

## Removal of phosphate from coating wastewater using magnetic Fe-Cu bimetal oxide modified fly ash

Ke Xu, He Tao and Tong Deng

### ABSTRACT

In this work, magnetic Fe-Cu bimetal oxide modified fly ash was used to remove phosphate from coating wastewater. The influences of pH, dosage amount and adsorption time on the removal of phosphate were investigated. The experimental results showed that pH had a significant effect on the adsorption of phosphate. The removal percentage of phosphate reached a maximum at pH 10. The removal efficiency of phosphate increased with the increase in adsorbent dosage. A kinetic study showed that the phosphate adsorption was well described by a pseudo second order model. The adsorption isotherm of phosphate could be described by the Langmuir model and Freundlich model. The Langmuir maximum capacity  $Q_0$  was 12.69 mg/g and the value of  $n$  of the Freundlich model was 3.82. The experimental results indicated that magnetic Fe-Cu bimetal oxide modified fly ash was a potential adsorbent for the removal of phosphate from the wastewater.

**Key words** | adsorption, fly ash, magnetic Fe-Cu bimetal oxide, modification, phosphate, removal

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### INTRODUCTION

As a main nutrient, phosphate is essential for the growth of organisms in most ecosystems. However excessive amounts of phosphate may cause eutrophication of surface waters (Carpenter 2005). Thus it is necessary to reduce phosphate for eutrophic water. Environmental researchers have proposed and applied many phosphate removal methods including chemical precipitation (de-Bashan & Bashan 2004), physicochemical processes (Mishra *et al.* 2010) and enhanced biological P removal (Gouider *et al.* 2011). Among these techniques, adsorption is known to be more useful and economical. Many materials have been used as adsorbents for removal of phosphate. These adsorbents include fly ash (Pengthamkeerati *et al.* 2008; Lu *et al.* 2009; Xu *et al.* 2010), red mud (Huang *et al.* 2008; Zhao *et al.* 2009; Yue *et al.* 2010), aluminum hydroxide (Guan *et al.* 2007; Yang *et al.* 2007; Kawasaki *et al.* 2010), iron oxide (Persson *et al.* 1996; Zeng *et al.* 2004; Rentz *et al.* 2009; Wu *et al.* 2011), zirconium oxide (Chitrakar *et al.* 2006; Biswas *et al.* 2008; Liu *et al.* 2008; Zheng *et al.* 2009) and manganese dioxide (Mustafa *et al.* 2006). An innovative

technology that has gained increasing attention involves solid-liquid separation and employs adsorbents with magnetic properties. Magnetic separation is now widely used in many fields (Ren *et al.* 2008; Zhang *et al.* 2008). In this study we attempted to use magnetic Fe-Cu bimetal oxide modified fly ash for the removal of phosphate from zinc phosphate coating wastewater. Zinc phosphate is a crystalline coating that is formed on a metal substrate. It is mainly used for the surface treatment of metal surfaces due to its corrosion resistance and wear resistance. The zinc phosphate coating process plays a significant role in automotive and outdoor applications. However, the presence of phosphate in the process wastewater leads to pollution when discharged directly into the environment. Hence, the removal of phosphate is necessary to meet the discharge limit in order to control eutrophication. This study used batch adsorption experiments to investigate the influence of pH, dosage amount, and adsorption time on the removal of phosphate from the coating wastewater using magnetic Fe-Cu bimetal oxide modified fly ash. The

kinetics of the adsorption and the adsorption isotherms were also studied.

## MATERIALS AND METHODS

### Materials and reagents

The fly ash used in this work was obtained from a coal-burning power plant. The wastewater was obtained from the zinc phosphate coating process of an automotive assembly plant. The phosphate concentration in the wastewater was 9.94 mg/L. The chemicals and reagents used in this work were of analytical reagent grade. Deionized water was used for preparing solutions.

### Preparation of magnetic Fe-Cu bimetal oxide modified fly ash

The Fe-Cu bimetal oxide modified fly ash was prepared according to the following procedure: 1 mol/L iron(II) sulfate heptahydrate and 1 mol/L copper sulfate pentahydrate was mixed in the molar ratio of 2:1, a given amount of fly ash was added into the solution, the slurry was heated to 70 °C, 3 mol/L NaOH was slowly added under vigorous stirring until the pH reached 11. The mixture was then aerated uniformly by pumping air through porous glass to promote an oxidization reaction; the precipitate showed magnetism during the oxidization. Then the precipitate was filtrated and dried at 70 °C. The dry material was ground and used for the removal of phosphate.

### Sorption studies

A sorption experiment was carried out to measure phosphate removal by the magnetic Fe-Cu bimetal oxide modified fly ash. The adsorbent was added to phosphate-containing wastewater, the pH was adjusted to a given value, then the mixture was shaken for various times at 25 °C. After being shaken, the mixture was magnetically separated, and the residual phosphate concentration in the solution was measured spectrophotometrically using the molybdenum-blue ascorbic acid method. The experiments

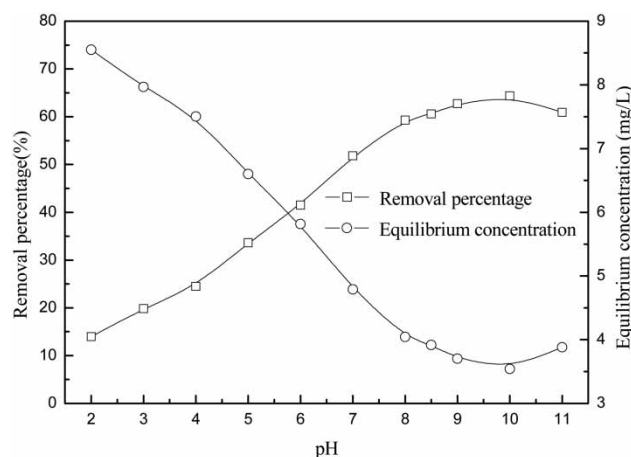
were duplicated under identical conditions, and average values were calculated and used.

## RESULTS AND DISCUSSION

### Effect of pH on the removal of phosphate

The effect of pH on the removal of phosphate is shown in Figure 1.

From Figure 1 it can be seen that when the pH increased from 2 to 8 the removal percentage of phosphate increased significantly from 13.97 to 59.31%, and the residual phosphate concentration in the treated water decreased from 8.55 to 4.04 mg/L. Then the removal percentage of phosphate increased gradually with the increase in pH until the removal percentage of phosphate reached the maximum 64.37% at a pH of 10. When the pH exceeded 10, the removal percentage of phosphate decreased with the increase in pH. In practical application, the pH of the treated wastewater should meet the requirement of the wastewater discharge standard. According to the wastewater discharge standard, the pH range of the discharged water must be 6 to 9. Considering these factors, a pH of 8.5 was used for the subsequent experiments. At this pH the removal percentage of phosphate was 60.57%, which was slightly less than the maximum.



**Figure 1** | Effect of pH on phosphate removal (initial concentration 9.94 mg/L, adsorbent dosage 0.05 g/100 ml, 2 h, 25 °C).

## Effect of adsorbent dosage on the removal of phosphate

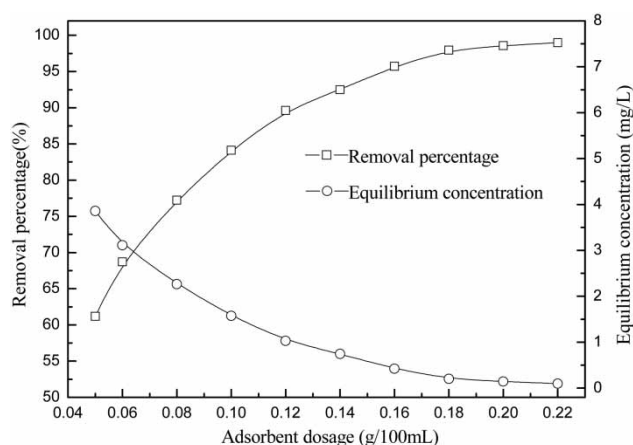
The effect of adsorbent dosage on the removal of phosphate is shown in Figure 2.

From Figure 2, it can be seen that when the adsorbent dosage increased from 0.05 g/100 ml to 0.18 g/100 ml, the removal percentage of phosphate increased significantly from 61.18 to 97.97%, and the residual concentration of phosphate decreased from 3.86 to 0.202 mg/L. After the adsorbent dosage exceeded 0.18 g/100 ml, the removal percentage of phosphate increased slowly with the increase of adsorbent dosage. The experimental results indicated that the optimum adsorbent dosage for phosphate removal was 0.18 g/100 ml; at this adsorbent dosage the residual concentration of phosphate was 0.202 mg/L. This was less than 0.5 mg/L, the maximum allowable loading for the first-rate criterion required by the Integrated Wastewater Discharge Standard.

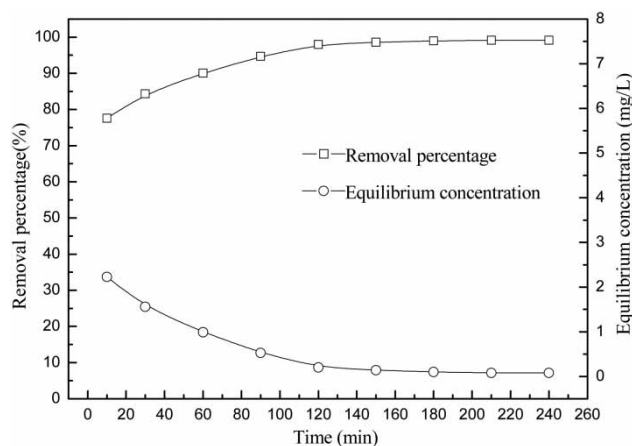
## Effect of contact time on the removal of phosphate

The effect of contact time on the removal of phosphate is shown in Figure 3.

From Figure 3, it can be seen that the process of phosphate adsorption showed two different steps. In the first step, a rather fast uptake of phosphate occurred within 120 min and the adsorption percentage of phosphate reached 97.97%, with the residual concentration of phosphate decreasing to 0.202 mg/L. The first step was then



**Figure 2** | Effect of adsorbent dosage on phosphate removal (initial concentration 9.94 mg/L, 2 h, pH 8.5, 25 °C).



**Figure 3** | Effect of contact time on the phosphate removal (initial concentration 9.94 mg/L, adsorbent dosage 0.18 g/100 ml, pH 8.5, 25 °C).

followed by a relatively slow stage until the adsorption of phosphate reached equilibrium when the contact time was 210 min.

In order to further understand the characteristics of the absorption process, the pseudo first order equation (Equation (1)), pseudo second order equation (Equation (2)), and intraparticle diffusion model (Equation (3)) were used to fit experimental data obtained from the adsorption experiments.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

$$q_t = k_i t^{0.5} + C \quad (3)$$

where  $q_e$  and  $q_t$  are the adsorption capacity of the adsorbate (mg/g) at equilibrium and at time  $t$  (min);  $k_1$  and  $k_2$  are the pseudo first order and pseudo second order rate constants,  $k_i$  is the intraparticle diffusion rate constant and  $C$  is the intercept. The linear fit results of the three kinetic models are shown in Table 1.

Of the three kinetic equations tested, the pseudo second order model was the most suitable in describing the adsorption kinetics of phosphate on the adsorbent. The calculated kinetic parameter  $k_2$  was 0.027 g/min/mg, the calculated adsorption capacity at equilibrium  $q_{ecal}$  was 6.776 mg/g and the experimental adsorption capacity at equilibrium

**Table 1** | Characteristic parameters and determination coefficient of kinetic data of phosphate adsorption according to the three models

Pseudo first order				Pseudo second order				Intraparticle diffusion		
$k_1$	$q_{ecal}$	$q_{eexp}$	$r^2$	$k_2$	$q_{ecal}$	$q_{eexp}$	$r^2$	$k_i$	$C$	$r^2$
0.028	2.505	6.612	0.981	0.027	6.776	6.612	1	0.119	5.008	0.901

$q_{eexp}$  was 6.612 mg/g. The  $q_{eexp}$  was similar to  $q_{ecal}$ . This also suggested that the experiment results fitted better with the pseudo second order model.

The pseudo first order and pseudo second order kinetic models cannot identify the adsorption mechanism, and the intraparticle diffusion model is commonly used to characterize the sorption process. According to this model, if the rate limiting step is diffusion of adsorbate within the pores of the adsorbent particle, a graph between the amount of adsorbate adsorbed and the square root of time should give a straight line passing through the origin. When the plots do not pass through the origin, this is indicative of some degree of boundary layer diffusion control, and intraparticle diffusion is not the only rate-limiting step. The linear fit plot of the kinetic data in this experiment, according to the intraparticle model, did not pass through the origin ( $C = 5.008$ ), which revealed that the adsorption of phosphate on the modified fly ash was a complex process involving boundary layer diffusion, intraparticle diffusion and surface adsorption. In phosphate adsorption, the initial rapid adsorption might be attributed to the diffusion of phosphate through the solution to the external surface of the adsorbent by electrostatic attraction, or the boundary layer diffusion of solute molecules. The following slow adsorption indicated that intraparticle diffusion was the dominant mechanism of phosphate adsorption.

The adsorption rate of this adsorbent was relatively moderate when compared with other adsorbents reported in the literature. For example, the equilibrium time of this adsorbent was 3.5 h, while the time required to reach equilibrium was 6 h in the removal of phosphate using hydroxy-aluminum pillared bentonites (Yan *et al.* 2010) and phosphate sorption reached equilibrium at 24 h when using magnetic iron oxide nanoparticles (Yoon *et al.* 2014). However, the adsorption rate of this adsorbent was relatively slower when compared with ground burnt patties, which reach adsorption equilibrium at 40 min (Rout *et al.* 2014).

## Sorption isotherms

The phosphate adsorption isotherm is shown in Figure 4. From Figure 4 it can be seen that the phosphate adsorption capacity increased considerably with the increase in phosphate concentration. This indicates that the adsorbent had a high affinity for the phosphate, and that phosphate could be effectively removed from solution. The isotherm data on phosphate adsorption were fitted to Langmuir and Freundlich equations.

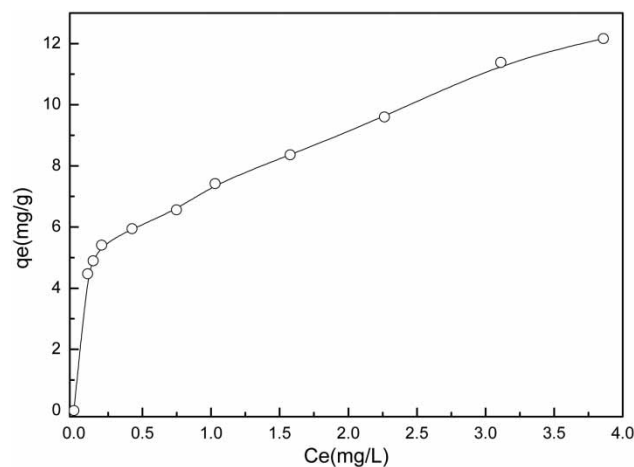
Langmuir equation:

$$C_e/q_e = 1/(Q_0)C_e + 1/(Q_0 \cdot K_L) \quad (4)$$

where  $q_e$  is the amount of phosphate adsorbed per unit of sorbent (mg/g),  $C_e$  is the phosphate concentration in equilibrium solution (mg/L),  $Q_0$  is the Langmuir maximum capacity (mg/g), and  $K_L$  is a constant related to the binding strength of phosphate.

Freundlich equation:

$$\ln q_e = (1/n) \ln C_e + \ln K_f \quad (5)$$

**Figure 4** | Phosphate adsorption isotherm of the modified fly ash.

where  $K_f$  and  $n$  are constants related to the adsorption capacity and the energy of adsorption.

Linearized forms of the Langmuir and Freundlich isotherms for phosphate adsorption are shown in Figure 5, and Equations (6) and (7).

Langmuir equation,  $r^2 = 0.964$ :

$$c_e/q_e = 0.0788c_e + 0.0367 \quad (6)$$

Freundlich equation,  $r^2 = 0.965$ :

$$\ln q_e = 0.2615 \ln c_e + 2.0599 \quad (7)$$

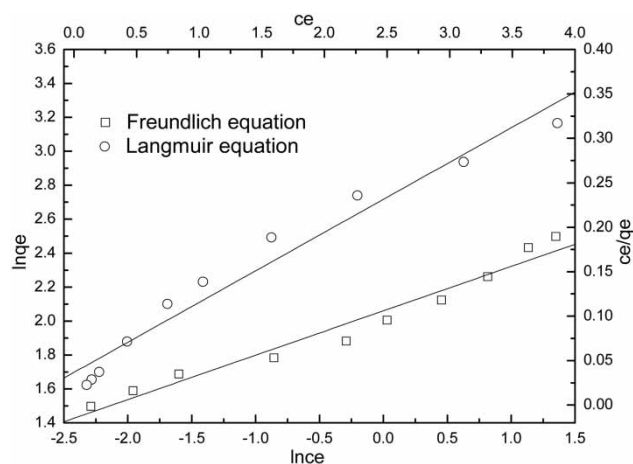
The  $Q_0$  and  $K_L$  values for the Langmuir isotherm, the  $K_f$  and  $n$  values for the Freundlich isotherm and the regression coefficients of the equations are shown in Table 2.

It can be seen that the adsorption data fitted well with the Langmuir model and the Freundlich model. The Langmuir maximum capacity  $Q_0$  was 12.69 mg/g. The value of

$n$  of the Freundlich model was 3.82. These results indicate effective adsorption of phosphate by the modified fly ash.

### Comparison with other adsorbents for removal of phosphate

Many kinds of adsorbents have been used to remove phosphate from wastewater. To illustrate the potential in the use of the modified fly ash for removal of phosphate from wastewater, a comparative evaluation of the adsorption capacities of various phosphate adsorbents reported in the literature are presented in Table 3. From Table 3 it can be seen that the phosphate sorption capacity of the modified fly ash was slightly lower than that of metal-loaded orange waste and is almost equivalent to that of hydroxy-aluminum pillared bentonite. The phosphate sorption capacity of the modified fly ash was relatively greater than that of magnetic biochar, magnetic iron oxide,  $\text{ZnCl}_2$ -activated carbon, ground burnt patties and zeolite. The results indicate that modified fly ash is a potential adsorbent for the removal of phosphate.



**Figure 5** | Linearized form plot of Freundlich and Langmuir isotherms for phosphate adsorption on the modified fly ash.

**Table 2** | The  $Q_0$  and  $K_L$  values for the Langmuir isotherm, the  $K_f$  and  $n$  values for the Freundlich isotherm and the regression coefficients of equations

Langmuir			Freundlich		
$Q_0$ (mg g <sup>-1</sup> )	$K_L$ (l mg <sup>-1</sup> )	$r^2$	$K_f$	$n$	$r^2$
12.69	2.15	0.964	7.85	3.82	0.965

### CONCLUSIONS

In this work, magnetic Fe-Cu bimetal oxide modified fly ash was used to remove phosphate from coating wastewater. The influences of pH, dosage amount and adsorption time

**Table 3** | Phosphate adsorption by different adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
Modified fly ash	12.69	Present study
Magnetic biochar	1.24	Chen <i>et al.</i> (2011)
Magnetic iron oxide	5.03	Yoon <i>et al.</i> (2014)
$\text{ZnCl}_2$ -activated carbon	5.1	Namasivayam & Sangeetha (2004)
Hydroxy-aluminum pillared bentonite	12.7	Yan <i>et al.</i> (2010)
Metal-loaded orange waste	14	Biswas <i>et al.</i> (2007)
Ground burnt patties	0.41	Rout <i>et al.</i> (2014)
Zeolite	2.15	Sakadevan & Bavor (1998)

on the removal of phosphate were investigated. The experimental results showed that pH had a significant effect on the adsorption of phosphate. The removal percentage of phosphate reached a maximum at pH 10. The removal efficiency of phosphate increased with the increase in adsorbent dosage. Kinetic study showed that the phosphate adsorption was well described by a pseudo second order model. The adsorption isotherm of phosphate could be described by the Langmuir model and Freundlich model. The Langmuir maximum capacity  $Q_0$  was 12.69 mg/g and the value of  $n$  of the Freundlich model was 3.82. The experimental results indicated that the magnetic Fe-Cu bimetal oxide modified fly ash was a potential adsorbent for the removal of phosphate from wastewater.

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