



Study on Phosphate Removal from Aqueous Solution Using Fe-Mn-Zn Trimetal Oxide Modified Fly Ash

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ABSTRACT

In this work the adsorption of phosphate using the Fe-Mn-Zn trimetal oxide modified fly ash was studied. The experimental results showed that the adsorbent could effectively remove phosphate in the pH range 4 to 9 and the maximum phosphate adsorption was at pH 8.0. Kinetic study showed that the phosphate adsorption was well described by pseudo-second-order model. The removal efficiency of phosphate increased with the increase of adsorbent dosage and the decrease of the initial concentration. The adsorption of phosphate could be well described by Langmuir isotherm, the Langmuir constant Q_0 was 19.22mg/g. Comparative phosphate adsorption study of the untreated fly ash and the modified fly ash showed that modification with Fe-Mn-Zn trimetal oxide could significantly enhance the phosphate adsorption of the fly ash. The Fe-Mn-Zn trimetal oxide modified fly ash was a potential adsorbent for the removal of phosphate from aqueous systems.

INTRODUCTION

Phosphorus is an essential resource and material, it is widely used in the areas of agriculture and industry. However, if the amounts of phosphate supply to water is excessive, eutrophication of water bodies may happen. Therefore, the removal of phosphate from waters is an effective method for the control of eutrophication in natural waters. The main methods used for phosphate removal are chemical precipitation, biological treatment and adsorption. Chemical precipitation method is effective in the removal of phosphate. Lime, alum and ferric chloride are the common precipitants used for phosphate removal. However, the cost of the process is high and large amount of sludge is produced during the treatment of the wastewater. Biological treatment is widely used in the removal of organophosphorus chemicals in food and domestic wastewater. The disadvantages of this method is that it is sensitive to the variations in chemical composition and temperature of wastewater. Adsorption is a comparatively more useful and economical method for phosphate removal. In recent years, considerable attention has been paid to the investigation of different types of adsorbents, such as fly ash (Cheunga & Venkitachalamb 2000, Lu et al. 2009, Pengthamkeerati et al. 2008), red mud (Yue et al. 2010, Zhao et al. 2009), slag (Xue et al. 2009, Yang et al. 2009), aluminum hydroxide (Guan et al. 2007, Kawasaki et al. 2010, Yang et al. 2007), iron oxide (Persson et al. 1996, Rentz et al. 2009, Zeng et al. 2004), niobium oxide (Rodrigues & Silva 2010), zirconium oxide (Biswas et al. 2008, Chitrakar

et al. 2006, Liu et al. 2008) and manganese dioxide (Mustafa et al. 2006). Coal fly ash has been given great attention as a potential adsorption material for phosphate removal in recent years since it is easily available and cost-effective. However, the adsorption capacity of the fly ash was relatively low. In order to enhance phosphate adsorption we attempted to modified fly ash with Fe-Mn-Zn trimetal oxide and the modified fly ash was used to remove phosphate from aqueous solution. The influences of pH, dosage amount, adsorption time and the initial concentration on the removal of phosphate from the aqueous solution were investigated. In addition, 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 major phases of the fly ash were quartz, mullite, hematite and amorphous silicate. The main components of the fly ash were SiO_2 (56.81%), Al_2O_3 (23.37%), Fe_2O_3 (4.74%), CaO (9.32%), MgO (0.89%), K_2O (0.95%) and Na_2O (0.32%). The chemicals and reagents used in this work were of analytical reagent grade. Deionized water was used for preparing solutions. Stock solutions of phosphate was prepared by dissolving KH_2PO_4 in deionized water.

Preparation of Fe-Mn-Zn trimetal oxide modified fly ash: The Fe-Mn-Zn trimetal oxide modified fly ash was prepared according to the following procedure: 0.105 mol iron(II)

sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.03 mol zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and 0.06 mol manganese sulfate tetrahydrate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) were dissolved in deionized water, 15 g 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 slurry was aerated by pumping air through porous glass to promote an oxidization reaction and the precipitate showed magnetism during the oxidization. Then the precipitate was filtrated and dried at 70°C . The material was ground and used as adsorbent for the removal of phosphate.

Sorption studies: Sorption experiment was carried out to measure the phosphate removal by the Fe-Mn-Zn trimetal oxide modified fly ash. The adsorbent was added to phosphate solutions of varying concentration prepared from KH_2PO_4 stock solution. The pH was adjusted to a given value, then the mixture was shaken for various times at 25°C . After being shaken, the adsorbent was separated from the solution using a magnet and the residual phosphate concentration in the solution was measured spectrophotometrically using the molybdenum-blue ascorbic acid method.

RESULTS AND DISCUSSION

Effect of pH on the removal of phosphate: The effect of pH on the removal of phosphate is shown in Fig. 1. It could be seen that phosphate removal percentage fluctuated when the pH increased from 4 to 9. The removal of phosphate reached to the maximum 93.76% at the pH of 8 and the residual phosphate concentration of the treated water was 0.624 mg/L. From Fig. 1, it could also be seen that in the pH range of 4 to 9, the removal percentage of phosphate was above 90% and the residual phosphate concentration was less than 1 mg/L. The experiment results suggested that the adsorbent could effectively remove phosphate in a relatively wide pH range.

Effect of adsorbent dosage on the removal of phosphate: The effect of adsorbent dosage on the removal of phosphate is shown in Fig. 2. It could be seen that when the adsorbent dosage increased from 0.08 g/100mL to 0.16 g/100mL, the removal percentage of phosphate increased significantly from 65.28% to 94.32%, the residual concentration of phosphate decreased from 3.47 mg/L to 0.57 mg/L. After the adsorbent dosage exceeded 0.16 g/100mL, the removal percentage of phosphate increased gradually with the increase of adsorbent

dosage. From Fig. 2, it could also be seen that when the adsorbent dosage was 0.14 g/100mL, the removal percentage of phosphate reached 89.77%, the residual concentration was 1.02 mg/L which was close to 1.0 mg/L, the maximum allowable loading for second-rate criterion required by Integrated Wastewater Discharge Standard. In practice, the adsorbent dosage of 0.15 g/100mL was used for phosphate removal.

Effect of contact time on the removal of phosphate: The effect of contact time on the removal of phosphate is shown in Fig. 3. It could be seen from the figure that the rather fast uptake of phosphate occurred within 2 h. The adsorption percentage of phosphate could reach 93.72% at the contact time of 2h and the residual concentration of phosphate decreased to 0.63 mg/L. After the contact time exceed 2h, the removal percentage increased gradually. When the contact time was 3h the adsorption percentage of phosphate reached 95.18%, the residual concentration of phosphate decreased to 0.48 mg/L which was less than 0.5 mg/L, the maximum allowable loading for first-rate criterion required by Integrated Wastewater Discharge Standard. Fig. 3 also showed that the adsorption of phosphate reached equilibrium when the contact time was 3.5 h.

In order to further understand the characteristics of the absorption process, the pseudo-first-order equation (eq. 1) (Bulut & Tez 2003), pseudo-second-order equation (eq. 2) (Ho & McKay 2000) and intra-particle diffusion model (eq. 3) (Wu et al. 2009) were applied to fit experimental data obtained from the adsorption experiments.

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

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

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

The parameter 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 intra-particle diffusion rate constant and C is the intercept. The linear fit results of the three kinetic models are given in Table 1.

From Table 1, it could be found that of the three kinetic equations tested, the pseudo-second-order model was the most suitable in describing the adsorption kinetics of phos-

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

K_1	Pseudo-first-order			Pseudo-second-order				Intra-particle diffusion		
	q_{ecal}	q_{eexp}	r^2	k_2	q_{ecal}	q_{eexp}	r^2	k_i	C	r^2
0.0401	4.490	6.363	0.740	0.0378	6.473	6.363	0.999	0.0793	5.269	0.941

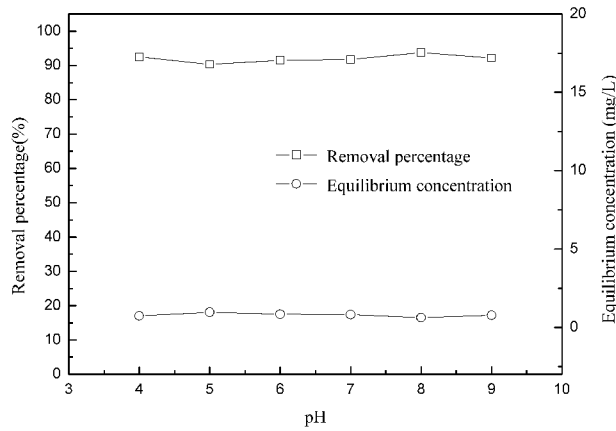


Fig. 1: Effect of pH on the phosphate removal (initial concentration 10mg/L, adsorbent dosage 0.15g/100mL, 2h, 25°C).

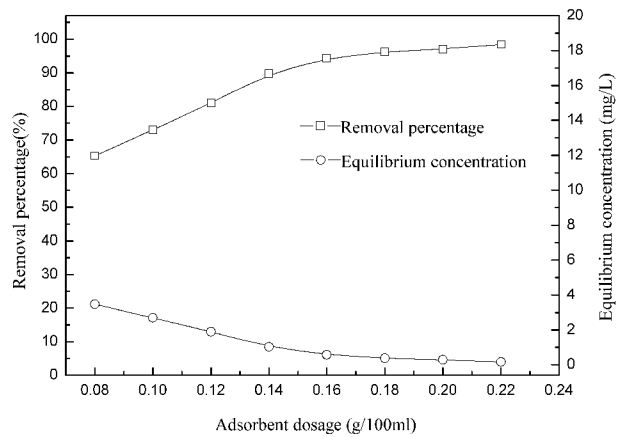


Fig. 2: Effect of adsorbent dosage on the phosphate removal (initial concentration 10mg/L, 2h, pH8.0, 25°C).

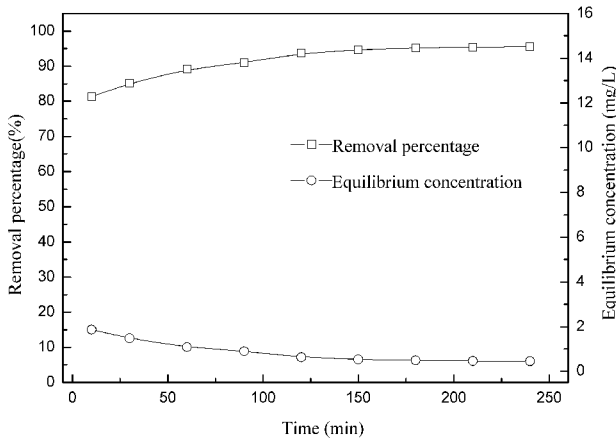


Fig. 3: Effect of contact time on the phosphate removal (initial concentration 10mg/L, adsorbent dosage 0.15g/100mL, pH 8.0, 25°C).

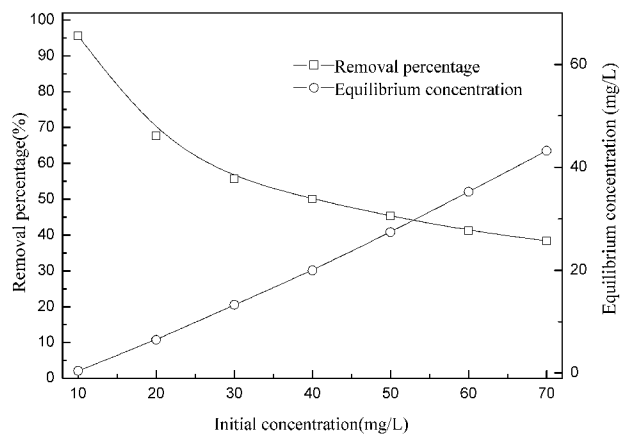


Fig. 4: Effect of initial concentration on the phosphate removal (adsorbent dosage 0.15g/100mL, pH 8.0, 3.5h, 25°C).

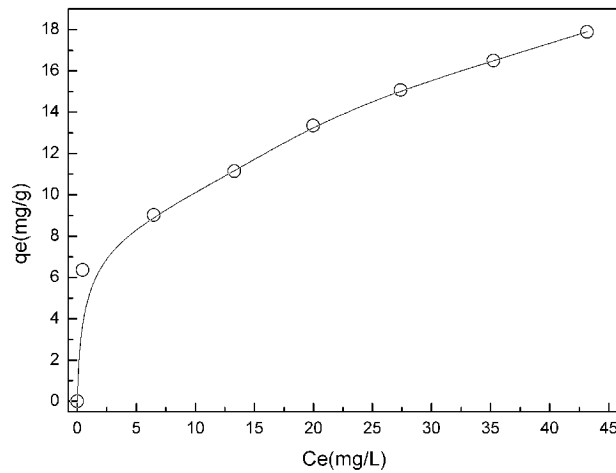


Fig. 5: Phosphate adsorption isotherm of the modified fly ash.

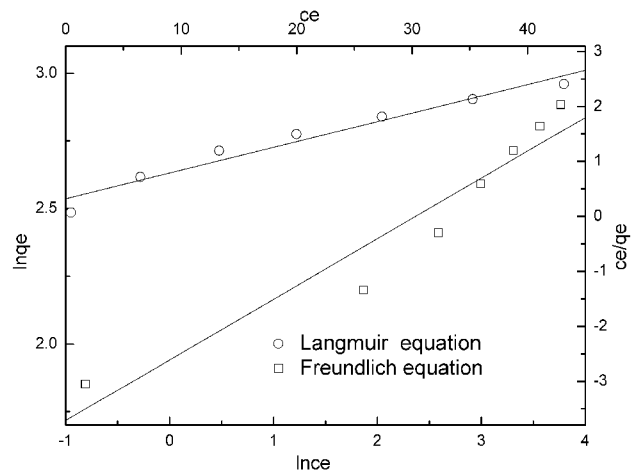


Fig. 6: Linearized form plot of Freundlich and Langmuir isotherms for phosphate adsorption on the modified fly ash.

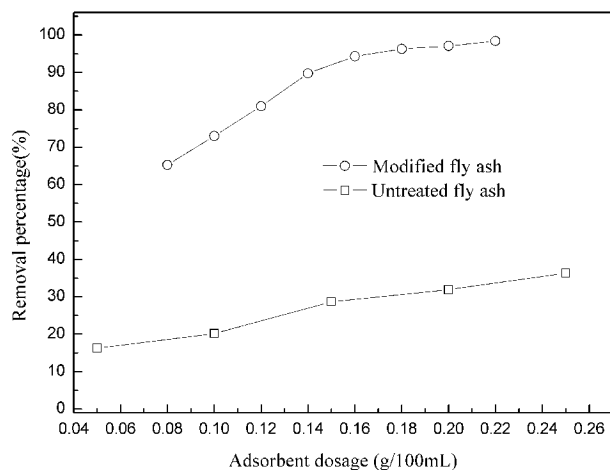


Fig. 7: Effect of adsorbent dosage on the phosphate removal of the untreated fly ash and the modified fly ash (initial concentration 10mg/L, 2h, pH8.0, 25°C).

phosphate adsorption on the modified fly ash. The calculated kinetic parameter k_2 was 0.0378 g/min/mg, the calculated adsorption capacity at equilibrium q_{ecal} was 6.473 mg/g and experimental adsorption capacity at equilibrium q_{eexp} was 6.363 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.

Effect of initial concentration on the removal of phosphate: The effect of initial concentration on the removal of phosphate is shown in Fig. 4. It was found that the adsorption of phosphate on the modified fly ash was strongly dependent on the initial concentration. As seen in Fig. 4, the percentage of adsorption decreased when initial concentration of phosphate increased. This decrease of phosphate adsorption may be attributed to the fact that at higher phosphate concentration, the number of active sites on adsorbent surface were not enough to accommodate phosphate ions. However, at low phosphate concentration, the ratio of surface active sites to total phosphate were high and therefore phosphate ions could interact with the active sites on adsorbent surface sufficiently.

Sorption isotherms: The phosphate adsorption isotherm of the modified fly ash is shown in Fig. 5. It could be found that the phosphate adsorption capacity considerably increased with the increase of phosphate concentration. This indicated that the modified fly ash had a high affinity for the phosphate and that phosphate could be effectively removed from solution. The isotherm data of phosphate adsorption were fitted to Langmuir and Freundlich equations.

Langmuir equation :

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

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

Freundlich equation:

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

Where K_f and n are constants related to adsorption capacity and energy of adsorption.

Linearized forms of Langmuir and Freundlich isotherms for the phosphate adsorption on the modified fly ash are shown in Fig. 6, eq. 6 and eq. 7.

Langmuir equation, $r^2 = 0.9526$

$$c_e/q_e = 0.3208 + 0.0523c_e \quad \dots(6)$$

Freundlich equation, $r^2 = 0.9090$

$$\ln q_e = 1.9411 + 0.2238 \ln c_e \quad \dots(7)$$

It could be seen that adsorption data of phosphate by the modified fly ash fitted better with Langmuir model. The Langmuir constant Q_0 was 19.22mg/g.

Effect of modification on the phosphate removal by the fly ash: In order to investigate the effect of modification on the phosphate removal by the fly ash, the phosphate removal percentage at different adsorbent dosage by the modified fly ash and the untreated fly ash was compared. The experiment results are shown in Fig. 7.

From Fig. 7 it could be found that for the modified fly ash and the untreated fly ash the phosphate removal percentage all increased with the increase of adsorbent dosage, but the phosphate removal percentage by the modified fly ash was higher than that of the untreated fly ash when the adsorbent dosage was same. The experiment results suggested that modification could significantly enhance the adsorption ability of the fly ash.

CONCLUSIONS

From the experimental results in this work, the following conclusions could be drawn:

1. The modified fly ash could effectively remove phosphate in the pH range of 4 to 9 and the maximum phosphate adsorption was at pH 8.0.
2. Kinetic study showed that the phosphate adsorption was well described by pseudo-second-order model.
3. The removal efficiency of phosphate increased with the increase of adsorbent dosage and the decrease of the initial concentration.

4. The adsorption of phosphate could be well described by Langmuir isotherm, the Langmuir constant Q_0 was 19.22mg/g.
5. Modification with Fe-Mn-Zn trimetal oxide could significantly enhance the phosphate adsorption of the fly ash.

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