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Removal of Phosphate from Aqueous Solution with Modified Bentonite

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Abstract: Bentonite combined with sawdust and other metallic compounds was used to remove phosphate from aqueous solutions in this study. The adsorption characteristics of phosphate on the modified bentonite were investigated, including the effects of temperature, adsorbent dosage, initial concentration of phosphate and pH on removal of phosphate by conducting a series of batch adsorption experiments. The results showed that 98% of phosphate removal rate was obtained since sawdust and bentonite used in this investigation were abundantly and locally available. It is concluded that modified bentonite is a relatively efficient, low cost and easily available adsorbent for the removal of phosphate from aqueous solutions.

Key words: adsorption; phosphate; sawdust; bentonite

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1 INTRODUCTION

Nowadays, most regions in China suffer from environmental problems due to phosphorous loading to surface and ground water from municipal wastewater containing detergents and concentrated agricultural activities including soil fertilization, feedlots, dairies, and pig and poultry farms. Numerous studies showed that nutrients (nitrogen and phosphorus) are one of the leading causes of water quality problems in rivers, lakes, and estuaries, resulting in eutrophication, increased fish mortality and outbreaks of microbes.

At the current rate of exploitation, the high quality portion of the resource of mined rock phosphate will be largely depleted in less than 100 years, if another source of high-quality phosphate is not identified. This will place a burden on agricultural production, because lower grade phosphates will have to be used, significantly increasing production costs. Phosphates recovered from wastewater plants might be a viable source of industrial raw material for manufacture of phosphate fertilizers. Currently, such phosphorus is regarded more as a contaminant than a resource. This perspective has started to change in recent years[1].

The most common approach for removing phosphate from wastewater is precipitation with metallic salts because phosphate makes a precipitate with calcium, magnesium, or iron ions[2]. However, in the case of a lower concentration of phosphate, the removal of phosphate is difficult and more sludge is produced. The studies of phosphorus immobilization by adsorption have been attracting more and more research interest in recent years for the saving of phosphate resources and the recycling of phosphate. Some researchers focus on activated alumina, iron-based compounds, layered double hydroxides, hydrotalcite, yttrium carbonate, and polymeric ligand exchanger while others put more attention on natural materials and their modifications, such as boehmite and goethite[3], and even solid wastes, such as fly ash, blast furnace slag and alum sludge[4–6].

Bentonite is enriched with the oxides of aluminum, iron and calcium, and silica. It was modified by loading Mg–Al hydroxides and then calcined with sawdust at 450 ℃ for 5 h. This work aims to identify the influential factors of phosphate immobilization on this kind of adsorbent while the preparation conditions, such as the dosage of each material, calcination temperature and the mechanisms of solid reactions will be reported in other papers.

2 PHOSPHATE IMMOBILIZATION EXPERIMENTS

2.1 Materials

The natural bentonite (Ca–betonite) was purchased from Ningmin County, Guangxi Zhuang Autonomous Region, China. The bentonite was purified and modified to become Na^+-bearing clay by adding sodium chloride before use. Aluminum nitrate and manganese nitrate obtained from Xilong Chemical Company, Guangdong Province, China, had a chemical purity of 99%, and

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were used as received.

Sawdust was obtained from a pulp mill and was ground first with a pulverizer, and then sieved, collected and stored in airtight containers at room temperature until use.

2.2 Adsorbent

1% concentration by weight of Na^+-bearing bentonite solution was firstly mixed with a 0.75 mol/L solution of the mixture solution of NaOH(aq) and Na_2CO_3, and then put in a beaker. 3.5 mol/L solution of $Mg(NO_3)_2\cdot 6H_2O(aq)$ and $Al(NO_3)_3\cdot 6H_2O(aq)$ was added dropwise to Na^+-bentonite mixture under vigorous stirring. Hydrothermal treatment under 60 ℃ was required to improve the crystallinity of the product for 24 h. The suspension was centrifuged and then washed with deionized water until sodium ion concentration was very low. The solids were mixed with aqueous sawdust and calcined at 450℃ for 5 h. The resulting product was ground and sieved with 200-mesh sieve, and collected and stored in airtight containers at room temperature until use.

2.3 Analysis of Phosphate

Phosphate was analyzed by the molybdenum blue method[7]. Molybdenum acid ammonium solution, 2.0 mL, and an L-ascorbic acid solution, 1.0 mL, were added to the sample solution. After 15 min, the absorbance at a wavelength of 700 nm with UV–visible recording spectrophotometer (U3210, Hitachi, Tokyo, Japan) using 10 mm matched quartz cells.

2.4 Adsorption Experiment

Adsorption experiments were carried out by adding certain weight of adsorbent and 50 mL water containing 30 mg/L P in each of 250 mL Erlenmeyer flasks. The flasks were placed in a thermostat shaker and the solution was agitated at a given temperature for a particular period of time respectively. After the stipulated contact time, the conical flasks were taken from the shaker and the content was centrifuged and the concentration of phosphate in the suspension was determined.

Batch equilibration experiments were conducted using the phosphate stock solutions containing 30 mg/L P. The amount of phosphate adsorbed onto the adsorbent at equilibrium was calculated by the equation:

$$q_t = (C_0 - C_e)V/m\ ,$$

where q_t is the amount adsorbed per unit gram of adsorbent (mg/g) in t time, C_0 the initial concentration (mg/L), C_e the equilibrium concentration (mg/L), V the solvent quantity (mL), and m the weight of the adsorbent (g).

The percentage of adsorbed phosphate was determined from the ratio of the concentrations of phosphate present in the solution and particulate phases as follows:

$$\eta = \left[(C_0 - C_e)/C_0\right] \times 100\%\ .$$

3 RESULTS AND DISCUSSION

3.1 Effect of Adsorbent and Adsorbate Dosage

The percentages of adsorbed phosphate varying with amounts of adsorbent and phosphate removal are presented in Fig.1. As expected, the amount of phosphate adsorption increases with the increase of adsorbent dosage, which indicates that the adsorption depends upon the availability of binding sites for phosphate. When the adsorbent content is 0.76 g/L, the percentage of adsorbed phosphate reaches 98%.

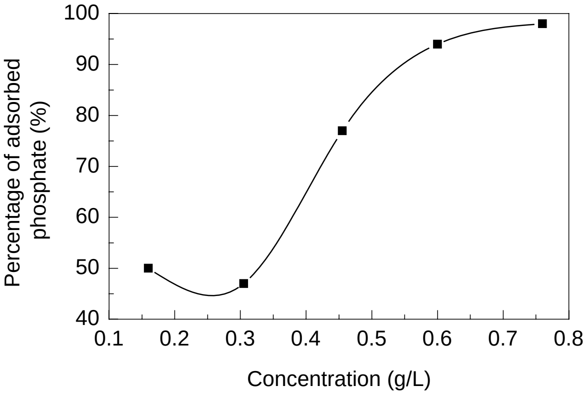

Fig.1 Effect of adsorbent dosage

3.2 Effect of Time

The phosphate adsorption results showed that adsorption equilibrium was attained in about 120 min (see Fig.2). There was no further change in equilibrium concentration up to 240 min.

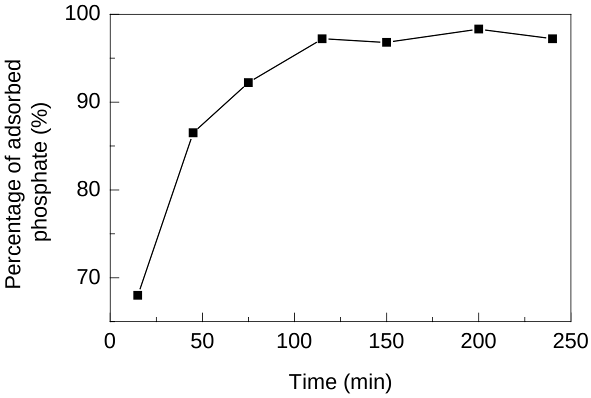

Fig.2 Effect of time

3.3 Effect of pH

The effect of pH value in the solution on immobilization of phosphate was studied by keeping the dosage of adsorbent at 0.76 g/L and contact time in 120 min, and varying the pH from 2 to 11. The pH of the solution was adjusted with 1 mol/L HCl or 1 mol/L NaOH solution and measured by a pH meter. Fig.3 represents the effect of pH on the percentage of phosphate adsorption. It is evident from the figure that the percentage of phosphate immobilized increases with the increase of pH from 2 to 8, and then decreases with the increase of pH. In wastewater applications, most common and successful methods to precipitate phosphate involve the dissolved cation Al^{3+}. Solubility diagrams for metal phosphates in pure water show that when aluminum and magnesium are present, variscite $AlPO_4$ and $Mg_3(PO_4)_2$ are the stable solid phases in the low pH range below 6.5. The minimum variscite solubility occurs at pH 6. At higher pH values (>6.5), the aluminum chemistry becomes increasingly governed by the formation of oxides and hydroxides[8], and these conditions are more ideal for the precipitation of phosphate with calcium (contained in bentonite) as apatites and hydroxyapatites. The highest percentage of phosphate adsorption occurring at the pH around 5 can be explained with this principle.

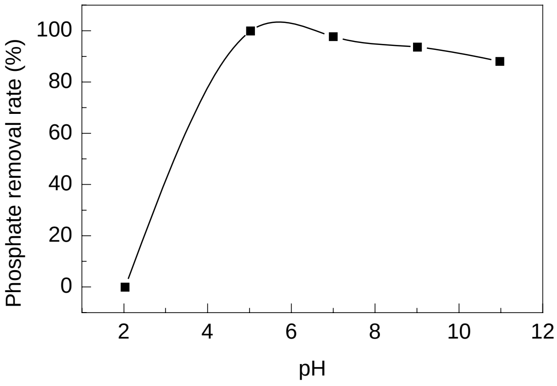

Fig.3 Effect of initial pH

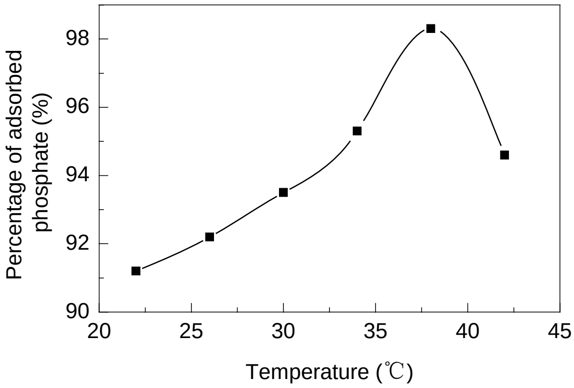

Fig.4 Effect of temperature

3.4 Effect of Temperature

The effect of temperature on phosphate adsorption was studied in the range 24~42℃. It was found that the percentage of phosphate adsorption increased when the temperature increased to 38℃. However, when the temperature further increased, the adsorption decreased, as shown in Fig.4, probably desorption took place.

3.5 Adsorption Isotherm

In order to determine the rate constant of adsorption, the monolayer Langmuir theory[9] was used to describe the adsorption of phosphate on modified bentonite. The linear form of the Langmuir isotherm model can be represented by the following equation:

$$\frac{C_{\mathrm{e}}}{q_{\mathrm{e}}}=\frac{1}{Q_{\mathrm{m}}b}+\frac{C_{\mathrm{e}}}{Q_{\mathrm{m}}},$$

where q_e is equilibrium phosphate content on adsorbent (mg/g), C_e equilibrium phosphate concentration in solution (mg/L), Q_m monolayer capacity of the adsorbent (mg/g), and b adsorption constant (L/mg).

The Langmuir constants were determined after linearizing the equations through linear regression analysis. The calculated values of the constants in Langmuir equations and the regression coefficients (r^2) are given in Table 1, showing that Langmuir adsorption models were suitable for the adsorption of phosphate.

Table 1 The calculated values of the constants in Langmuir equations

Adsorbent	Q_m (mg/g)	b (L/mg)	r^2
Modified bentonite	34.48	1.53	0.9905

3.6 Kinetics of Adsorption

The pseudo-second-order model[10] can be represented in the following form:

$$dq_t/dt=k_2(q_e-q_t)^2,$$

where k_2 is the pseudo-second-order rate constant [g/(mg·min)], and q_e the equilibrium adsorption (mg/g) for the pseudo-second-order adsorption. The following form can be obtained by integrating the above equation for boundary conditions of t=0 to t=t and q_0=0 to q_t=q_t:

$$\frac{t}{q_t}=\frac{1}{k_2q_{\mathrm{e}}^2}+\frac{1}{q_{\mathrm{e}}}t\,.$$

The rate constant values with the correlation coefficient are listed in Table 2. It can be seen that the correlation coefficient (r^2) is 0.9978 and the calculated q_e values for pseudo-second-order model agree well with the experimental data, which indicates that the adsorption process follows the pseudo-second-order rate expression[11].

Table 2 Kinetic parameters for phosphate adsorption on modified bentonite.

Adsorbent	k_2 [g/(mg·min)]	$q_{e,cal.}$ (L/mg)	r^2	$q_{t,exp.}$ (L/mg)	$q_{t,cal.}$ (L/mg)
Modified bentonite	1.7×10^{-2}	33.089	0.9978	11.54	33.590

4 CONCLUSIONS

The following points in this study may be summarized:

(1) The amount of phosphate adsorption on the modified bentonite increases with the increase of adsorbent content in the aqueous solution, which indicates that the adsorption depends upon the availability of binding sites for phosphate.

(2) The equilibrium of phosphate adsorption was attained in about 120 min.

(3) The highest percentage of phosphate adsorption occurred at the pH range from 5 to 8.

(4) The amount of phosphate adsorption increases with the increase of temperature, which indicates that the adsorption depends upon the availability of binding sites for phosphate, but the desorption probably took place at about 40℃.

(5) While the adsorbed amount of phosphate increased with the increase of phosphate concentration, the percentage of phosphate adsorption decreased with the increase of phosphate concentration.

(6) The experimental data were correlated reasonably well by Langmuir adsorption isotherm and the isotherm parameters (Q_m and b) were calculated.

(7) Adsorption of phosphate on the modified bentonite followed the pseudo-second-order rate expression.

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