



Removal mechanism of phosphate from aqueous solution by fly ash

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ABSTRACT

This work studied the effectiveness of fly ash in removing phosphate from aqueous solution and its related removal mechanism. The adsorption and precipitation of phosphate by fly ash were investigated separately in order to evaluate their role in the removal of phosphate. Results showed that the removal of phosphate by fly ash was rapid. The removal percentage of phosphate in the first 5 min reached 68–96% of the maximum removal of phosphate by fly ash. The removal processes of phosphate by fly ash included a fast and large removal representing precipitation, then a slower and longer removal due to adsorption. The adsorption of phosphate on fly ash could be described well by Freundlich isotherm equation. The pH and Ca^{2+} concentration of fly ash suspension were decreased with the addition of phosphate, which suggests that calcium phosphate precipitation is a major mechanism of the phosphate removal. Comparison of the relative contribution of the adsorption and precipitation to the total removal of phosphate by fly ash showed that the adsorption accounted for 30–34% of the total removal of phosphate, depending on the content of CaO in fly ash. XRD patterns of the fly ash before and after phosphate adsorption revealed that phosphate salt ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) was formed in the adsorption process. Therefore, the removal of phosphate by fly ash can be attributed to the formation of phosphate precipitation as a brushite and the adsorption on hydroxylated oxides. The results suggested that the use of fly ash could be a promising solution to the removal of phosphate in the wastewater treatment and pollution control.

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1. Introduction

Removal of phosphate from wastewater by chemical precipitation and advanced biological treatment has been widely investigated [1]. Among numbers of removing techniques, adsorption is known more useful and economical [1]. The application of low cost and easily available materials in wastewater treatment has recently attracted great interest. Fly ash, a by-product of coal-burning power plants, has been used as a potential adsorbent for removal of phosphate, heavy metals and organic pollutants for water pollution control or wastewater treatment [2–10]. Batch and column experiments, as well as field tests demonstrated that fly ash had high P adsorption capacity [11–16]. Ugurlu and Salman [10] found that a Turkish fly ash was an efficient adsorbent for phosphate removal due to the high concentration of calcite present. Chen et al. [12] reported that the maximum phosphate adsorption (Q_m) of 15 Chinese fly ashes was in a range from 5.51 to 42.55 mg/g. The most effective removal of phosphate occurred in alkaline conditions for high calcium fly ash, near neutral pH for medium calcium fly ash, and low calcium fly ash immobilized little phosphate in

whole pH range. Khelifi et al. [17] developed porous carrier from the mixture of zeolitized fly ash and slag to remove phosphate and ammonium on the aquatic environment. Significant difference in the efficiency of phosphate removal among different fly ashes was attributed to the different Ca content and pH of fly ashes. Cheung and Venkitachalam [2] indicated that alkaline precipitator fly ash possessed the highest phosphate sorption capacity with a Q_m of 13.8 mg/g in terms of its Langmuir isotherm parameter.

Because of the progress controlling phosphate discharge from industrial processes, the phosphate discharge of non-point sources, such as domestic and agricultural wastewater, is recently becoming more significant [1]. Therefore, treatment of sewage discharged from agricultural processes and rural communities for the removal of phosphate is required. For this purpose, different on-site treatment techniques, such as constructed wetland and soil filtration systems, have been launched. These systems may be an appropriate and economically attractive on-site treatment solution for agricultural and domestic wastewaters [1,2,4,14,16]. In practice use, fly ash and other industrial waste slags are often used as the adsorbent or filter for the constructed wetland and soil filtration systems [1,2,14].

The process of adsorption and precipitation has been reported as the main mechanism of phosphate removal by fly ash. Tsitouridou and Georgiou [18] studied three fly ashes with different calcium contents and found that the removal of phosphate was involved in an adsorption and/or precipitation process. Cheung and Venki-

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tachalam [2] indicated that phosphate removal by two fly ashes with high and low calcium content was primarily due to the precipitation of phosphate with Ca^{2+} ions in solution. Oguz [19] suggested that the removal of phosphate by a medium calcium fly ash predominantly took place by precipitation mechanism, ion exchange and weak physical interaction between the surface of sorbent and the metallic salts of phosphate. Chen et al. [12] concluded that phosphate immobilization by fly ash was controlled by Ca ingredient (especially CaO and CaSO_4) and Fe ingredient (especially Fe_2O_3). Johansson and Gustafsson [20] ruled out the formation of amorphous calcium phosphate and/or octacalcium phosphate as the major P removal mechanism, and suggested direct formation of hydroxyapatite as the predominant mechanism of phosphate removal. Although it is generally acceptable that the phosphate removal by fly ash involved adsorption and/or precipitation mechanism, the interaction of phosphate and Ca is not well known. Extensive studies have been conducted to optimize the conditions of phosphate removal by fly ash and to explore innovative treatment methods for the removal of phosphate from aqueous solution. This paper reports on the feasibility of using fly ash to remove phosphate ions from aqueous solution and possible mechanism of phosphorus retention by fly ash from aqueous solution. An attempt was made to investigate the adsorption and precipitation separately by treating fly ash with acid before use, so as to evaluate the individual role of adsorption and precipitation and provide new insight into the mechanism of the phosphate removal.

2. Materials and methods

2.1. Fly ash

Three fly ashes used in this work, coded as FA1, FA2 and FA3 for identification, were obtained from three coal-burning power plants, eastern China. The pH of fly ash was determined with a pH meter in a 1:5 (w/v) ash/water suspension after equilibrium for 24 h. Particle size of the ashes was measured by a combination of sieving and laser beam techniques [21]. Sieving was used for the determination of particles coarser than 150 μm . Elemental analysis was carried out by a wet chemical method, involving hydrofluoric acid digestion and measurement by atomic absorption spectrophotometry (AAS). The pH development of fly ash in water was monitored by a pH meter. 10 g of fly ash was suspended in 50 mL of water by continuous stirring. The immediate pH of the solution and its following development in the next period of 24 h were recorded. The chemical composition of fly ash used was summarized in Table 1. The fly ash was treated with a 3% HCl (v/v) for 24 h and then filtered and washed thoroughly with deionized water. The residual was dried at 110 °C and used for adsorption studies.

Table 1
Chemical composition and physical parameters of three fly ashes used in the work

Component	FA1	FA2	FA3
pH	10.9	10.9	12.1
Electric conductivity (EC, S/m)	1.14	1.06	5.64
SiO_2 (%)	49.51	47.23	43.06
Al_2O_3 (%)	31.12	34.23	28.00
Fe_2O_3 (%)	5.36	6.32	8.63
CaO (%)	5.436	5.54	10.82
Particle size distribution (%)			
>0.15 mm	14.5	4.9	0.6
0.15–0.05 mm	43.7	35.5	46.3
0.05–0.02 mm	36.9	53.5	46.0
<0.002 mm	4.9	6.1	7.1
Density (g/cm^3)	1.93	2.20	2.29

X-ray diffraction (XRD) analyses were performed on a Rigaku D/Max 2550 PC (Rigaku Corporation, Japan) diffractometer employing a Cu $\text{K}\alpha$ radiation (40 kV, 40 mA) in a 2θ range of 2–80° at a scanning rate of 2°/min. Particle morphology of fly ash was observed using a scanning electron microscopy (SEM). Fly ash particles were mounted onto SEM sample stub and observed in a Philips XL 30 ESEM operating at 20 kV.

2.2. Batch adsorption experiments

Kinetics of phosphate removal: The standard phosphate solutions with different concentration were prepared from the stock solution of 5000 mg/L of KH_2PO_4 . 0.5 g of fly ashes and acid-treated fly ashes were respectively weighed and equilibrated in 50 mL centrifuge tubes containing 25 mL of 100 mg/L phosphate solution at room temperature. The tubes were stopped and continuously shaken at a spinning speed of 120 cycles/min. The shaking was interrupted momentarily at predetermined time intervals for the tube to be removed. The suspension was filtered to determine the concentration of phosphate. The tests using deionized water, 40 and 120 mg/L phosphate solution, respectively, were also conducted following the similar procedure and the supernatants were used to determine pH and concentrations of Ca^{2+} ions.

Adsorption isotherm test: Using a 50 mL centrifuge tube, 0.5 g sample was weighed and equilibrated in 25 mL solution containing different concentration of phosphate (50–2000 mg/L) for 6 h at room temperature. At the end of the 6 h period, the suspension was centrifuged. The supernatant was filtered and then was analyzed for phosphate concentration. The amount of phosphate sorbed was calculated from the difference between the initial and measured concentrations. The residual solid of adsorption test with 2000 mg/L phosphate solution was dried and used for XRD analysis.

2.3. Measurement methods

All measurements were performed in duplicate and the data was expressed as the average of two values and standard deviation. The phosphate concentrations were determined using the molybdenum blue spectrophotometric method according to procedure stated in APHA [22]. The concentrations of Ca^{2+} ions were determined by EDTA titrimetric method [23]. The relative error between the duplicate samples was used to assess data precision. The criteria assigned for the relative error was less than 10%, in most of the cases less than 5%. When the relative error exceeded the criterion, the data were discarded and a third experiment conducted until the relative error fell within an acceptable range.

3. Results and discussion

3.1. Characterization of fly ash and development of pH

The characterization of fly ash used is summarized in Table 1. The fly ash shows strong alkaline property with a pH ranging from 10.9 to 12.1. The main chemical components of fly ash are silicon, aluminum, iron, calcium and small amount of other elements (Table 1). SiO_2 and Al_2O_3 occupy about 71.1–81.5% of the fly ash. Fe_2O_3 and CaO compose about 10.8–19.5%. Particle size distribution of fly ash shows that about 42–59 wt% of the fly ash has particle diameter less than 50 μm . The SEM images (Fig. 1) show that fly ash mainly contains well-developed spherical particles with diameters of 10–50 μm and some irregular shaped particles. The spherical particles might be hollow particles filled with smaller spheres which are linked with the inner part of the particles. X-ray diffraction patterns show that the crystalline phases present in the fly ash are quartz, mullite and a lower content of magnetite.

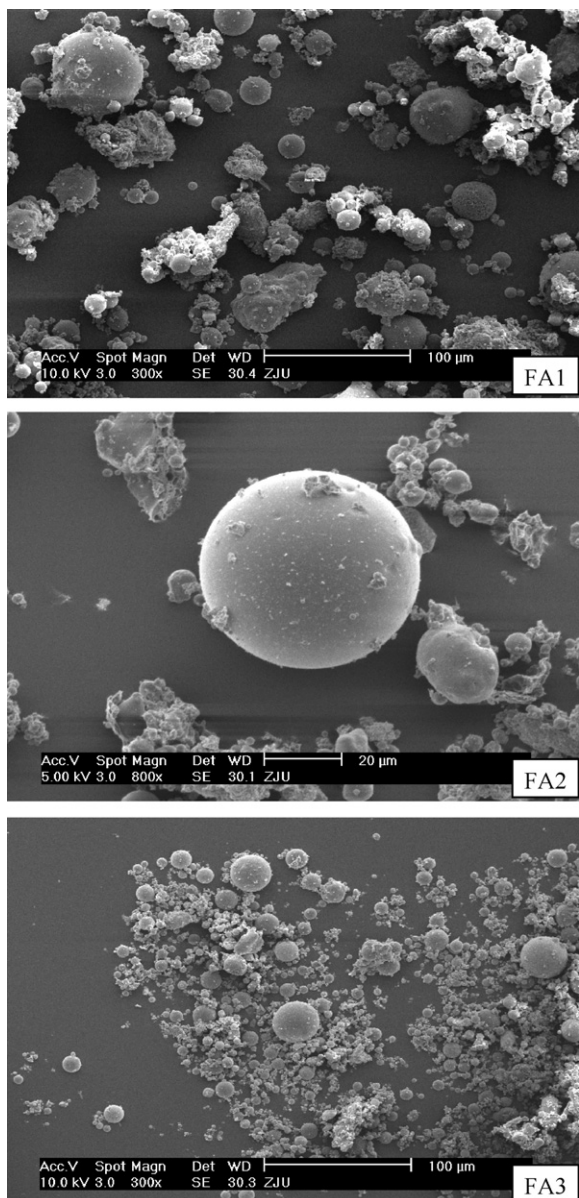


Fig. 1. Scanning electron microscopy (SEM) micrograph of fly ash.

The development of pH in fly ash suspension with time is presented in Fig. 2. In the case of FA3, the pH of the solution was almost constant at approximately 11.6. In the cases of FA1 and FA2, the pH of their solutions remained at the same level for a period of 24 h. With an addition of 40 and 120 mg/L of phosphate, the pH values of FA1 and FA2 decreased immediately to 7.3 and 7.6, respectively. Then, the pH gradually increased with contact time and reached a peak value at 24 h. The final pH values of the fly ash after reaction in deionized water are in the range of 10.8–11.6, while samples treated with a solution containing 120 mg/L phosphate have final pH values of 9.4, 9.7 and 11.5 for FA1, FA2 and FA3, respectively. The lower reduction of pH in FA3 is due to its higher CaO content. The high pH value of fly ash in deionized water is due to dissolution of Ca^{2+} from the sample into the solution. When phosphate is reacted with the fly ash, a large amount of calcium is removed from the solution, resulting in the precipitation of calcium phosphate. The formation of calcium phosphate suppresses the change of pH.

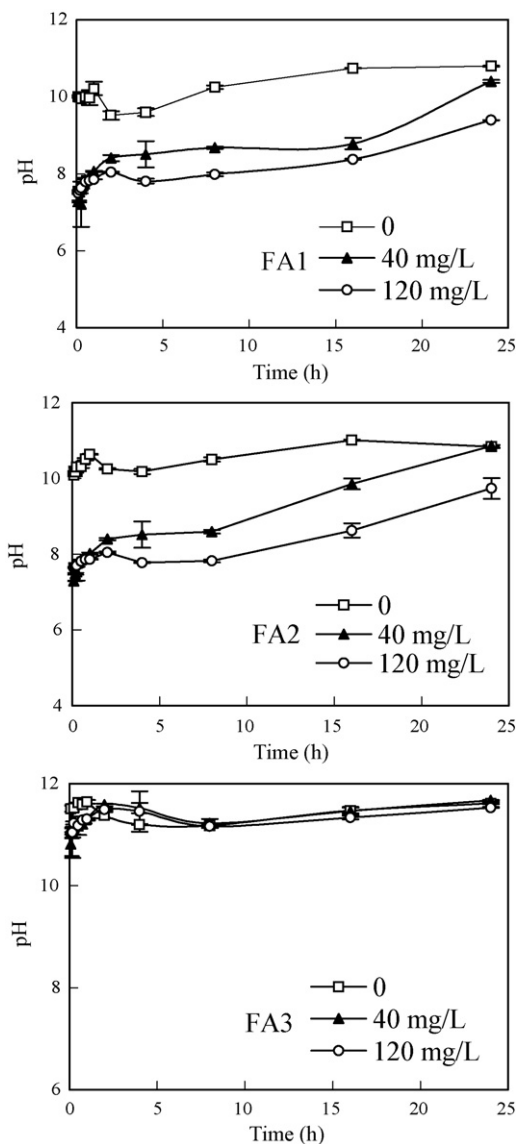


Fig. 2. The development of pH values in fly ash suspension with deionized water, 40 and 120 mg/L phosphate solution. Bars represent one standard deviation of the mean of two replicates.

3.2. Phosphorus adsorption kinetics

The kinetics of phosphate removal by fly ash are shown in Fig. 3 as a function of contact time from 5 min to 24 h. Results showed that the rate of phosphate removal by fly ash was quite rapid. The removal percentage of phosphate in the first 5 min was 69.7%, 68.4% and 95.6% of the maximum removal for FA1, FA2 and FA3, respectively. Fig. 3 also showed that the efficiency of phosphate removal of fly ash varied with the source of fly ash. The FA3 was superior to the others in terms of phosphate removal percentage. The kinetics of removal for FA3 showed that equilibrium was reached in about 15 min. There were no further increases in the percentage of phosphate removal up to 24 h. The rapid reaction is mainly attributed to the precipitation of applied phosphate with exchangeable and dissolved Ca rather than by adsorption. The liberated Ca^{2+} ions from the exchange sites or from the dissolution of CaCO_3 , CaO and CaOH most likely precipitate phosphate in an alkaline pH solution, which leads to high initial rate of phosphate removal. For FA1 and FA2,

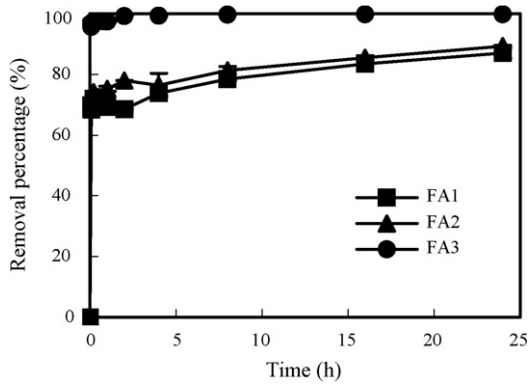


Fig. 3. Kinetics of phosphate removal by fly ash (initial phosphate concentration, 100 mg/L; dose of fly ash, 20 g/L). Bars represent one standard deviation of the mean of two replicates.

nearly 70% removal of phosphate was reached in the first 5 min and progressively increased with contact time. It was found that an initial large removal lasted only in a short time, followed by a further removal at low levels, but sustained over longer periods that refers to adsorption. Although the adsorption phase has the greater influence on the total removal of phosphate, the exact contribution of the adsorption phase to the removal of phosphate remains unclear.

3.3. Adsorption isotherm

The phosphate adsorption isotherms of fly ashes are shown in Fig. 4. The phosphate adsorption capacity considerably increased with the phosphate concentrations of applied solution increasing from 50 to 2000 mg/L. This indicated that fly ash had a high affinity for the phosphate and that phosphate was completely removed from dilute solution. The isotherm data on phosphate adsorption were fitted to two two-parameter equations (Freundlich and Langmuir model).

$$\text{Freundlich model: } q = kC^{1/n} \quad (1)$$

$$\text{Langmuir model: } \frac{C}{q} = \frac{C}{Q_m} + \frac{1}{bQ_m} \quad (2)$$

where C is the phosphate concentration in equilibrium solution (mg/L), q is the amount of phosphate adsorbed per unit of sorbent (mg/g), Q_m is the Langmuir sorption maximum (mg/g), k and n in the Freundlich model are constants related to adsorption capacity and energy of adsorption, and b is a constant related to the binding strength of phosphate.

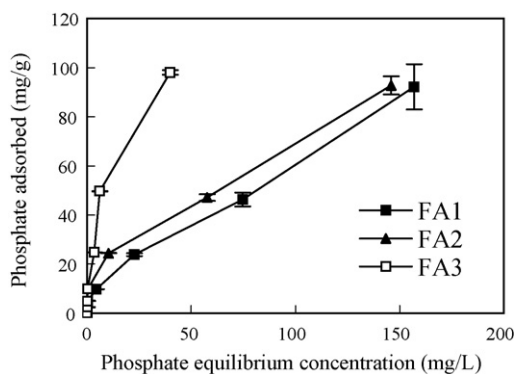


Fig. 4. Phosphate adsorption isotherms of fly ash. Bars represent one standard deviation of the mean of two replicates.

Table 2

Characteristic parameters and determination coefficients of the experimental data according to Freundlich and Langmuir equations

Adsorbent	Freundlich equation			Langmuir equation		
	1/n	k	R ²	Q _m (mg/g)	b	R ²
FA1	0.483	6.17	0.974	90.09	0.040	0.775
FA2	0.450	8.96	0.967	90.91	0.078	0.877
FA3	0.584	13.47	0.962	107.53	0.207	0.941

The values of the Freundlich and Langmuir constants and of the correlation coefficients for fly ash are presented in Table 2. Results showed that Freundlich equation gave a better fit than the Langmuir equation according to their correlation coefficients. In all case, correlation is lower with the Langmuir equation than with the Freundlich equation. This is in agreement with the result reported by Ugurlu and Salman [10], who found that adsorption data of phosphate by fly ash fitted better with Freundlich model. Our result was not in agreement with the findings of Chen et al. [12], who reported that both Langmuir and Freundlich equations were suitable for the description of phosphate adsorption isotherm by fly ash, but the Langmuir equation gave a better fit than the Freundlich equation according to their correlation coefficient. The fact that the Langmuir isotherm equation does not fit the experimental data may be due to inhomogeneous distribution of active sites on the surface of fly ash since the Langmuir equation assumes that the surface of adsorbent is homogeneous.

Linearized forms of Freundlich isotherms for the phosphate adsorption on fly ashes are given in Fig. 5. The Freundlich constant k , ranging from 6.17 to 13.47, varied widely, indicating large variations in the phosphate adsorption capacity of fly ashes. The Freundlich parameter could be compared with other published data in the literature. Chen et al. [12] reported that the values of k and $1/n$ for 15 Chinese fly ashes ranged from 0.11 to 8.35 and from 0.193 to 0.518, respectively. Cheung and Venkitachalam [2] found that the values of k and $1/n$ were 12.3 and 0.010 for the high calcium fly ash, and 0.113 and 0.580 for the low calcium fly ash, respectively.

3.4. Changes in calcium concentration and pH due to phosphate removal

It is suggested that phosphate removal depends on the dissolution of Ca^{2+} ions from the fly ash. In order to find out the relationship between pH and dissolution of Ca^{2+} from fly ash, a series of batch tests were performed. The results are shown in Fig. 6, which indicates that the Ca^{2+} concentration in the fly ash suspension was decreased with the addition of phosphate. The pH was also decreased with the addition of phosphate, and the effects were found particularly strong for FA1 and FA2. Phosphate removal

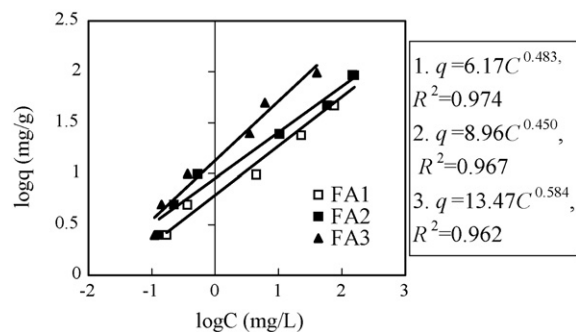


Fig. 5. Linearized form plot of Freundlich isotherm for phosphate adsorption on fly ash.

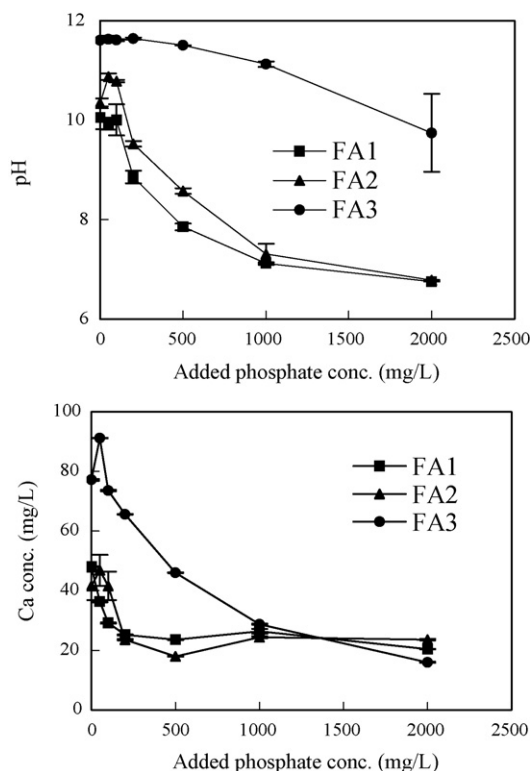


Fig. 6. The pH value and Ca^{2+} concentration as a function of the amount of phosphate added. Bars represent one standard deviation of the mean of two replicates.

was accompanied by a decrease in the Ca^{2+} ion concentration and pH value, which suggests a possible precipitation of calcium phosphate.

Phosphate may be removed by adsorption, and/or by precipitation of any of several calcium phosphates. However, the results are not consistent with adsorption, a most important phosphate retention mechanism. With adsorption, it is difficult to explain the concomitant decrease of Ca^{2+} concentration that occurred as a result of phosphate addition. The capacity of phosphate adsorption by fly ash was reduced by the removal of calcium salts. It is expected that the fly ash containing large amounts of calcium would adsorb phosphate and promote the precipitation of calcium phosphates. Phosphate concentration declined more rapidly due to its direct precipitation with calcium.

3.5. Mechanisms of phosphate removal by fly ash

Different mechanisms such as exchange, adsorption and precipitation have been proposed to explain the removal of phosphate from aqueous solutions. The pH of the solution plays a critical role in the rate and mechanism of the removal of phosphate. Generally, the removal of phosphate is accompanied by a decrease in the Ca^{2+} ion concentration and pH value (Fig. 6). In the case of FA3, Ca^{2+} concentration was decreased from 91.2 to 16.0 mg/L and the pH was decreased from 11.6 to 9.7 when the addition of phosphate was increased from 50 to 2000 mg/L. These results confirmed that phosphate reaction mechanism with calcium ingredients was through deposition as phosphate salts rather than trapped in Ca hydroxides floccule. It is known that high pH and Ca^{2+} concentration are favorable for the precipitation of calcium phosphate. The results suggested that phosphate removal was accomplished mainly by Ca^{2+} ion, depending on the dissolution of Ca^{2+} ion from the fly ash. Chen et al. [12] reported Ca ingredient (especially CaO and CaSO_4)

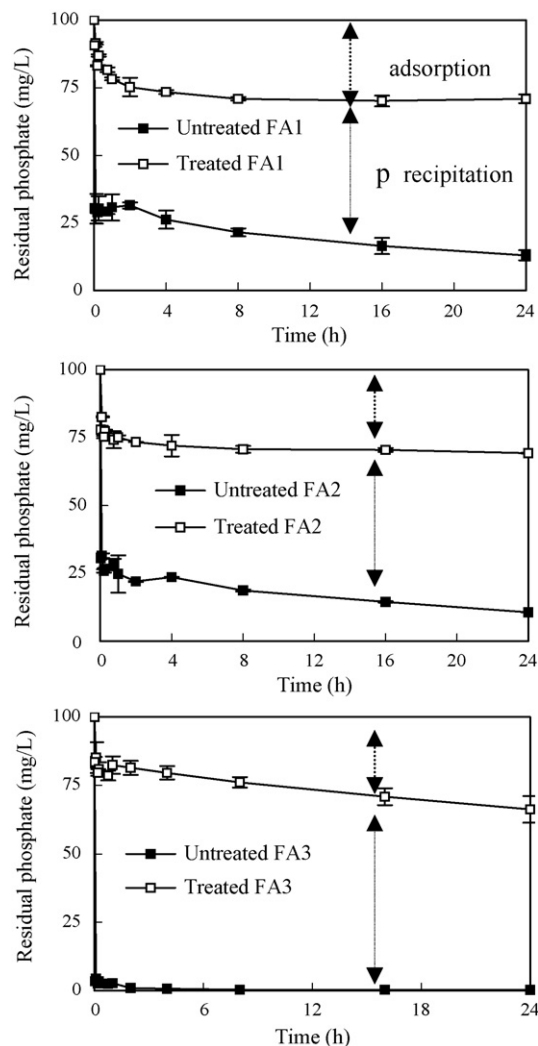


Fig. 7. Change of phosphate concentration with untreated and acid-treated fly ash (initial phosphate concentration, 100 mg/L; contact time, 6 h; dose of fly ash, 20 g/L). Bars represent one standard deviation of the mean of two replicates.

and Fe ingredient contributed primarily to phosphate immobilization. It was reported that chemical precipitation was dominant when pH was above 8 and adsorption was dominant when pH was below 6.

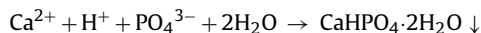
Chemisorption is another significant mechanism for the removal of phosphate. In order to compare the relative contribution of adsorption and precipitation to phosphate removal, the phosphate removal experiments of acid-treated fly ash were carried out. The removal of phosphate by the acid-treated fly ash could be attributed to the contribution of adsorption processes of phosphate by fly ash. The results are presented in Fig. 7, which shows strong effect of acid treatment on the removal of phosphate. With the untreated fly ash, phosphate concentration in aqueous solution was declined rapidly due to its direct precipitation with calcium. For example, the sample FA3 containing higher amount of calcium (CaO 10.82%) was able to remove almost all of phosphate from solution. However, the removal of phosphate by the acid-treated fly ash was considerably reduced as compared with that of the untreated fly ash. The results indicated that the reduction of Ca^{2+} concentration and pH of the solution by the acid treatment significantly affected phosphate removal. Comparison of removal of phosphate by the acid-treated and untreated fly ashes gave an evaluation of

the relative contribution of adsorption and precipitation to the total removal of phosphate. These results indicated that adsorption processes accounted for 30–34% of the total removal of phosphate. The possible adsorption mechanism for the removal of phosphate could be an adsorption process through the ligand exchange between phosphate and hydroxide groups on the surface of the hydroxylated Fe and Al oxides. Phosphate adsorption through ligand exchange reactions could be predominate when the surfaces of Fe and Al oxides are protonated, which results in the surfaces positively charged. This explanation can be supported by the fact that iron and aluminum oxides had higher adsorption capacity for phosphate [12].

The above results suggested that the calcium phosphate precipitation could be predominate mechanism for the phosphate removal. Fractionation of phosphate sorbed by fly ash revealed that loosely bound P fraction and/or CaMg-P fraction were the dominant forms of the immobilized phosphate [12]. The extent of phosphate removal by these adsorbents appears to be related to the percent CaO and/or Ca^{2+} ions released to the solution via hydration and

dissolution. This also explained that the Qm value had a significantly positive correlation with total Ca content. This observation is consistent with the findings of Johansson and Gustafsson [20] and Agyei et al. [11], who suggested that the adsorption of phosphate was mainly due to the formation of calcium phosphate.

Fig. 8 showed X-ray diffraction patterns of fly ash before and after phosphate reaction. The fly ash has specific chemical composition diffraction peaks at different 2θ ($^\circ$), indicating the presence of mullite, quartz and corundum. After phosphate adsorption process, two sharp and intense peaks of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) appeared in X-ray diffraction pattern of fly ash, indicating that phosphate salts are present on the structure of fly ashes. According to ion activity product calculation of different calcium phosphate phases, several calcium phosphate may be formed, including amorphous calcium phosphates (ACP), octacalcium phosphate (OCP, $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$), tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$) and hydroxyapatite (HAP, $\text{Ca}_5\text{H}(\text{PO}_4)_3\text{OH}$), depending on the pH and the composition of calcium and phosphate (H_2PO_4^- or HPO_4^{2-}) of the solution. Calcium phosphate precipitation depends on the formation of stable nuclei after which crystal growth takes place, and on the degree of supersaturation. The state of supersaturation is generally developed by increasing calcium, OH and phosphate concentrations in the solution. High total Ca^{2+} concentration and high pH are normally required for the precipitation of calcium. Abbona and Barronet [24] reported that ACP and octacalcium (OCP) could not be formed in an alkali solution having a pH of above 8. Johansson and Gustafsson [20] showed that hydroxyapatite (HAP) is the major form of calcium phosphate precipitates. The XRD results suggested that the major precipitate during the removal of phosphate by fly ash was brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). The crystals of brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) are formed on the surfaces of seed particles through the reaction below:



In addition to brushite, the presence of small amount of other precipitates such as HAP, tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and calcium hydrogen phosphate (CaHPO_4) are not excluded.

4. Conclusions

Based on results of this work, it is concluded that the fly ash removes phosphate from aqueous solution rapidly, and that removal effectiveness is associated with the content of calcium in the fly ash. The removal processes of phosphate include a fast and large removal representing precipitation, then a slower and longer removal due to adsorption. The adsorption isotherm of phosphate on fly ash can be well described by Freundlich equation. The removal of phosphate is accompanied by a reduction of Ca^{2+} concentration and pH of the solution. Phosphate may be removed by adsorption and/or by precipitation of calcium phosphate. The relative contribution of adsorption to the total removal of phosphate accounts for 30–34%. The mechanism of phosphate removal by fly ash is related to the formation of phosphate calcium precipitates. XRD results confirm that the precipitation of phosphate by Ca as a brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) precipitation is the main process responsible for the removal of phosphate. Results of this work indicated that the use of fly ash could be a promising solution to the removal of phosphate in the wastewater treatments.

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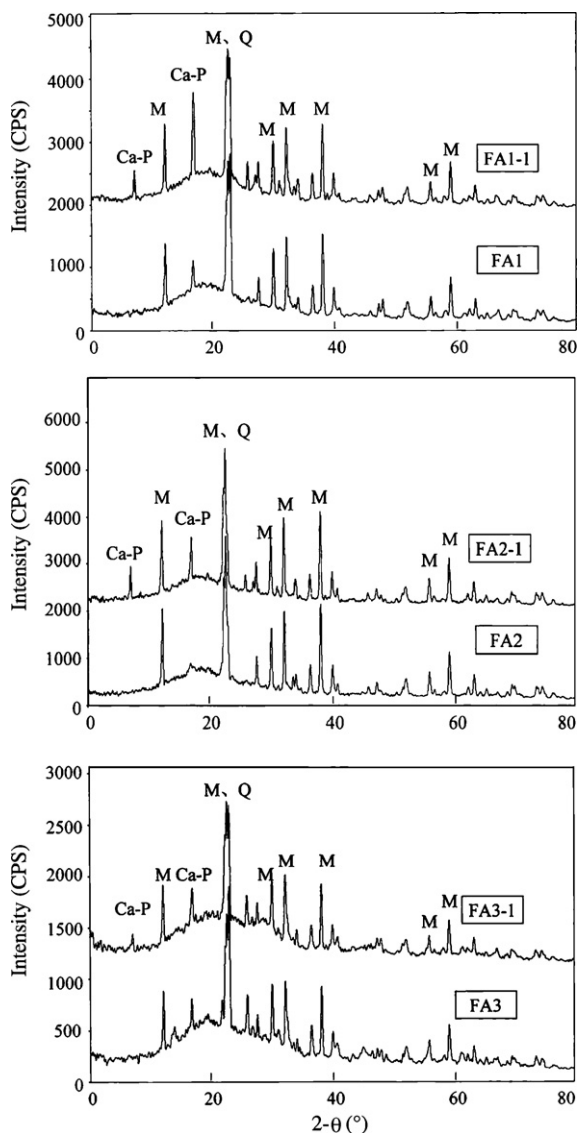


Fig. 8. X-ray diffraction diagrams of fly ash before (FA1, FA2 and FA3) and after (FA1-1, FA2-1 and FA3-1) adsorption (initial phosphate concentration = 2000 mg/L). M—mullite ($\text{Al}_{1.272}\text{Si}_{0.728}\text{O}_{4.864}$), Q—quartz (SiO_2), Ca-P—brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

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