized in Figure 2. According to Fig. 2, AAT3 had highest adsorption capacities than the H400 and AT, which were 0.69 mg/g, 0.56 mg/g and 0.64 mg/g, respectively, at the phosphate initial concentration of 200 mg/L. It is noted here that H400 had higher adsorption capacities than AT when the initial phosphate concentration was below 200 mg/L. The adsorption data were fitted with the Langmuir isotherm:

\[ q = \frac{q_m b C}{1 + b C} \]

Where \( q \) (mg/g) and \( C \) (mg/L) are the equilibrium concentrations of an adsorbate on the attapulgite and in the aqueous solution, respectively. \( b \) is adsorption isothermal constant (Table 2). The adsorption data agree with the Langmuir isotherm reasonably. Some studies showed that attapulgite clay on phosphorus adsorption capacity of about 2.1 mg/g [8] and 3.7 mg/g [10]. 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 [7]. Therefore, data on P adsorption capacity should only be compared when similar experimental conditions have been employed [5].
Fig. 2 Adsorption isotherms of natural attapulgite (AT), H400 and AAT3 plotted as equilibrium adsorbed amount \( (q) \) vs. equilibrium concentration \( (C_e) \) at 25 °C

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) | \( R^2 \) |
| AT              | 0.42              | 0.07                  | 0.979 | 25.04 | 0.999 |
| H400            | 0.89              | 0.04                  | 0.995 | 21.41 | 0.999 |
| AAT3            | 0.47              | 0.21                  | 0.927 | 148.93| 0.999 |

3.3 Phosphate adsorption kinetic results
In Figure 3, the results of phosphate adsorption kinetic data for AT, H400 and AAT3 at 25 °C are presented. The AAT3 had fast kinetics than AT and H400, the majority of phosphate adsorption on the AAT3 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/AT, H400 and AAT3 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 AT and 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 AT, from 0.22 mg P/g at pH 3.0 to 0.02 mg P/g at pH 10.0. Similar trends were also observed for phosphate adsorption on fly ash [1] 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. While for AT, it seems complicated that adsorption capacity reached to 0.27 mg/g at pH 4.0, then decreased to 0.14 mg/g at pH 7.0, and pH had greater influence on H400 than on AT. 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 AT, H400 and AAT3 ($C_0=200$ mg/L)

Fig. 4 Impact of pH on phosphate adsorption capacity of AT and H400 ($C_0=200$ mg/L)

4 Conclusions
The performance characteristics were investigated to remove phosphate for heated attapulgites and acid activated attapulgites. It has been demonstrated that the natural attapulgite in Xuyi county 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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