



Sulphuric Acid Modification of Fly Ash for Enhanced Phosphate Removal from Wastewater

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ABSTRACT

The modification of fly ash with sulphuric acid for the enhanced phosphate removal was investigated. In the modification process the fly ash was slurried with water and blended with concentrated sulphuric acid, followed by curing. It was found that modification of fly ash with sulphuric acid could significantly enhance the phosphate immobilization ability of the fly ash. The optimum modification conditions were determined as follows: the proportion of water : concentrated sulphuric acid : fly ash was 1.5 mL : 0.3 mL : 5 g, reaction temperature and time was 100°C and 1.5 h. In the phosphate immobilization process it was found that the optimum pH for phosphate removal was 7.0. The removal percentage of phosphate increased with the increase of adsorbent dosage. Adsorption of phosphate by the modified fly ash was rapid, the removal percentage of phosphate could reach the maximum in 10 minutes. The optimum temperature for phosphate removal was between 20°C and 30°C. The adsorption of phosphate by the modified fly ash could be described well by Langmuir isotherm equation, the Langmuir constant Q_0 was 4.37 mg/g.

INTRODUCTION

Phosphate is widely used in industry and agriculture. Many domestic, industrial and farming wastewaters contain phosphate. Excessive discharge of phosphate can cause eutrophication. Therefore, it is important to control phosphate concentration in wastewater. Several methods including chemical precipitation, biological treatment and adsorption have been used to remove phosphate from wastewater. In these removing techniques, adsorption has attracted more attention because it is known as more useful and economical. Coal fly ash is getting more attractive in phosphate removal other than commercial adsorbents due to its low cost and abundance (Cheung & Venkitachalam 2000, Yildiz 2004, Gray & Schwab 1993, Ugurlu & Salman 1998, Agyei et al. 2002, Chen et al. 2007, Drizo et al. 1999, Li et al. 2006, Pengthamkeerati et al. 2008). However, the phosphate removal efficiency of raw fly ash was relatively low. In this study, we attempted to modify the fly ash with sulphuric acid in order to improve the phosphate sorption capacity. The modified fly ash was used to remove phosphate from wastewater of primary settling tank. The influence of sulphuric acid amount, water amount, reaction temperature, reaction time on the modification of the fly ash and the influences of adsorption time, pH, dosage amount and temperature on the removal of phosphate from wastewater of primary settling tank using modified fly ash were investigated.

MATERIALS AND METHODS

Materials and reagents: The fly ash used in this work was obtained from a coal-burning power plant. The wastewater containing phosphate was obtained from the primary settling tank of a wastewater treatment plant. All chemicals and reagents used were of analytical reagent grade. Deionized water was used for preparing solutions. Stock solution of phosphate was prepared by dissolving KH_2PO_4 in deionized water.

Physical and chemical measurements: X-ray diffraction (XRD) analysis was carried out on Phillips X'Pert diffractometer with $\text{Cu K}\alpha$ radiation. The pH in solution was measured using a pH meter with glass electrode. Sorption of phosphate was measured spectrophotometrically using the molybdenum-blue ascorbic acid method.

Modification of the fly ash: A specified amount of water was added into 5 g fly ash, the mixture was stirred, then a given amount of concentrated sulphuric acid was added, after well agitated the mixture was cured at given temperature for a period of time for the further reaction between fly ash and sulphuric acid.

Sorption studies: Sorption experiment was carried out to measure the phosphate removal by the modified fly ash. The adsorbent was added to the wastewater, the pH was adjusted to a given value, then the mixture was shaken for a

particular length of time at a specified temperature. After being shaken, the mixture was filtered and the supernatant was measured for phosphate concentration.

RESULTS AND DISCUSSION

Modification of the fly ash with sulphuric acid: In the modification process, the fly ash was mixed with water and sulphuric acid, then the mixture was cured at a given temperature for a period of time. The effect of sulphuric acid amount, water amount, reaction temperature and time were studied. The modified fly ash prepared under different conditions was used for the removal of phosphate from aqueous solution. The phosphate removal condition was kept consistent as follows: initial phosphate concentration 60 mg/L, adsorbent dosage 1 g/100mL, pH 7.0, temperature 25°C, contact time 1 h.

Effect of sulphuric acid amount on the modification of the fly ash: The effect of sulphuric acid amount on the modification of the fly ash is shown in Fig. 1. It could be seen that sulphuric acid addition had significant effect on the phosphate removal of the fly ash. The removal percentage of phosphate by the untreated fly ash was 4.4%, the residual phosphate concentration was 57.4 mg/L. When the sulphuric acid addition was 0.3 mL for 5 g fly ash, the removal percentage of phosphate increased to 97.2%, the residual phosphate concentration decreased to 1.7 mg/L. It could also be seen that after the sulphuric acid amount exceeded 0.3 mL, the phosphate removal percentage increased slowly with the increase of sulphuric acid. In practice, 0.3 mL sulphuric acid was optimum amount for the modification of 5 g fly ash.

X-ray diffraction patterns of the untreated fly ash and the modified fly ash (Fig. 2) showed that the major phases present in the untreated fly ash were quartz, mullite, hematite, CaO and amorphous silicates. The amorphous silicates may contain calcium (Goodarzi 2006), iron (Kutchko & Kim 2006), aluminium (Grubb et al. 2000) and other metals. When the fly ash was modified with sulphuric acid, water soluble salt of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ appeared in the modified fly ash. Calcium, aluminium and iron could dissolve into water and form precipitates with phosphate when the modified fly ash was used for the removal of phosphate. Therefore, phosphate removal efficiency of the modified fly ash was enhanced.

Effect of water amount on the modification of the fly ash: The effect of water amount on the modification of the fly ash is shown in Fig. 3. It could be seen that the phosphate removal of the modified fly ash was improved as water was added for wetting the fly ash before the addition of sulphuric acid. When the fly ash was not mixed with water, the

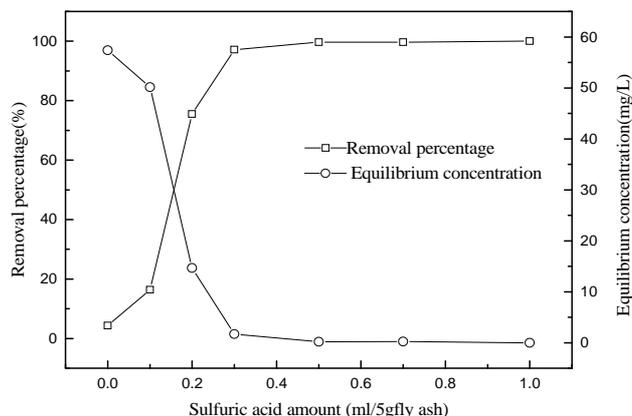


Fig. 1: Effect of sulphuric acid amount on the modification of the fly ash. (2 mL water/5g fly ash, 100°C, 2 h).

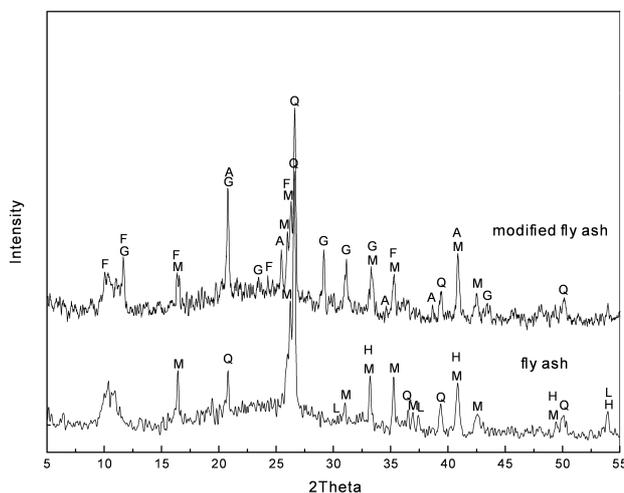


Fig. 2: XRD pattern of the untreated fly ash and the modified fly ash. M-mullite, Q-quartz, H-hematite, L-CaO, G- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, A- $\text{Al}_2(\text{SO}_4)_3$, F- $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

phosphate removal percentage of the modified fly ash was 93.05%, and the residual phosphate concentration after sorption was 4.17 mg/L. When the fly ash was mixed with 1.5 mL water before the addition of sulphuric acid, the phosphate removal percentage of the modified fly ash increased to 97.18%, and the residual phosphate concentration after sorption decreased to 1.69 mg/L. The reason was that, too low moisture seemed not to ensure the necessary fluidity of the fly ash for the homogeneous mixing of sulphuric acid and the fly ash. In addition, the moisture led to the dilution heat when concentrated sulphuric acid was added to the fly ash slurry, which prompts the reaction of fly ash with sulphuric acid, and hence improved the modification efficiency. From Fig. 3, it could also be seen that in the water amount range from 0 to 1.5 mL, the phosphate removal per-

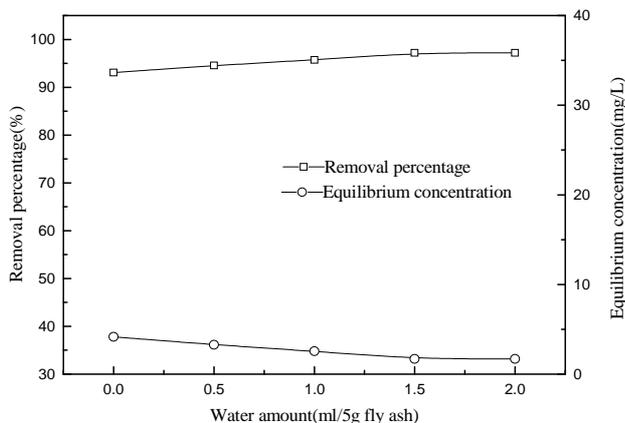


Fig. 3: Effect of water amount on the modification of the fly ash (0.3 mL sulphuric acid/5 g fly ash, 100°C, 2 h).

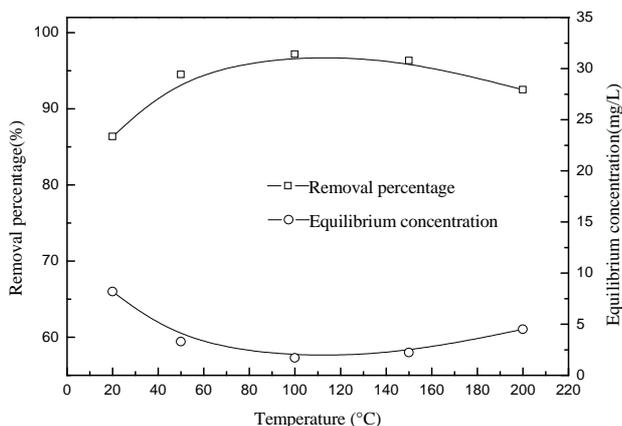


Fig. 4: Effect of temperature on the modification of the fly ash (1.5 mL water/5g fly ash, 0.3 mL sulphuric acid/5g fly ash, 2h).

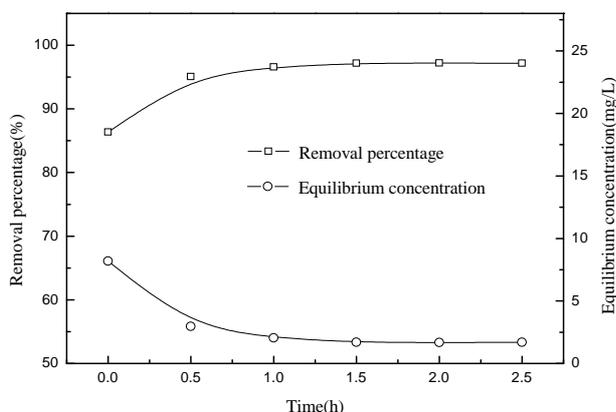


Fig. 5: Effect of time on the modification of the fly ash. (1.5 mL water/5g fly ash, 0.3 mL sulphuric acid/5 g fly ash, 100°C).

centage of the modified fly ash increased with the increase of water amount. When the water amount exceeded 1.5 mL, the phosphate removal percentage of the modified fly ash kept almost constant with the increase of water amount. Therefore, the optimum water amount was 1.5 mL for 5 g fly ash.

Effect of temperature on the modification of the fly ash:

The fly ash blended with water and sulphuric acid was preferably allowed to age at a given temperature for a period of time to increase the degree of conversion of the metal component to water-soluble sulphates. The effect of temperature on the modification of the fly ash is shown in Fig. 4.

From Fig. 4, it could be seen that when the temperature was below 100°C, the phosphate removal of the modified fly ash enhanced with the increase of temperature. The reason was that, increase of temperature could prompt the reaction between the fly ash and sulphuric acid. From Fig. 4, it could also be seen that the phosphate removal percentage reached to the maximum value when the temperature was 100°C. Then the further increase of the temperature actually decreased the phosphate removal efficiency of the modified fly ash. This was probably because the side reaction was induced at high temperature and resulted in the formation of insoluble components, which was not favourable for the dissolution of calcium, aluminium and iron from the modified fly ash. Therefore, the temperature should be limited within 100°C.

Effect of time on the modification of fly ash:

The effect of time on the modification of the fly ash is shown in Fig. 5. It could be seen that a period of curing was conducive to the full reaction of fly ash with sulphuric acid, thereby improving the adsorption properties of the modified fly ash. In Fig. 5, time zero meant that fly ash mixed with water and sulphuric acid was directly used for phosphate removal without curing. Under this condition, the phosphate removal percentage of the modified fly ash was 86.35%, the residual phosphate concentration after sorption was 8.19 mg/L. With the increase of curing time, the phosphate removal efficiency of the modified fly ash enhanced significantly. When the curing time was 1.5 h, the phosphate removal percentage of the modified fly ash reached to the maximum value of 97.8%, the residual phosphate concentration after sorption decreased to 1.69 mg/L. Then, the further increase of the curing time did not significantly affect the phosphate removal percentage of the modified fly ash. Therefore, the suitable curing time was 1.5 hours.

Phosphate immobilization:

In the phosphate immobilization experiments, the modified fly ash was prepared under the previously optimized conditions as follows: the ratio of water : sulphuric acid : fly ash was 1.5

mL : 0.3 mL : 5 g, the mixture was cured at 100°C for 1.5 h. In the phosphate immobilization experiments, the effects of pH, dosage amount, contact time and temperature on the removal of phosphate from the wastewater of the primary settling tank were studied.

Effect of pH on the removal of phosphate: The effect of pH on the removal of phosphate is shown in Fig. 6. It could be seen that when pH increased from 3 to 4, the removal percentage of phosphate increased significantly. When the pH value was higher than 4.0, the removal percentage of phosphate increased slowly until the pH 7.0. At this pH, the phosphate removal percentage reached the maximum. After pH 7.0, the removal efficiency of phosphate decreased with the increase of the pH. After the pH is higher than 8.0, the removal percentage of phosphate increased to a certain extent. From the effect of pH on phosphate removal it could be seen that the suitable pH for the removal of phosphate was 7.0. The experimental results also showed that for the wastewater containing 3.55 mg/L phosphate, when pH was 7.0 and the dosage of modified fly ash was 0.1 g/100 mL, the removal percentage of phosphate was 98.78%, the equilibrium concentration of phosphate in the treated water was 0.043 mg/L which was less than 0.5 mg/L, the maximum allowable loading for first-rate criterion required by Integrated Wastewater Discharge Standard (China Bureau of Environmental Protection 1997).

Effect of adsorbent dosage on the removal of phosphate: The effect of adsorbent dosage on the removal of phosphate is shown in Fig. 7. It could be seen that when the adsorbent dosage increased from 0.03 g/100 mL to 0.1 g/100 mL, the removal percentage of phosphate increased significantly. After the adsorbent dosage exceeded 0.1 g/100 mL, the removal percentage of phosphate increased slowly with the increase of adsorbent dosage. For the wastewater containing 2.53 mg/L phosphate, when the dosage of modified fly ash was 0.1 g/100 mL, the removal percentage of phosphate could reach 99.50%, the equilibrium concentration of phosphate in the treated water decreased to 0.013 mg/L. The experimental data showed that the modified fly ash could effectively remove phosphate in wastewater.

Effect of contact time on the removal of phosphate: The effect of contact time on the removal of phosphate is given in Table 1. It could be seen that the adsorption of phosphate by the modified fly ash was rapid, the adsorption could reach the equilibrium in 10 minutes, then the further increase of contact time did not significantly affect the removal percentage of phosphate and the residual concentration of phosphate. The relatively rapid adsorption rate was favourable for the removal of phosphate by the modified fly ash. The shorter time which the modified fly ash required to

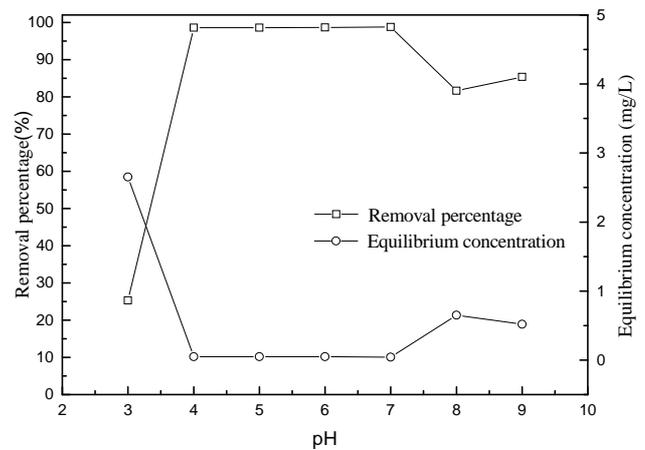


Fig. 6: Effect of pH on the phosphate removal by the modified fly ash. (initial phosphate concentration 3.55 mg/L, adsorbent dosage 0.1 g/100 mL, temperature 30°C, time 1 h).

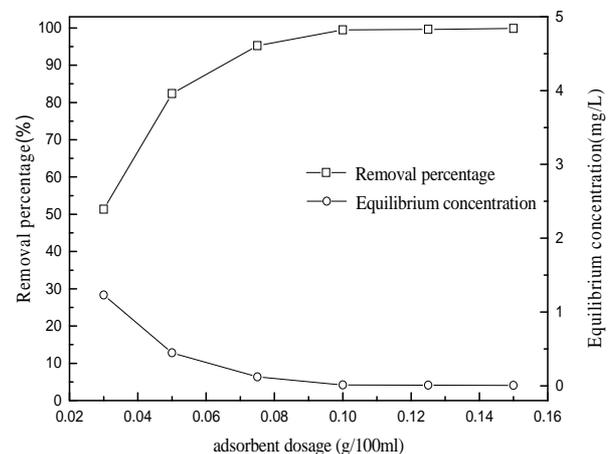


Fig.7: Effect of adsorbent dosage on the phosphate removal by the modified fly ash. (initial phosphate concentration 2.53 mg/L, pH 7.0, temperature 30°C, time 1h).

reach equilibrium also indicated that the removal of phosphate was mainly attributed to the precipitation reaction (Lu et al. 2008, Lu et al. 2009).

Effect of temperature on the removal of phosphate: The effect of temperature on the removal of phosphate is given in Table 2, which shows that when the temperature increased from 20°C to 30°C, the adsorption percentage of phosphate increased slightly. Thereafter, the adsorption percentage of phosphate decreased significantly when the temperature exceeded 30°C. The experimental results showed that in the phosphate removal process, the suitable temperature range was 20°C to 30°C.

Sorption isotherms: The phosphate adsorption isotherm of the modified fly ash is shown in Fig. 8, which indicates that the phosphate adsorption capacity considerably increased

Table 1: Effect of contact time on the phosphate removal by the modified fly ash.

| Time(min) | Removal percentage (%) | Equilibrium concentration (mg/L) |
|-----------|------------------------|----------------------------------|
| 5 | 98.24 | 0.0625 |
| 10 | 98.71 | 0.0458 |
| 15 | 98.62 | 0.0489 |
| 25 | 98.86 | 0.0405 |
| 35 | 98.76 | 0.0440 |
| 45 | 98.81 | 0.0422 |
| 60 | 98.76 | 0.0440 |

Initial phosphate concentration 3.55 mg/L, adsorbent dosage 0.1 g/100 mL, pH 7.0, temperature 30°C.

Table 2: Effect of temperature on the phosphate removal by the modified fly ash.

| Temperature (°C) | Removal percentage (%) | Equilibrium concentration (mg/L) |
|------------------|------------------------|----------------------------------|
| 20 | 98.56 | 0.051 |
| 30 | 98.78 | 0.043 |
| 40 | 66.08 | 1.204 |
| 50 | 61.80 | 1.356 |
| 60 | 58.00 | 1.491 |
| 70 | 57.50 | 1.509 |

Initial phosphate concentration 3.55 mg/L, adsorbent dosage 0.1 g/100 mL, pH 7.0, time 1h

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 wastewater.

The isotherm data on phosphate adsorption were fitted to Langmuir and Freundlich equations. Linearized forms of Langmuir and Freundlich isotherms for the phosphate adsorption on the modified fly ash are shown in Fig. 9. 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 4.37 mg/g.

CONCLUSION

The modification of fly ash with sulphuric acid could significantly enhance the immobilization ability of the fly ash. The factors affecting the fly ash modification were investigated to optimize the modification process. The optimal modification conditions were determined as follows: the proportion of water : concentrated sulphuric acid : fly ash was 1.5 mL : 0.3 mL : 5 g, reaction temperature and time are 100°C and 1.5 h respectively. In the phosphate immobilization process it was found that the optimum pH for phosphate removal was 7.0. The removal percentage of phosphate increased with the increase of adsorbent dosage. Adsorption of phosphate by

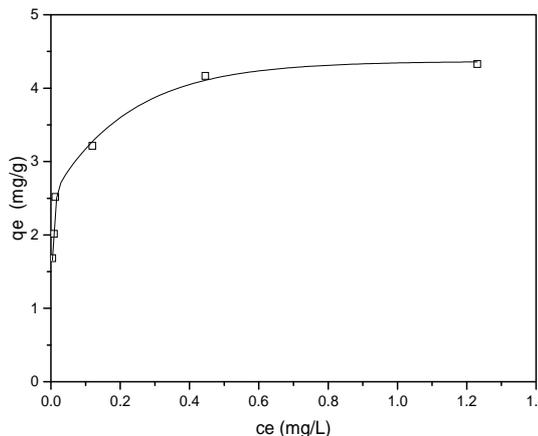


Fig. 8: Phosphate adsorption isotherm of modified fly ash. (pH 7.0, temperature 30°C).

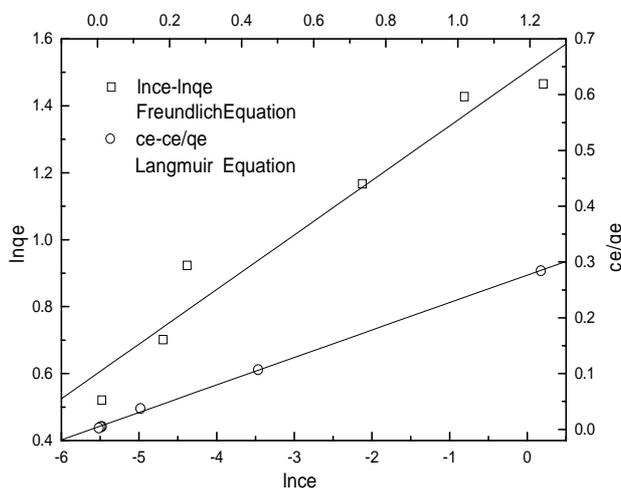


Fig. 9: Linearized form plots of Freundlich and Langmuir isotherms for phosphate adsorption on modified fly ash.

the modified fly ash was rapid, the removal percentage of phosphate could reach the maximum in 10 minutes. The optimum temperature for phosphate removal was between 20°C and 30°C. The adsorption of phosphate by the modified fly ash could be described well by Langmuir isotherm equation, the Langmuir constant Q_0 was 4.37 mg/g.

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