

Phosphate removal from aqueous solutions on fly ash with medium calcium content

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Abstract—Excessive discharge of phosphate into water bodies may cause eutrophication and affect the natural water quality. The adsorption behavior of phosphate from aqueous solution on fly ash was investigated by a medium calcium fly ash in weak acid solution. Experimental findings showed that removal of phosphate was pH-dependent with the maximum adsorption capacity at the initial solution pH of 5.0-7.0. The increment in the initial phosphate concentration and temperature enhanced the adsorption capacity. Kinetic studies of phosphate followed the pseudo-second-order model. The predominant removal mechanism was ligand exchange reaction on the basis of desorption experiment. The adsorbed phosphate was difficult to leach to the environment from the waste fly ash.

Keywords: Fly Ash, Medium Calcium Content, Kinetics, Phosphate Removal Mechanism, Desorption

INTRODUCTION

Phosphate is essential for the growth of photosynthetic algae and cyanobacteria in the most ecosystems. However, excessive discharge of phosphate may cause eutrophication and subsequent deterioration of water quality [1]. Phosphate removal is important in the control of eutrophication of water bodies. Traditional biological treatments and chemical precipitation are generally suitable for phosphate removal with high concentration, while adsorption is comparatively more economical and highly effective in low phosphate concentrations.

In recent years, considerable attention has been paid to cheap and readily available adsorbents [2-8]. Fly ash is one of the major industrial solid wastes produced during the combustion of coal in the electricity generation process. Since fly ash is enriched with SiO₂ and contains a portion of unburned carbon, this waste possesses the potentiality of a low-cost adsorbent to remove various hazardous materials [6-11]. The results of batch and column experiments showed that fly ash is a good sorbent for removal of phosphate from wastewaters. Oguz [12] found the maximum phosphate sorption capacity of the fly ash was defined as 71.87 mg/g. Chen et al. [2] reported that the maximum phosphate adsorption of 15 Chinese fly ashes was in a range from 5.51 to 42.55 mg/g. The significant difference in the efficiency of phosphate removal among different fly ashes was attributed to the different calcium content in fly ash. Many documents reporting the removal of phosphate with fly ash were dominated by calcium-rich ash. The primary mechanism was the precipitation of phosphate with calcium ions in solution at elevated pH. However, the related literatures did not elucidate the immobilization of phosphate on fly ash with medium or low calcium. In this paper, we tried to elucidate the removal mechanism

of phosphate on medium calcium ash by desorption experiments.

MATERIALS AND METHODS

1. Adsorbents Characterization

Raw coal fly ash was collected at the electrostatic precipitator in a full-scale power-plant in China. The chemical compositions of the sample mainly contained SiO₂ (47.2%), Al₂O₃ (27.2%), Fe₂O₃ (15.7%) and CaO (4.5%) (obtained from the plant). Raw fly ash dried at 105 °C overnight was sieved under different particle size. Fly ash particles with size ranging from 75 to 96 μm were collected and pretreated in a furnace at 350 °C for 30 minutes, and kept in a desiccator for further adsorption study.

The surface area and total pore volume of the fly ash were measured through N₂ adsorption at -196 °C using a TRISTAR-3000 surface area analyzer (Micromeritics). They were 2.04 m²/g and 0.012 cm³/g, respectively. pH of zero charge (pH_{pzc}=8.4) of the sample was determined using pH drift method by a PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co. LTD.) [10].

2. Adsorption Study

The synthetic wastewaters were prepared by dissolving phosphate (potassium dihydrogen phosphate) in de-ionized water to produce a stock solution of 1 g/L. In the adsorption study, the phosphate solutions with P concentration ranging from 5 to 50 mg/L were prepared from the stock solution. Batch experiments were carried out by agitating 100 mL of phosphate solution and 0.6 g of fly ash in a 250 mL conical flask. After stirring, the suspensions were separated by centrifugation. The residual concentration of phosphate solution was determined measured using the molybdenum blue spectrophotometric method with a UV-2102PC uv-visible spectrometer (Uicol Instrument Co., Ltd.) [13]. The effect of solution pH on phosphate removal was investigated similarly as described above by changing the initial pH (2-12) adjusting by dilute HCl or NaOH. All experiments were conducted for three times and were found reproducible.

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3. Desorption Study

About 1.0 g of phosphate-loaded adsorbent was added to 100 mL of solution and the mixtures were stirred at 150 rpm for three days. Samples were separated by centrifugation and phosphate was recycled. The solutions included de-ionic water, 0.5 mol/L HCl, 0.5 mol/L NaOH, dilute hydrochloric acid (pH=5) and dilute alkali (pH=9).

4. Error Analysis

The optimization procedure required error indicators to be defined to evaluate the validity of the isotherm and kinetics model to the experimental data. The correlation coefficient (r^2) is used widely to determine the model parameters in phosphate adsorption process. In addition, root mean square error (RMSE) was defined to evaluate these models:

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (q_{exp} - q_{cal})^2}{N}} \quad (1)$$

where q_{exp} and q_{cal} are the experimentally measured and model prediction for the amount of phosphate adsorbed, respectively. Smaller RMSE represents that data from the model is similar to the experimental value, whereas larger value points out the difference between them.

RESULTS AND DISCUSSION

1. Effect of pH and Ionic Strength

Solution pH is an important factor controlling the surface charge of the adsorbent and the degree of ionization of the materials in the solution [14]. The pH was varied from 2.5 to 12.0 at different ionic strength to determine its effect on phosphate removal. Fig. 1 illustrates the effect of the initial solution pH and ionic strength on phosphate removal. It is clear that the removal of phosphate was maximum at initial pH of 5.0-7.0 and decreased above and below this pH.

The effect of pH values on the phosphate removal was explained by a complex mechanism. Because the pK_{a1} and pK_{a2} of phosphate were 2.2 and 7.2 [15], HPO_4^{2-} and $H_2PO_4^-$ were the main ionic species in pH range of 2.5-12.0. The surface of fly ash was positively charged ($pH_{pzc}=8.4$) due to high hydrolysis reaction of the surface of

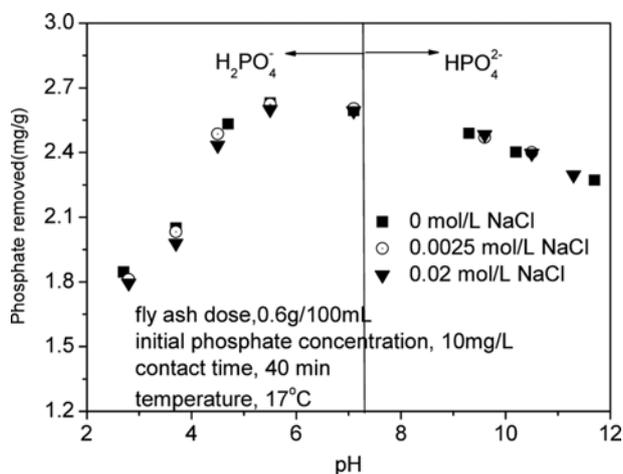


Fig. 1. Effect of pH and ionic strength on phosphate removal.

Fe_2O_3 and Al_2O_3 at the optimum pH of 5.0-7.0, while the predominant ionic of phosphate was $H_2PO_4^-$. Dominant anionic $H_2PO_4^-$ acted as two hydrogen bond donors as well as two hydrogen bond acceptors. In this pH range it formed strong intermolecular O-H...O type hydrogen bond on the surface of fly ash (ligand exchange adsorption). Moreover, the electrostatic attraction between fly ash and anionic phosphate favored the efficient high removal of phosphate.

At acid solution, the phosphate removal reduced with decreasing the pH value. This reduction could be attributed the competitive adsorption of hydrogen ion, which decreased the ligand exchange adsorption of phosphate on surface of metal oxide. In addition, precipitation of calcium rapidly decreased in acid solution. All resulted in the quick decrement of phosphate removal. When pH increased at basic solution (pH>8.4), the surface of fly ash was negatively charged and the predominant ionic of phosphate was HPO_4^{2-} . The strong electrostatic repulsion interaction between fly ash and phosphate hindered the adsorption of HPO_4^{2-} on fly ash. Precipitation reaction was an important mechanism on removal of phosphate on fly ash in alkali solution. However, the low calcium (with CaO content of 4.5%) failed to favor to the precipitation of calcium with HPO_4^{2-} in high basic solution. These results led to the decreasing of phosphate removal with the increment of pH in basic solution. Due to the ligand exchange between phosphate and hydroxide groups on the surface of fly ash, a relatively high removal efficiency was acquired in basic solution.

Fig. 1 shows that the ionic strength (with NaCl as electrolyte) had little effect on the removal of phosphate, which revealed the physical interaction was not the preferential removal mechanism.

2. Adsorption Kinetic

The effect of contact time for the removal of phosphate was studied for 120 min (Fig. 2). The initial adsorption of phosphate on fly ash was very rapid in the first 10 minutes, and then the phosphate adsorption rate gradually increased with the prolongation of contact time. After 40 minutes of contact, the removal of phosphate acquired the maximum value. Based on these results, forty minutes was taken as the equilibrium time in batch adsorption experiments.

To understand the comprehensive adsorption mechanisms and interactions of phosphate onto fly ash, the pseudo-first and sec-

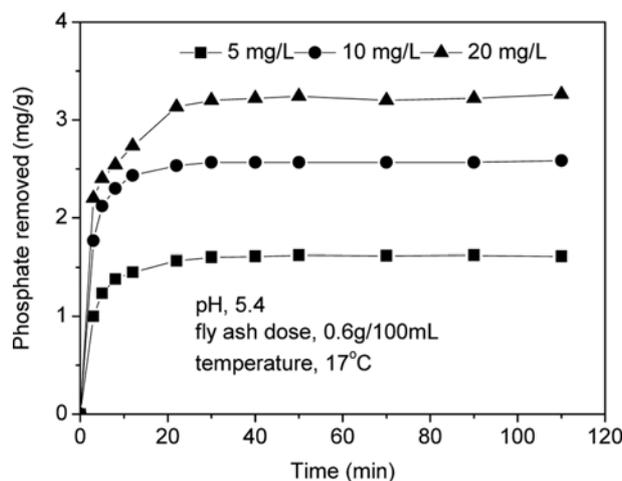


Fig. 2. Effect of contact time on phosphate removal.

Table 1. Adsorption rate constants of the first and second-order kinetic

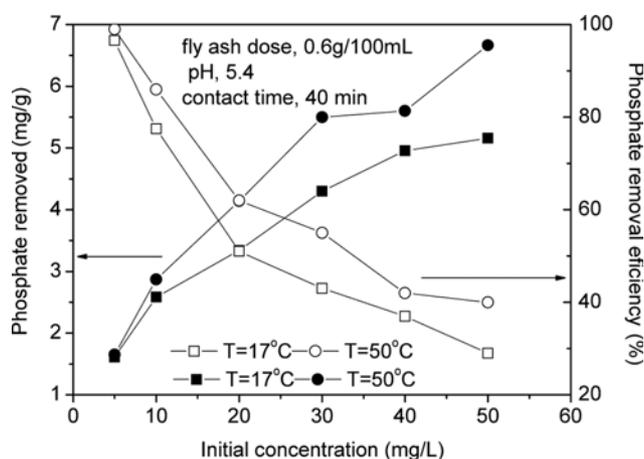
		5 mg/L	10 mg/L	20 mg/L
First-order kinetic modal	q_{exp} (mg/g)	1.670	2.584	3.340
	q_{cal} (mg/g)	1.591	2.544	3.382
	k_1 (1/min)	0.297	0.693	0.751
	r^2	0.991	0.995	0.956
	RMSE	0.042	0.172	0.372
Second-order kinetic modal	q_{cal} (mg/g)	1.673	2.647	3.382
	k_2 (g/(mg·min))	0.540	0.752	0.500
	r^2	0.997	0.997	0.990
	RMSE	0.021	0.047	0.086

ond-order kinetic adsorption models were employed to analyze these data. The pseudo-first and second-order kinetic models are the most common models to study the adsorption kinetics on fly ash. The two equations are given by Eq. (2) and (3).

$$q = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q = \frac{k_2 q_e t}{1 + k_2 t} \quad (3)$$

where q (mg/g) is the amount of material adsorbed at time t , q_e (mg/g) is the adsorption capacity at equilibrium, k_1 (1/min) and k_2 (g/(mg·min)) represent the rate constant of the first-order model and second-order model. Batch dynamic parameters were obtained using non-linear regression analysis (MATLAB 7.5) and shown in Table 1. The correlation coefficients for the first-order and second-order kinetics were very similar at the concentration of 5 and 10 mg/L. The r^2 values of second-order were higher than that of the first-order model in the solution with 20 mg/L. However, the relatively lower RMSEs (RMSE=0.021-0.086) in the second-order model were obtained in all ranges of initial phosphate concentrations. All the results indicated the second-order kinetic model well fitted the experiment data. Based on the pseudo-second-order model, these observations indicated that the rate of phosphate adsorption process was controlled by the chemisorption process, which depended

**Fig. 3. Effect of initial concentration and temperature on phosphate removal.**

on the chemical character of fly ash and phosphate [10].

3. Effect of Initial Concentration and Temperature

The removal experiments were performed in a phosphate concentration range of 5-50 mg/L at 17 and 50 °C. The effect of the initial concentration and temperature on the removal is presented in Fig. 3. As the initial concentration increased, the phosphate removal efficiency decreased from >95% to <40%. By comparison, the phosphate adsorption capacities increased with the increment of the initial concentration.

Also, increasing adsorption temperature intensified phosphate adsorption, especially at higher concentration. When the adsorption temperature increased from 17 to 50 °C, phosphate capacities were increased from 1.61 to 1.65 mg/g for the initial phosphate concentration of 5 mg/L and from 5.16 to 6.67 mg/g for the initial phosphate concentration of 50 mg/L. These results suggested that the process is endothermic.

4. Desorption of Phosphate

To determine the predominant removal mechanisms, adsorbent samples were extracted after equilibrium. In water solution, the desorption efficiency was only 3.13%, indicating the loose physical adsorption by weak bond was not the dominant form of phosphate removal [16]. In case of 0.5 mol/L HCl, the desorption phosphate was denoted precipitation fractionation with calcium ions in solution [2]. The value was 18.46%, which revealed that precipitation was one of the removal mechanisms. Very high desorption of phosphate (51.59%) was found in sodium hydroxide solution. In strong basic solution, hydroxyl ion was exchanged with the phosphate on the surface of fly ash, resulting in the breakage of ligand bond between phosphate and fly ash. This fact suggested the ligand exchange reaction was the predominant mechanism [6]. In addition, the desorption rate of phosphate was about 6.47% in dilute hydrochloric acid and 7.89% in dilute alkali. These results indicated that the phosphate was difficult to leach to the environment from the waste fly ash.

CONCLUSIONS

The removal of phosphate on fly ash was investigated by batch experiments. Adsorption of phosphate was found to be dependent on the initial pH of solution and was maximum at initial pH of 5.0-7.0. The phosphate adsorption amount increased with the incremental initial concentration and the experiment temperature. Desorption of phosphate suggested the predominant removal mechanism was ligand exchange reaction. The adsorbed phosphate was difficult to leach to the environment from the waste fly ash in near neutral solution.

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