



Adsorption removal of phosphate from aqueous solution by active red mud

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Abstract

Red mud is the waste of alumina industry and has high TiO_2 and Fe_2O_3 content which are active components for the adsorption of anion pollutants. In this study, the uptake of phosphate by red mud activated by heat treatment and acid-heat treatment was investigated. The factors influencing the adsorption were also investigated. The result showed that the red mud sample treated using acid-heat method at 80°C with 0.25 mol/L HCl for 2 h achieved the highest phosphate removal. For the heat-activated red mud, the sample heated at 700°C for 2 h performed better than the other heat treatment. Phosphate removal by the activated red mud was significantly pH dependent, and pH 7 was the optimal pH for phosphate removal. The adsorption fits Langmuir isotherm model well and the maximum adsorption capacities of the acid-heat activated red mud and the heat activated samples were 202.9 mgP/g and 155.2 mgP/g, respectively.

Key words: phosphate removal; red mud; activation; adsorption

Introduction

Excess phosphate presenting in wastewater is one of the main causes of eutrophication. Wastewater treatment techniques mainly include: physical, chemical, and biological methods. Among them, physical methods were inefficient in phosphate removal. Despite the removal up to 97% of the total phosphate, the enhanced biological treatment can be highly variable due to operational difficulties (Clark *et al.*, 1997). Chemical treatment is widely used for phosphate removal. Adsorption is one of the techniques which would be comparatively useful and economical for phosphate removal. In recent years, considerable attention has been paid to low-cost adsorbents such as alum sludge (Galarneau and Gehr, 1997), red mud (Shiao and Akashi, 1977; López *et al.*, 1998; Pradhan *et al.*, 1998), fly ash (Oguz, 2005) and other waste materials (Agyei *et al.*, 2000, 2002) as adsorbents for adsorption of phosphate from wastewater economically.

Red mud (RM) is the waste by-product during the alkaline leaching of bauxite in the Bayer Process. It causes serious environmental problems due to its high alkalinity and large amount. Environmental and economical concerns have led to an ongoing research to find effective ways to utilize the abundant and widely available RM (Shannon and Verghese, 1976) to remove phosphate. Several active constituents such as alumina, iron oxide present in RM.

RM has been used to remove fluoride (Çengelöğlu *et al.*, 2002), hexavalent chromium (Erdem *et al.*, 2004) and dyes (Wang *et al.*, 2005) from aqueous solution, and is also one of the suitable materials for phosphate adsorption (Shiao and Akashi, 1977; Altundoğan and Tümen, 2003). Although the RM was found to be a good phosphate removal medium for wastewater (Shannon and Verghese, 1976), the direct use of RM without activation as adsorbent for water treatment is not appropriate due to the high dosage. In this study, RM was activated with different methods and used for the removal of phosphate.

1 Materials and methods

1.1 Materials

The red mud used in the present study was obtained from Shandong Aluminium Industry Corporation, Shandong, China. It was 100 mesh particle sized, washed, and air-dried as received. The heat-treatment was carried out by heating samples at different temperature. At the end of the treatment, the powder was ground in a mortar and sieved through a 100 mesh sieve.

The acid-heat activation of red mud was performed in a glass reactor fitted with a stirrer and a thermometer. The stirring speed was held constant by means of a digital controlled stirrer. A constant temperature circulator was used to maintain the desired temperature in the reactor. The samples were loaded into the glass reactor and the ratio of liquid to solid was 20 ml/g. The effect of hydrochloric

acid concentration on activation was tested by acidified raw red mud with a specified amount of known concentration (0.01, 0.05, 0.25, 0.5, 1 mol/L HCl) at specific temperature. The effect of temperature on acid-heat activation was carried out at 25, 40, 60, 80, 100°C for 2 h, and the effect of heating time on acid-heat activation was carried out for 0.5, 1, 2 and 3 h. At the end of the experiment, the mixture was centrifuged for 10 min at 7000 r/min. The residue was washed with distilled water and dried at 100°C overnight.

1.2 Analytical methods

The removal of phosphate was measured using the ascorbic acid method with a HACH DR/4000U spectrophotometer, according to APHA Standard Methods (Arnold, 1985). The specific surface area of the samples was determined by the BET nitrogen gas sorption method using an Accelerated Surface Area and Porosimetry (AS-AP2000, Micromeritics Co.).

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, washed and then rinsed four times with deionised water. Deionised water was used for the preparation of solutions. All experiments were conducted in duplicate and the average values were used for data analysis.

1.3 Adsorption studies of red mud

Adsorption studies were carried out by shaking 20 ml of 155 mg/L phosphate (KH_2PO_4 , calculated as P) solution at 180 r/min with 0.1 g sorbent in the bottles capped with glass screws for 4 h at 25°C, and a background electrolyte of 0.01 mol/L KCl was used as diluent for all the batch experiments. After equilibrium, the samples were centrifuged at 5000 r/min for 10 min and a clear aliquot of the supernatant was taken and analyzed for phosphate. The amount of phosphate adsorbed per unit of adsorbents (X) was calculated as Eq.(1).

$$X = (C_i - C_e) V/m \quad (1)$$

where, X is the concentration of the phosphate adsorbed, C_i and C_e are the initial and final concentrations of the phosphate in solution, respectively, V is the solution volume, and m is the mass of adsorbent. Blank runs, with only 20 ml of 0.01 mol/L KCl solution, were conducted

simultaneously under the same conditions to account for phosphate adsorbed by the glass container.

The effect of time, pH and initial concentration on the phosphate removal was investigated based on the sorption studies. The reaction time of batch studies was executed for a series of time until equilibrium was achieved. The effect of pH on the removal was carried out by adjusting pH of the solution from 1.0–11.0 using 1 mol/L HCl or 1 mol/L NaOH. Solutions of different initial concentrations were used to investigate the effect of concentration on the phosphate removal.

2 Results and discussion

2.1 Effect of different active treatments on the removal of phosphate

The red mud samples were activated with either heat treatment or acid-heat treatment, consequently the composition of the activated red mud samples was different (Table 1), which resulted in different efficiency of phosphate removal (Figs.1 and 2). The acid-heat treatment red mud significantly enhanced the phosphate removal from aqueous solution.

The chemical composition of red mud and the composition of acid-heat activated and heat activated red mud samples are also listed in Table 1.

It can be seen from Fig.1 that the phosphate removal

Table 1 Composition and properties of the raw and activated red mud (RM)

Composition	RM	RM700 ^a	RMAH ^b
SiO ₂ (wt%)	19.14	22.45	17.96
Fe ₂ O ₃ (wt%)	12.76	13.05	12.91
Al ₂ O ₃ (wt%)	6.93	7.06	9.85
CaO (wt%)	46.02	45.23	32.33
MgO (wt%)	1.15	1.14	1.73
TiO ₂ (wt%)	3.43	4.25	4.22
K ₂ O (wt%)	1.20	0.64	0.56
Na ₂ O (wt%)	2.37	1.86	1.73
Loss on ignition	5.73	1.65	1.98
pH	11.70	11.94	7.63
S_{BET} (m ² /g)	14.09	15.69	21.76

^a RM700: the red mud sample calcined at 700°C for 2 h; ^b RMAH: the red mud sample treated with 0.25 mol/L HCl at 80°C for 2 h; ^c S_{BET} : surface area of the raw and activated red mud.

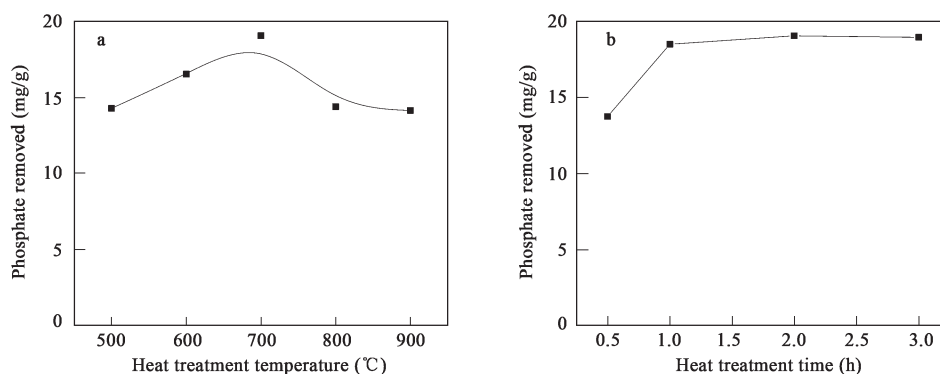


Fig. 1 Effect of heat treatment temperature (a) and time (b) on heat activation of red mud. (a) heat treatment time 2 h; (b) heat treatment temperature 700°C.

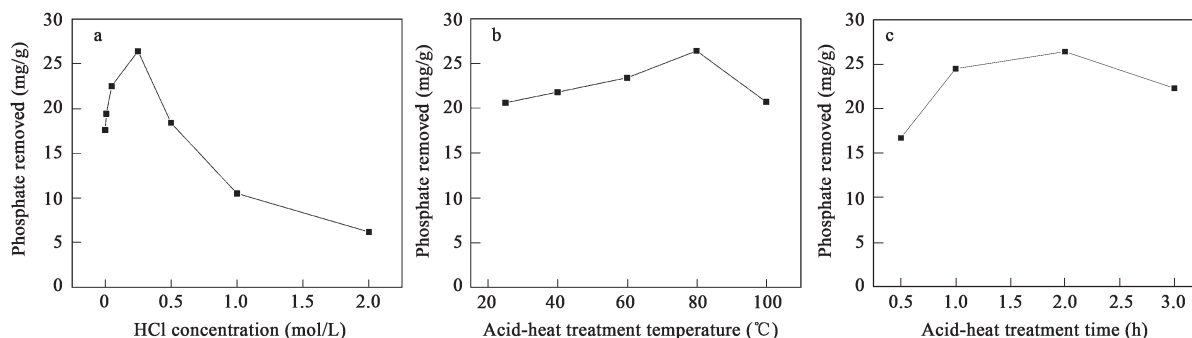


Fig. 2 Effect of HCl concentration (a); temperature (b) and time (c) on acid-heat activation of red mud. (a) activation temperature 80°C; (b) HCl concentration 0.25 mol/L and activation time 2 h; (c) HCl concentration 0.25 mol/L and activation temperature 80°C.

by the red mud sample calcined at 700°C for 2 h (RM700) achieves 19.1 mgP/g, which is higher than those of red mud samples heated at other temperatures. The heating time also influences the heat activation capability. For example, at 700°C, the activation of heat treatment accomplish in the first 2 h. After that, the removal does not increase with the treatment time as shown in Fig.1b. During the calcination, the surface area of the red mud enlarges gradually. The expulsion of water leads to the development of porosity (Cornell and Schwertmann, 1996). The phosphate removal is efficient comparatively when the red mud sample is calcined at 700°C, the phosphate removal would decrease with temperature increase or time last. This is due to the decomposition of some hydroxyl groups, calcite and the sintering shrinkage of red mud when it is calcined.

As for the acid-heat treatment process, HCl concentration significantly influences the activation of red mud (Fig.2a). When the HCl concentration changes from 0.001 mol/L to 2 mol/L, the phosphate removal increases at first and the highest adsorption of 26.4 mg/g is achieved when the HCl concentration is 0.25 mol/L. Then the removal decreases steadily. Except for HCl concentration, both activation time and temperature also influence the activation of red mud. From Fig.2b we can see when the activation temperature increases from room temperature to 80°C, the phosphate removal increased. After that, the phosphate removal decreases with the increase of temperature. The effect of acid-heat activation time on activation capability shows that phosphate removal increases until time is up to 2 h, and then declined (Fig.2c). The phosphate removal of the red mud treated with dilute HCl (0.001, 0.01 and 0.05 mol/L) (the phosphate removal is 17.6, 19.4 and 22.5 mgP/g respectively) does not achieve the capacity as high as the sample treated with 0.25 mol/L HCl at 80°C for 2 h (RMAH) (the phosphate removal was 26.4 mgP/g). Maybe this is due to the fact that appropriate concentration of HCl can enhance the positive charge on the surface of the metal oxide colloid in the RM which is a complex mixture of different minerals. When this activated RM was added in the phosphate solution, phosphate was apt to be adsorbed on the surface of the activated RM. Simultaneously calcium and some other acid-soluble salts were dissolved partially, some coarse exterior and new cavities appeared during the acidification process. The surface area of RMAH is listed in Table 1, it can be seen that treatment

with appropriate concentration of HCl can improve the surface areas of the RM samples, resulting in the increase of phosphate removal (Fig.2a). However, during acid-heat process, when the HCl concentration or the activation temperature was too high, or the activation time was too long, the loss of acid-soluble fractions such as hematite and calcite in the residue was likely to take place. Thus the soluble Ca, Fe and Al in the residue decreased, which may play an important role in the removal of phosphate from aqueous solution, and the phosphate removal decreased consequently.

2.2 Effect of contact time on the removal

The effect of contact time on the removal of phosphate is shown in Fig.3. After the initial rapid reaction, phosphate sorption of the raw and activated red mud is kept steadily. As seen from the Fig.3, the phosphate removal reaches the peak value in the first 4 h. Thus, 4 h is selected as a consistent time to investigate the effect of initial phosphate concentration and pH on the sorption capacity.

2.3 Sorption isotherm

The Langmuir isotherm was used to simulate the phosphate sorption isotherm. The Langmuir isotherm model assumes uniform energies of sorption onto the surface with no transmigration of adsorbate in the plane of the surface, and it can be presented by Eq.(2)

$$X = \frac{X_m k C_e}{1 + k C_e} \quad (2)$$

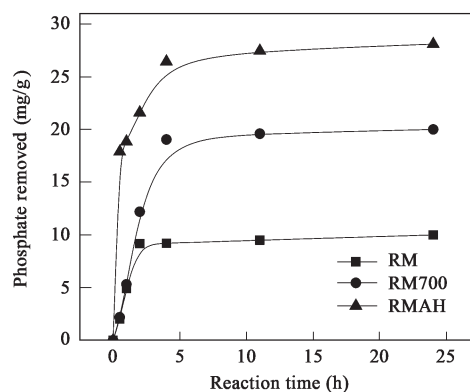


Fig. 3 Effect of contact time on the phosphate removal by the activated red mud (RM). RM700 and RMAH are the same as that in Table 1.

where, X is equilibrium phosphate concentration on adsorbent (mg/g), X_m is monolayer capacity of the adsorbent (mg/g), k is adsorption constant, C_e is equilibrium phosphate concentration in solution (mg/L).

The phosphate adsorption isotherms are shown in Fig.4, the symbols in the figures expressed the data obtained in the adsorption experiment, and the lines stand for the Langmuir isotherm simulation. The results of this study show that phosphate uptake increases with the increase of the equilibrium phosphate concentration for each adsorbent.

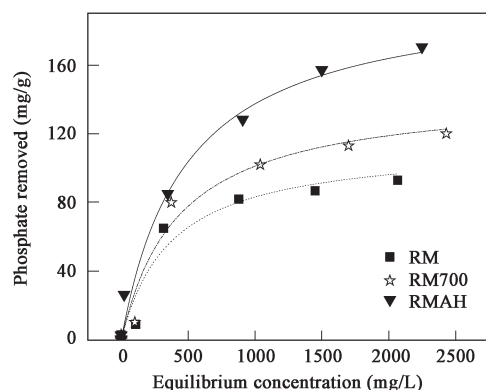


Fig. 4 Langmuir adsorption isotherm simulated the effect of equilibrium concentration on phosphate removal (reaction time is 4 h, temperature is 25°C). RM700 and RMAH are the same as that in Table 1.

The isotherm data were calculated from the least squares method and the values of the parameters of the Langmuir model and the related correlation coefficients (R^2) are listed in Table 2. The parameters indicate that the activated RM can enhance the phosphate removal effectively. The RMAH can achieve up to 202.9 mgP/g of the maximum adsorption capability, and the maximum adsorption capability of the RM700 is 155.2 mgP/g, whereas it is only 95.8 mgP/g for the RM. As for the related correlation coefficients of samples, they are 0.96, 0.99 and 0.99 for the RM, RM700 and RMAH, respectively. The results show that the Langmuir equation simulates the sorption equilibrium data well. The trend indicates that chemisorption is taking place in the system.

Table 2 Langmuir parameters of phosphate adsorption by the activated red mud (RM)

Sample	X_m (mg/g)	k	R^2
RM	95.86	0.0027	0.96
RM700	155.20	0.0035	0.99
RMAH	202.93	0.0021	0.99

2.4 Effect of pH on the phosphate removal

The phosphate removal by the activated red mud is shown in Fig.5 when pH was 1, 3, 5, 7, 9 and 11, and the pH of the solution was also determined after the phosphate removal by the activated red mud (Fig.6). The phosphate removal of the samples reaches maximum at pH 7, after that the removal of phosphate decreases with the increase of pH. A similar behavior was also reported for

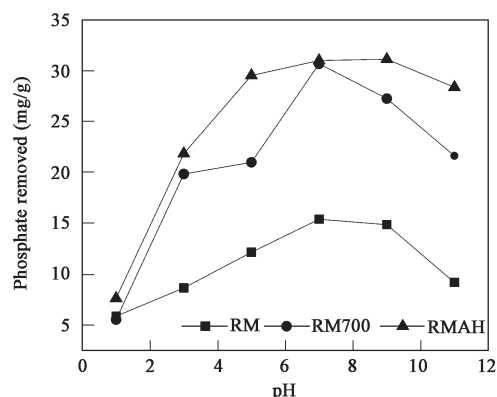


Fig. 5 Effect of pH on the phosphate removal by the activated red mud (RM). RM700 and RMAH are the same as that in Table 1.

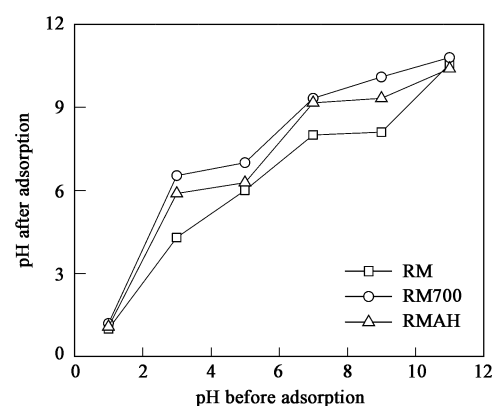


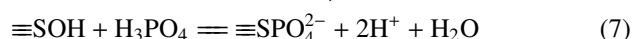
Fig. 6 pH of the solution after the phosphate removal by the activated red mud (RM). RM700 and RMAH are the same as that in Table 1.

the adsorption of anionic species from aqueous solution on the activated red mud (Pradhan *et al.*, 1999; Genç *et al.*, 2004). A ligand exchange mechanism took place in the sorption of phosphate onto the samples, and the sorption reaction may be written with the following ligand exchange reactions.

When the red mud was added into a solution, there exists such surface hydrolysis reactions depending on pH:



When phosphate exists in the solution, then these sorption reactions take place depending on pH:



Here, $\equiv\text{SOH}$ represent sample surface of the red mud. When the pH increased, the amount of H_3PO_4 decreased and the acidic phosphates (H_2PO_4^- , HPO_4^{2-}) were the predominant aqueous species (Stumm and Morgan, 1996). Since anion adsorption was coupled with a release of OH^- ions, the adsorption was favored at low pH values. When the pH increased above 7.0, a gradual decrease in the

percentage of adsorption was observed, it may be due to the competition between OH^- and phosphate ions.

3 Conclusions

The uptake of phosphate by the heat activated and acid-heat activated red mud was compared in this study and the factors influencing the red mud activation were investigated. The phosphate sorption capacity can be enhanced by the activation. In the heat activation process, the optimum activation was the red mud calcined at 700°C for 2 h, and in the acid-heat active process, the red mud activated at 80°C with 0.25 mol/L HCl for 2 h performed the best. The pH has a significant effect on phosphate sorption. At pH 7, the RMAH and RM700 achieved 31.0 and 30.7 mgP/g removal from solution with the initial phosphate concentration of 155 mgP/L. The Langmuir isotherm model indicated that the maximum sorption capacity of phosphate by the RMAH and RM700 was 202.9 mgP/g and 155.2 mgP/g.

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