Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22516

116 (2018) 232–241
June

Phosphate removal from industrial wastewater effluent using modified coal fly ash

Prashant Dhanke[a,*], Abhijeet Patil[a], Vivek Kore[a], Pavan Thakare[b], Unmesh Patil[a], Sameer Wagh[c]

[a]*Chemical Engineering Department, Padmabhooshan Vasantraodada Patil Institute of Technology, Sangli, MH 445001, India, Tel. +91233 2366398, dbpchem@gmail.com (P. Dhanke), abhi.kiran.89@gmail.com (A. Patil), vivekskore@gmail.com (V. Kore), unmeshp9@gmail.com (U. Patil)*
[b]*Research and Development Department , Engineers India Limited, New Delhi 110 066, India, Tel. +91126763269, email: pavan.thakare@eil.co.in (P. Thakare)*
[c]*Chemical Engineering Department, Laxminarayan Institute of Technology, Nagpur, MH 440 033, India, Tel. +91 712 256 110, email: vansam2522@rediffmail.com (S. Wagh)*

Received 16 December 2017; Accepted 13 May 2018

ABSTRACT

Phosphate in a water act as a primary nutrient for the algae and water bodies present in that water. This present phosphate is also responsible for the excess growth of algae through eutrophication in stationary water. High level of phosphate reduces the oxygen present in the water. Reduced oxygen is indirectly harmful to aquatic life present in the water. Excessive growth of algae can be reduced by removing the phosphate from water. Coal based fly ash (CFA) using adsorption method proved itself best technique for the removal of phosaphate from water. Oxides of aluminum iron and calcium in CFA is responsible for the phosphate adsorption from water. In this research work laboratory scale experiments were carried out using (CFA) and Modified coal based fly ash (MCFA). An effect of adsorbent concentration, contact time, pH and temperature were investigated for the phosphate removal from water.

Keywords: Modified coal fly ash; Phosphate; Adsorption isotherm; Adsorbent

---

1. Introduction

Phosphorus is the highly available mineral on the earth. Naturally inorganic phosphorus is available in the forms of mineral apatite ($Ca_5F(PO_4)_3$) as a phosphate. Phosphorus is the important nutrient for all the lives. Growth of the plants and water bodies present in water depends on the phosphorus. The phosphorus present in the effluent is acting as a growth controlling agent and hence this phosphorus is used by the plants and water bodies present in the water. In natural water and wastewaters, phosphorus exists almost exclusively in the form of phosphates. Phosphate is also exists in the different forms, such as orthophosphate, polyphosphate, and organically bound phosphate. Orthophosphate is produced by natural decay process in waste water. This form of phosphate in water is utilized by plants and water bodies for their growth. Phosphate acts as a fertilizer for plants and food supplement for animals. Another form of phosphate is polyphosphate used in the treatment of boiler feed water. Breaking of organic pesticides is also responsible for the production of phosphate. If the concentration of phosphate increases in the water, algae and other plants will flourish at high rate. This flourish mechanism decreases the dissolved oxygen in the water [1]. Concentration of polyphosphate in ground water increases due to discharge of fertilizer, domestic waste and industrial effluent. In the next stage polyphosphate in water will converted to orthophosphate by degradation. This produced polyphos-

---

*Corresponding author.

1944-3994 / 1944-3986

phate is more reactive and act as nutrients for the plants and water bodies present in that water. This will lead eutrophication. In this phosphate reduces dissolved oxygen and disturb aquatic life [2]. Eutrophication is responsible for the excessive growth of algae in all the type of water due to presence of excessive phosphate. Waste water from industry and municipal is responsible for increasing phosphate concentration. Hence to avoid Eutrophication, phosphate should be removed from water. Effluent quality can be improved by removing phosphate after secondary treatment on applying adsorption methods.

Coal based thermal power plant generates solid waste called fly ash in millions of tons worldwide. Production of fly ash is found to be 500 millions of tons or more worldwide [3]. In India coal is always a dominant fuel to meet energy demand. In recent, thermal power plant in India generates 130 metric tons of coal fly ash (CFA) annually. CFA utilization is very low as compared to available ash. Most of the CFA is used in terms of landfills and lagoons. Hence the disposal CFA seems serious issue [4]. CFA is generates in the fine powder form which leads different respiratory diseases when travels along the air. As an alternative utilization, CFA can be used for the water treatment effectively.

2. Material and methods

2.1. Modification of Coal based Fly ash (MCFA)

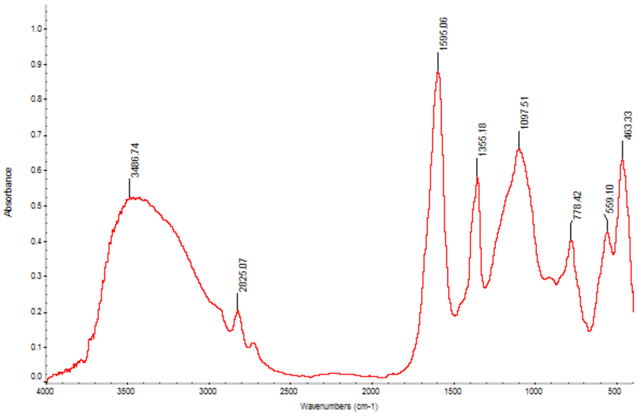
Fly ash was collected from NTPC Dadari, Haryana via Central Building of Research Institute (CBRI) Roorkee. CFA was washed using distilled water to remove other leachable matter. Washing of CFA was continuously with distilled water till water looks clear. Washed CFA was sieved thorough 106 µm mesh to get required particle size. In the next step CFA was dried for further use. Different amounts of distilled water like 1 ml, 2 ml, 3 ml and 4 ml were added to 5 g of CFA in different beakers. Each mixture was stirred properly and then added with different quantities of concentrated sulfuric acid ranging from 0.1 to 1.0 ml per 5 g of CFA. The mixtures were agitated again and cured at 100°C for 2–3 h till the mixtures became dry completely [5]. Obtained coal fly ash after the treatment was kept in air tight bottles till the final use. The optimum quantity of water and sulfuric acid for CFA modification was found to be 2 ml and 0.5 ml respectively where the phosphate removal was found greater than 99%. This MCFA was used as an adsorbent for proposed experimental work. The presence of functional group is responsible for the adsorption phenomena. Hence this functional group has been determined using FTIR technique for MCFA and CFA. The result of FTIR is shown in Fig. 1. Dissolved calcium in water react with phosphate and form calcium phosphate precipitate. Calcium oxide in water is responsible for the release of calcium. In MCFA, sulphuric acid was responsible to form calcium phosphate, aluminum phosphate and iron phosphate from soluble metal ions like calcium, aluminum and iron [6]. Hence MFCA improved immobility of phosphate.

2.2. Adsorbate (Phosphate solution)

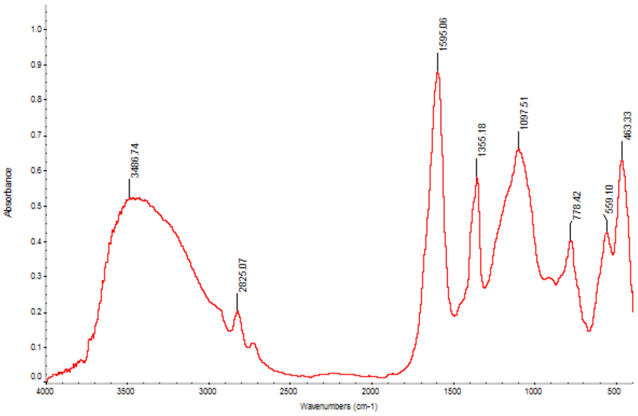
Potassium di-hydrogen ortho-phosphate (KH_2PO_4) of AR grade was taken as a source of PO_4^{3-} element. Stock solution of 1000 mg/l was prepared on dissolving phosphate in distilled water.

2.3. Characterization

Characterization of fly ash was carried out using standard analytical equipments. Specific surface area was calculated by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption isotherm (Micromeritics, CHEMISORB-2720). The Estimated surface area is 17.6 m^2/g for CFA and 26.9 m^2/g for MCFA. The presence of functional group was determined using FTIR technique (Thermo scientific, NICOLET 6700) for CFA and MCFA separately. The FTIR spectrum of CFA and MCFA is shown in Fig. 1. In the obtained FTIR spectra, 1595.06 cm^{-1} of frequency of CFA and 1624.23 cm^{-1} frequency of MCFA represents stretching of C=O bond, these stretching bonds denote active sites for the effective adsorption. The structure of CFA and MCFA was examined by scanning electron microscopy (SEM) couples with energy-dispersive X-ray analysis (EDX) for determination of elemental composition. The determined elemental composition of CFA and MCFA before adsorption is shown in Table 1. The SEM photograph of CFA and MCFA are shown in Figs. 2 and



(CFA)



(MCFA)

Fig. 1. FTIR analysis of CFA and MCFA.

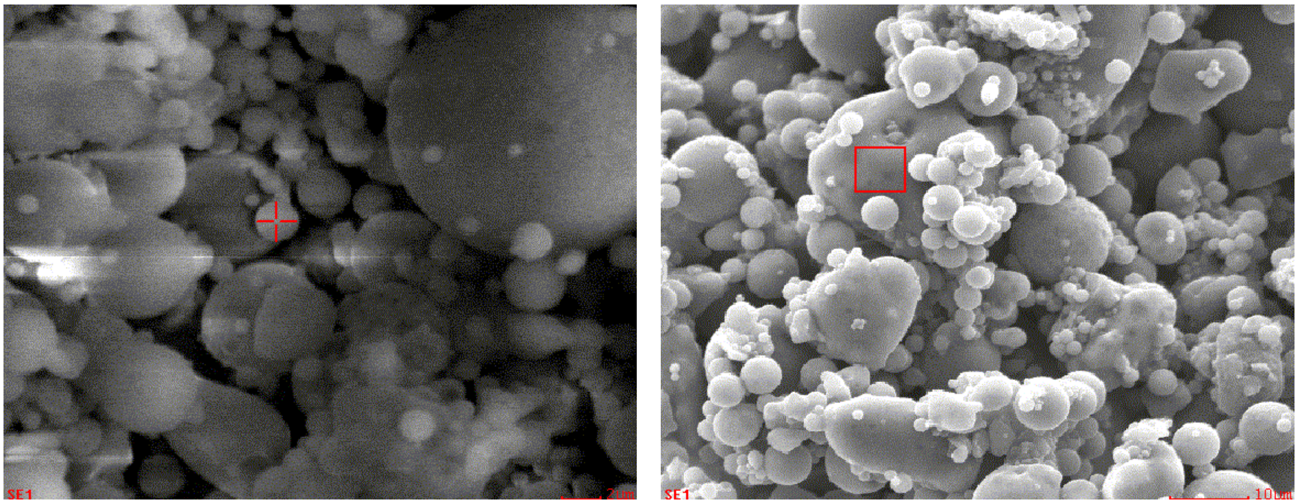
Table 1
Elemental composition of CFA and MCFA before adsorption

Element (CFA)	Wt (%)	Element (MCFA)	Wt (%)
C	18.50	S	0.65
O	29.37	O	30.08
Mg	1.15	Mg	0.42
Al	16.68	Al	28.12
Si	26.47	Si	34.94
K	1.54	K	1.33
Ca	1.29	Ca	0.78
Ti	1.31	Ti	2.19
Fe	3.69	Fe	1.52

3. The Elemental composition of MCFA before and after adsorption of phosphate is also given in Table 2.

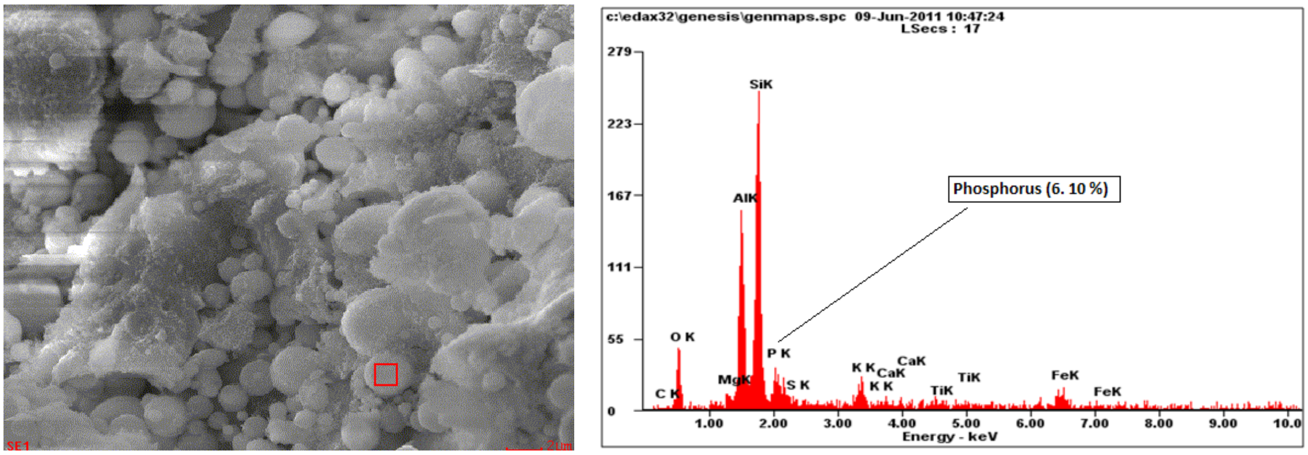
2.4. Analytical equipment

Solution spectrophotometry is a required and perfect analytical method for the analysis of water, especially for the determination of nitrogen and phosphorus. Hence the UV Spectrophotometer (Shimadzu, Japan; model UV 1800) was employed in the measurement of phosphate solutions using stannous chloride method [7]. A wavelength of 650 nm was used for this analysis. XRD analytical technique was used before and after adsorption of phosphate on MCFA. Adsorption rate of phosphate is directly affected by pH of solution [8,9]. The pH measurement was carried out by digital pH meter (EUTECH Instrument, Model pH 510). An Incubator shaker was used for all adsorption experiments.



(CFA) (MCFA)

Fig. 2. SEM photograph of CFA and MCFA before adsorption.



SEM photograph Elemental Spectra

Fig. 3. SEM and Elemental spectra of MCFA after adsorption.

Table 2
Elemental composition of MCFA

Element (Before)	Wt (%)	Element (After)	Wt (%)
O	30.05	C	2.07
Mg	0.42	O	18.39
Al	28.12	Mg	0.40
Si	34.94	Al	20.40
S	0.65	Si	37.13
K	01.33	P	6.10
Ca	0.78	S	0.64
Ti	02.19	K	3.87
Fe	01.52	Ca	0.98
		Ti	1.53
		Fe	8.46

2.5. Adsorption experiments

Set of different experiments were carried out using 50 ml of phosphate solution. In order to see the effect of different operating parameters, experiments were completed in 250 ml Stoppard conical flask for the removal of phosphate from prepared solution of known concentration using CFA and MCFA. The flasks were shaken on a speed of 180 rpm at temperature of 35°C. The pH of solutions was adjusted by the addition of 0.1 N H_2SO_4 and 0.1 N NaOH. The effect of different operating parameters, like initial phosphate concentration, adsorbent dose, time of contact, pH, and temperature were studied. Freundlich [10] and Langmuir [11] adsorption isotherm has been used to for the determination of equilibrium amount of phosphate adsorbed on CFA and MCFA. Similarly adsorption kinetic has been studied for the first order and second order model.

3. Result and discussion

3.1. Effect of adsorbent dose

The effect of adsorbent (CFA and MCFA) dose on the removal of phosphate from waste water was carried out at temperature of 35°C, 60 min contact time and initial concentration of 60 mg/l by varying the dose from 5 g/l to 80 g/l. Samples were collected at regular intervals and then analyzed for percentage phosphate removal. The results were plotted in terms of adsorbent dose Vs phosphate removal. It could be seen from Fig. 4 that for CFA the phosphate removal has been observed less with increasing adsorbent dose. Maximum phosphate removal was found up to the 48% at 40 g/l dose. Due to less phosphate removal, CFA dose was increased up to 80 g/l but no more change is observed in phosphate removal. On using MCFA it was observed that, as the dose increases slightly adsorption increases. MCFA achieved 98.2% of phosphate removal at dosage of 10 g/l. MCFA dose was kept continue up to 40 g/l but given slightly more removal. When the dosage increased to 20g/L, the phosphate removal increased slightly to 98.6% after that it become constant. The optimum dose was found 40 g/l for CFA and 10 g/l for MCFA for highest phosphate removal under given condition and which is shown in Fig. 4.

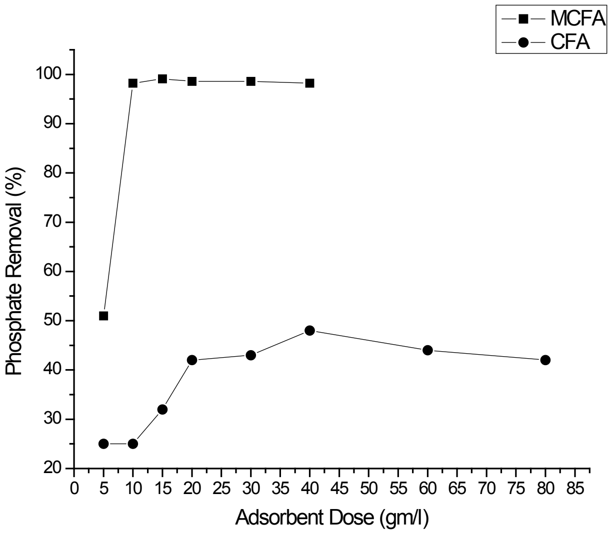


Fig. 4. Effect of adsorbent dose on phosphate removal (Temp. = 35°C, C_o = 60 mg/l, Contact time = 60 min).

3.2. Effect of pH

pH of phosphate solution have significant effect on phosphate removal. The pH of solution is important because the solubility of phosphates decreases with an increase in pH. The effect of pH on adsorption of phosphate from waste water on CFA and MCFA was studied by varying the pH from 2 to 11. The pH was adjusted by using 0.1 N sulfuric acid and 0.1 N sodium hydroxide. The pH was measured using digital pH Meter (EUTECH Instrument, Model pH 510). The results were plotted in terms of pH v/s Phosphate removal which is shown in Fig. 5. Effect of pH on phosphate removal was carried out on MCFA and CFA at Contact time of 60 min, phosphate concentration (C_o) 60 mg/l, and temperature 35°C with sufficient agitation. Adsorbent dose of 10 g/l (MCFA) and 40 g/l (CFA) was used, which was found optimum during effect of adsorbent dose. When CFA is used, it was observed that phosphate removal was not that much good, but there is a slight increment observed in phosphate removal with an increase in pH and maximum removal upto of 49% was found at the pH 8.4. While in case of MCFA, sharp increase in phosphate removal has been observed with an increase in pH from 2.5 to 4 and thereafter it increases slowly. It was observed that, towards acidic conditions, phosphate precipitation not found suitable [12]. Hence MCFA had maximum phosphate adsorption (>98%) over the pH range 6.5 to 11. Phosphate immobilization was governed by pH of solution. In case of MCFA, the phosphate removal was mainly by adsorption not by precipitation hence phosphate removal is comparatively very low. The maximum removal was found at neutral pH and similar results were found in alkaline condition. The optimum pH value for CFA is 8.5 and for MCFA it is 7.0 respectively.

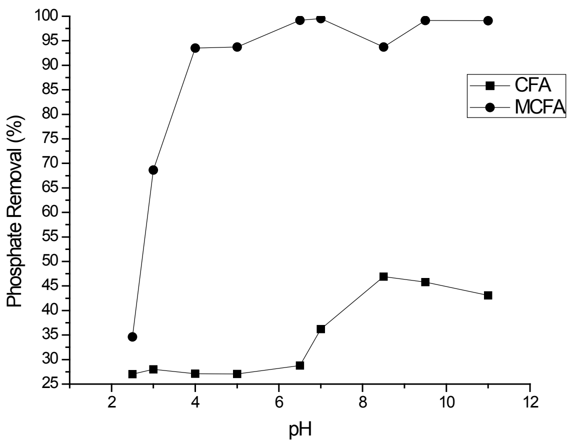


Fig. 5. Effect of pH on phosphate removal (%) using MCFA (Adsorbent dosage = 10 g m/l, Temp. = 35°C, C_o = 60 mg/l, Contact time = 60 min) and CFA (adsorbent dosage = 40 g m/l, Temp. = 35°C, C_o = 60 mg/l, Contact time = 60 min).

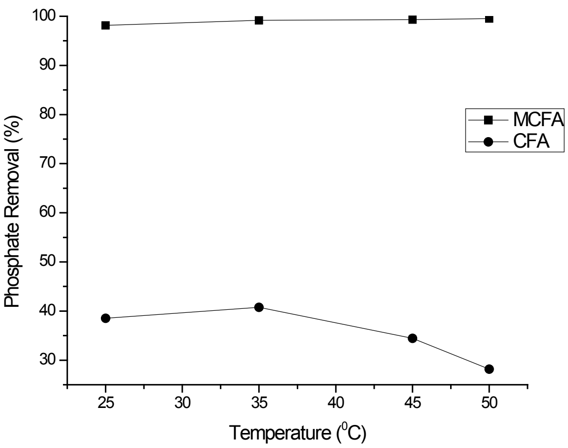


Fig. 6. Effect of temperature on phosphate removal using MCFA (Adsorbent dosage = 10 g m/l, pH = 7.0, C_o = 60 mg/l, Contact time = 60 min) and CFA (adsorbent dosage = 40 g m/l, pH = 8.4, C_o = 60 mg/l, Contact time = 60 min).

3.3. Effect of temperature

Obtained results were plotted for the temperature against phosphate removal which is shown in Fig. 6. For CFA, phosphate removal was decreased from 38.54 % to 28.18 % with increase in temperature from 25 to 50°C. For MCFA, change in the phosphate removal was negligible. Phosphate removal for MCFA was almost constant around 99 % with the increase in temperature. This condition is due the active participation of phosphate in precipitation mechanism rather than adsorption on MCFA. The temperature of 35°C found effective optimum for both the CFA and MCFA to remove more phosphate at 60 min contact time with initial concentration of 60 mg/l. Optimum ph of 8.4 and 7, similarly dose of 40 g/l and 10 g/l for CFA and MCFA was maintained to find the effect of temperature on phosphate removal.

3.4. Effect of contact time

It was observed that adsorption of phosphate by MCFA was rapid and hence equilibrium was reached in between 5 to 15 min. Further increases in contact time upto 60 min no significant effects on phosphate removal observed. Result were plotted and shown in Fig. 7. Time required to reach equilibrium by MCFA was less, which is indicates that phosphate removal is carried out by precipitation reaction. Similar trends were reported by Ugurlu and Salman (1998) for the adsorption of phosphate using fly ash [13]. In CFA adsorption only 40% phosphate removal achieved in first 60 min contact time, hence contact time was increased up to 360 min to find more phosphate removal, but only 50% was achieved in 360 min. The optimum contact time for MCFA and CFA from experiments was found to be 60 min respectively.

3.5. Effect of initial phosphate concentration

Effect of initial phosphate concentration was studied for the effective phosphate removal from given water samples. Phosphate concentration was varied for 60 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm and 1000 ppm using MCFA. Initial concentration of 60 ppm had given highest phosphate removal at 60 min contact, temperature 35°C and pH of 7, same condition was considered for above mentioned concentration level. The results were plotted which are shown below in Fig. 8. Phosphate removal upto 99% achieved at 60 ppm and 200 ppm within 15 min, after that seems constant up to 60 min. After increasing phosphate concentration from 200 ppm to 1000 ppm phosphate removal decreases continuously. At 1000 ppm concentration only 50% phosphate removal was obtained. At higher phosphate concentration higher energy sites get saturates and adsorption will starts on lower energy sites which results lower removal of phosphate. Phosphate removal at low concentration (60–200 ppm) is very important in terms of industrial applications using MCFA. Similar results were reported by P. Pengthamkeerati et al.

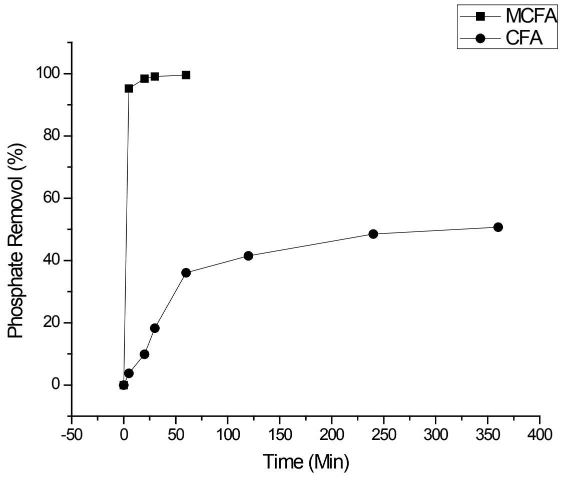


Fig. 7. Effect of contact time on the phosphate removal using MCFA (adsorbent dosage = 10 g m/l, pH = 7.0, C_o = 60 mg/l, Temp = 35°C) and CFA (adsorbent dosage = 40 g m/l, pH = 8.4, C_o = 60 mg/l, Temp = 35°C).

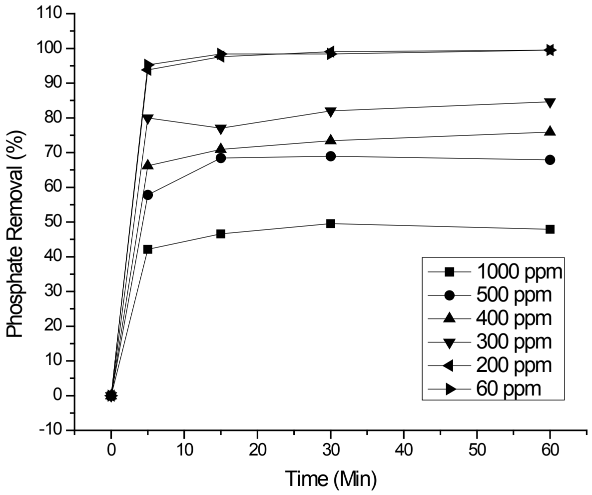


Fig. 8. Effect of initial concentration with respect to time on MCFA (contact time = 60 min, dose = 10 gm/l, pH = 7, Temp = 35°C).

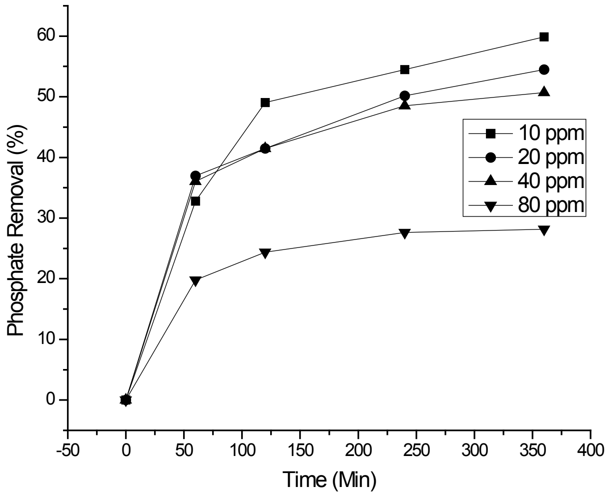


Fig. 9. Effect of initial concentration with respect to time on CFA (contact time = 360 min, dose = 40 g/l, pH = 8.4, Temp = 35°C).

Initial phosphate concentration from 10 ppm to 80 ppm was varied to find out phosphate removal using CFA at pH of 8.5 and temperature 35°C. Due to less capacity to remove phosphate by CFA initial concentration was considered less (10, 20, 40, 80 ppm) as compared to MCFA. Obtained results were plotted and shown in Fig. 9. Contact time was extended to 360 min to find out more removal by CFA, but not found significant, only lowest concentration (10 ppm) achieved 60% removal in 360 min. On comparing the results of CFA and MCFA, MCFA has more affinity to remove phosphate up to 200 ppm, which was very high as compared to CFA at same temperature (35°C).

3.6. Adsorption isotherm

Phosphate adsorption was increases with increase in the initial phosphate concentration on MCFA up to 200 ppm but it was limited on CFA, only 60 % adsorption was achieved for 10 ppm even increasing contact time up to 360 min. MCFA is more favorable for the phosphate adsorption as compared to CFA. The phosphate adsorption isotherms of MCFA and CFA are shown in Fig. 10. The phosphate adsorption capacity (mg of phosphates/g of fly ash) was found high in MCFA as compared to CFA. Adsorption isotherm such as Freundlich and Langmuir isotherm was used to describe the adsorption data. Optimization of adsorption was completed by the approximate correlation among equilibrium curves. Freundlich and Langmuir isotherm equations were used for this correlation. These isotherms are shown in Figs. 11, 12 and 13.

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{1}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L.q_m} \tag{2}$$

where 'q_e' is the amount of phosphate adsorbed per unit of sorbent (mg/g), 'K_f' and n are constants related to adsorption capacity and energy of adsorption, 'C_e' is the phos-

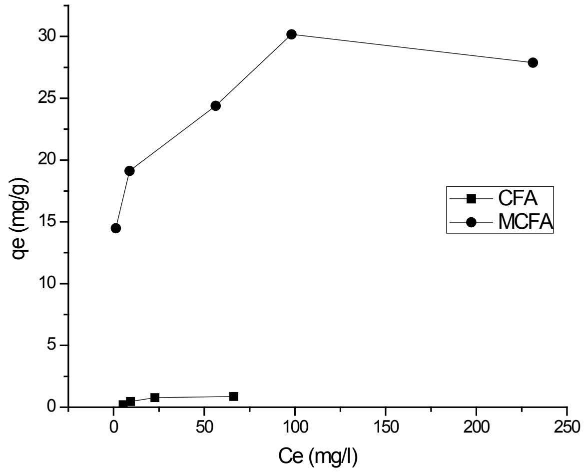


Fig. 10. Phosphate adsorption isotherm for MCFA and CFA.

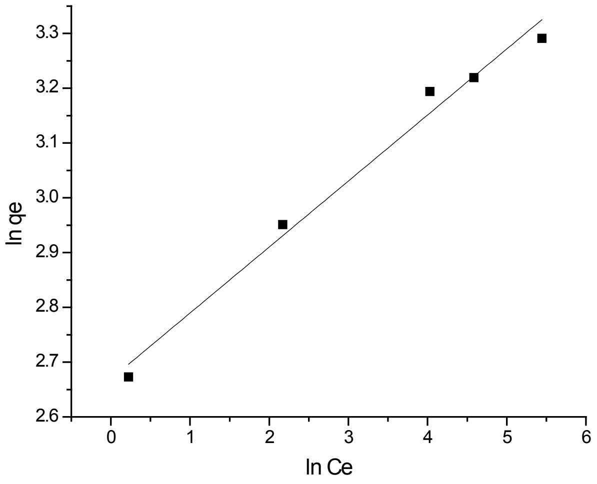


Fig. 11. Freundlich isotherm plot of MCFA (contact time = 60 min, dose = 10 gm/l, pH = 7, Temp = 35°C).

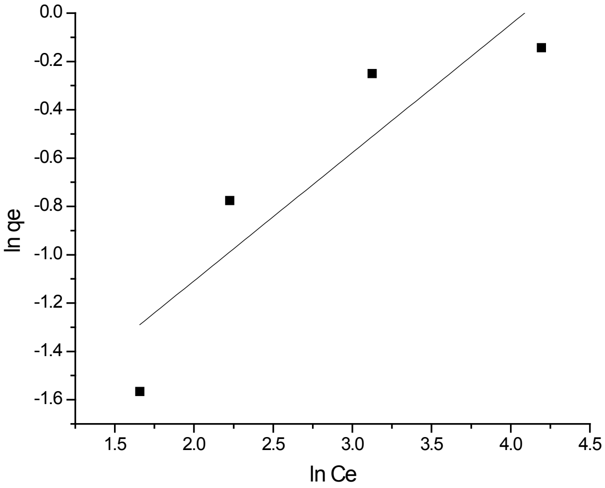


Fig. 12. Freundlich isotherm plot of CFA (contact time = 360 min, dose = 40 g m/l, pH = 8.4, Temp = 35°C).

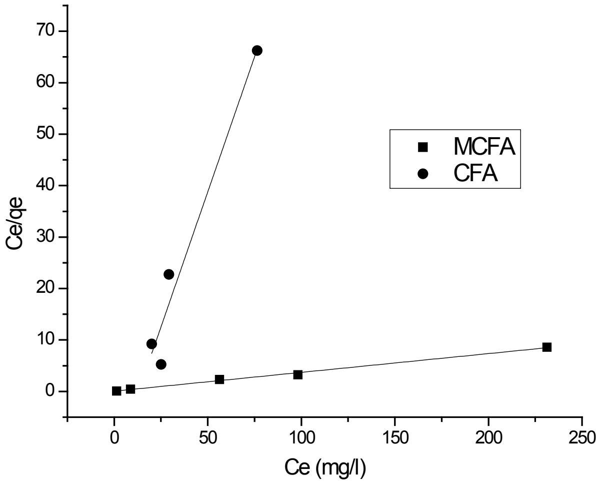


Fig. 13. Langmuir isotherm plot of MCFA (contact time = 60 min, dose = 10 g m/l, pH = 7, Temp = 35°C) and CFA (contact time = 360 min, dose = 40 g m/l, pH = 8.4, Temp = 35°C).

Table 3
Values of Freundlich isotherm

Adsorbent	K_f (l/mg)	$1/n$	R^2
MCFA	14.425	0.120	0.985
CFA	0.1142	0.530	0.818

Table 4
Values of Langmuir isotherm

Adsorbent	K_L (l/mg)	q_m (mg/g)	R^2
MCFA	0.6925	27.77	0.999
CFA	−0.0766	0.9532	0.960

phate concentration in equilibrium solution (mg/l), 'q_m' is the Langmuir sorption maximum or monolayer capacity (mg/g) and 'K_L' is a constant related to the binding strength of phosphate.

Experimental data was examined to meet the Freundlich model. The intercept values of K_f and slope of *1/n* was determined on plotting *ln* C_e with *ln* q_e for both MCFA and CFA separately which is shown in Figs. 11 and 12. The values of Freundlich constants of MCFA and CFA are shown in Table 3. Values in Table 3 shown that Freundlich fitted best for MCFA as compared to CFA, which indicates MCFA is favorable for better adsorption of Phosphate present in water. Langmuir isotherm is given by Eq. (2), in which constant was determined by plotting C_e with C_e/q_e for CFA and MCFA separately. The plotted graph is shown in Fig. 13 and obtained vales of constants in Table 4. It can be seen from Fig. 13 and Table 4 Langmuir isotherm model best fitted as compared to Fraundlich for MCFA with coefficient of 0.999. The higher K_1 value of MCFA as compared to K_l values of CFA indicates that rate of adsorption is fast on MCFA than that of CFA. The Langmuir constant (q_m) was 27.77 mg/g for MCFA, which is much greater than the Langmuir constant (q_m) of 0.9532 mg/g for CFA.

3.7. Adsorption kinetic

In proportion to find the mechanism of phosphate adsorption on MCFA and CFA, pseudo first order and pseudo second order kinetic model were used. The integrated equations proposed by Ho, Y.S [14] were used in the developing of kinetics. The kinetics of phosphate adsorption was reported for both CFA and MCFA. The order of model was determined by using Eqs. (3)–(7) developed by Ho, Y.S [14] and P. SethilKumar [15].

3.7.1. Pseudo first order model

In the investigation of phosphate adsorption mechanism on CFA and MCFA pseudo first order equation is

$$\frac{dq}{dt} = K_1\left(q_e - q_t\right) \tag{3}$$

where, q_t is the amount of adsorbate at time t (mg/g), $q_t = \frac{v(C_o - C_t)}{m}$; q_e is the adsorption capacity in equilibrium (mg/g), k_1 is the rate constant of pseudo-first order model (min^{-1}); t is the time (min); v is the volume of solution taken; m is the amount of adsorbent; C_o is the initial concentration of the solution; C_t is the concentration of solution at time t.

The resulting integrated equation with the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation is

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_{1t}}{2.303} \tag{4}$$

Rate constant (k_1) for the adsorption of phosphate was determined from the slope on plotting the graph of log (q_e – q_t) vs. *time* for different phosphate concentration. The graph of *log* (q_e – q_t) vs. *time* for MCFA and CFA is shown in Fig. 14 and Fig. 15. From the same graphs equilibrium adsorption capacity ($q_{e,cal}$) was determine by taking the intercept of

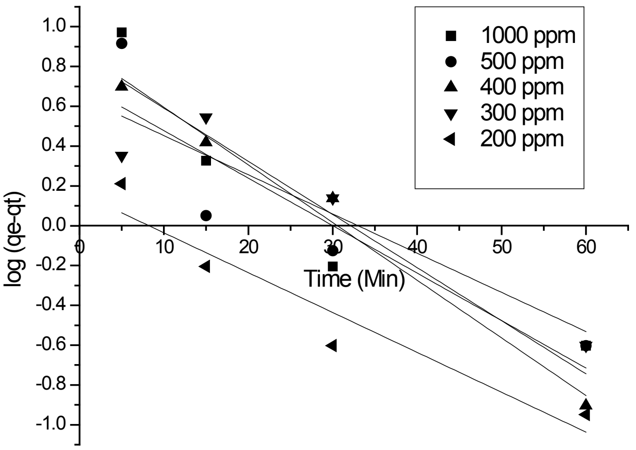


Fig. 14. Pseudo-first-order plot for adsorption of phosphates on MCFA for different phosphate concentration. (pH = 7.0, adsorbent dosage = 10 g m/l, temperature = 30°C).

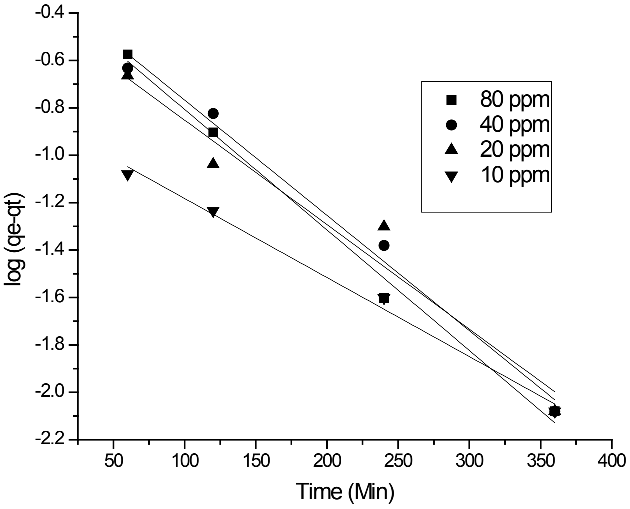


Fig. 15. Pseudo-first-order plot for adsorption of phosphate on CFA for different phosphate concentration. (pH = 8.4, adsorbent dosage 36 g/L, temperature = 30°C).

curves. Obtained values of correlation coefficients *(R^2)*, rate constants *(K_1)* and equilibrium adsorption capacity *($q_{e,cal}$)* are shown in Table 5 for the different phosphate concentration using CFA and MCFA as an adsorbent.

3.7.2. Pseudo second order model

The pseudo-second order model equation is

$$\frac{dq}{dt} = k_s\left(q_e - q_t\right)^2 \tag{5}$$

where k_s is the rate constant of pseudo-second order model (g/mg·min).

The resulting integrated equation with the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ is given by following equation

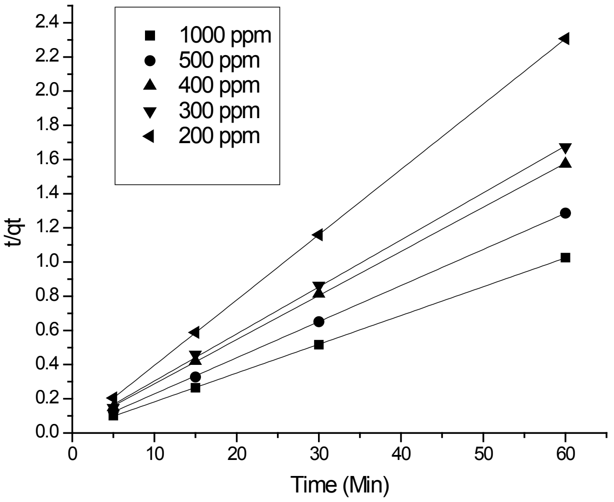


Fig. 16. Pseudo-second-order plot for adsorption of phosphate on MCFA for different phosphate concentration. (pH = 7.0, adsorbent dosage = 10 g m/l and Temp. 35°C).

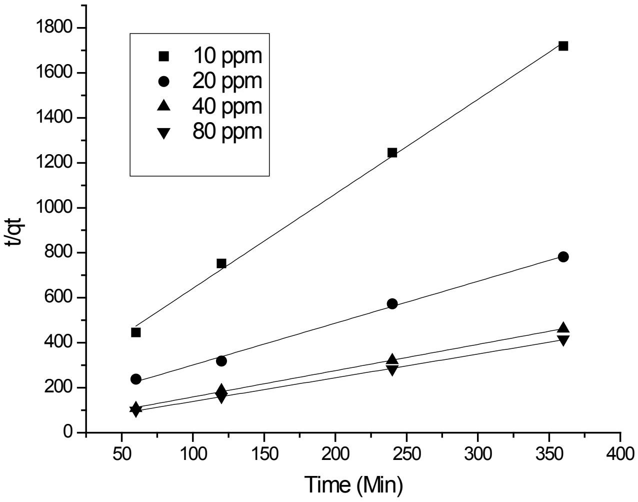


Fig. 17. Pseudo-second-order plot for adsorption of phosphate on CFA for different phosphate concentration. (pH = 8.4, adsorbent dosage = 36 g m/l and Temp. 35°C).

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \tag{6}$$

The initial sorption rate, h (mg/g min), as $t = 0$ can be defined as:

$$h = k_s q_e^2 \tag{7}$$

The graphs for t/q_t vs. *time* for CFA and MCFA was plotted for the determination of rate constant *(k_s)* from pseudo second order on taking slope of curves and from the intercept equilibrium adsorption capacity *($q_{e,cal}$)* was calculated for different phosphate concentration. The graph of t/q_t vs. *time* for CFA and MCFA is shown in Figs. 16 and 17.

Table 5
Pseudo first order and pseudo second order kinetics model for MCFA and CFA

Initial concentration (mg/l)	I^{st} order. rate constant (K_1)	II^{nd} order rate constant (K_s)	q_e values (I^{st} order)				q_e values (II^{nd} order)				R^2		*h*
			CFA		MCFA		CFA		MCFA		I^{st} Order	II^{nd} Order	
			$q_{e,\ cal.}$	$q_{e,\ exp.}$	$q_{e,\ cal.}$	$q_{e,\ exp.}$	$q_{e,\ cal.}$	$q_{e,\ exp.}$	$q_{e,\ cal.}$	$q_{e,\ exp.}$			
10	0.00690	0.07942	0.1419	0.2177	–	–	0.2381	0.2177	–	–	0.992	0.997	0.0045
20	0.00921	0.03011	0.3890	0.4604	–	–	0.5376	0.4604	–	–	0.958	0.996	0.0087
40	0.00921	0.03208	0.5248	0.7875	–	–	0.8568	0.7875	–	–	0.990	0.999	0.0235
80	0.01151	0.03290	0.5035	0.8750	–	–	0.9496	0.8750	–	–	0.992	0.999	0.0296
200	0.04606	0.11108	–	–	1.4586	26.125	–	–	26.3158	26.125	0.880	0.999	76.925
300	0.04376	0.02514	–	–	4.4566	36.125	–	–	37.037	36.125	0.813	0.999	34.485
400	0.06678	0.02155	–	–	7.65596	38.250	–	–	40.006	38.250	0.986	0.998	34.490
500	0.05297	0.02594	–	–	5.19995	46.875	–	–	47.619	46.875	0.884	0.999	58.821
1000	0.05988	0.01829	–	–	7.1940	58.750	–	–	62.50	58.75	0.918	0.997	71.445

Corresponding correlation coefficients *(R^2)* and adsorption rates (*h)* were calculated and are indicated in Table 5. Correlation coefficients *(R^2)* are close to one for pseudo second order kinetics for all initial phosphate concentration as compared to pseudo first order kinetics. Hence the adsorption of phosphate using CFA and MCFA has well fitted by pseudo second order kinetics. The chemisorptions are the rate limiting step. It can also be seen that the initial sorption rate *'h'* value for adsorption on MCFA are higher than that for adsorption on CFA. Experimental equilibrium adsorption capacity *($q_{e,\ exp}$)* and calculated equilibrium adsorption capacity *($qe,_{cal}$)* for both the model are nearer to each other. From the values of rate constants of pseudo-second order model, intraparticle diffusion rate is found significant. This adsorption occurs from external surface to the pores and then in to the internal surface of CFA and MCFA adsorbent.

4. Conclusion

From obtained results and discussion following conclusion is drawn:

1. Modification with acid on fly ash was more effective in the removal of phosphates from water. Untreated CFA showed limited phosphate adsorption capacity but modification by sulfuric acid on CFA could significantly increase its surface area and enhance the phosphate adsorption ability.
2. The phosphate removal by MCFA is highly dependent on the pH of solution. Percentage removal of phosphate increases with increasing in the pH. The optimum pH for removal of phosphate was found to be 7.0.
3. Maximum phosphate removal (>98 %) was found on the adsorbent dose of 10 g/L for MCFA, which can be considered as an optimum and effective adsorbent dosage at desired conditions.
4. Adsorption of phosphates on MCFA was rapid, hence adsorption of the phosphate could reach maximum (>95 %) in 5–15 min.
5. Adsorption of phosphate on MCFA is best described by Langmuir adsorption isotherm.
6. Phosphate immobilization capacity by MCFA has been improved significantly with the help of producing aluminum phosphate, calcium phosphate and iron phosphate in water.
7. Hence MCFA have more affinity towards the phosphate removal from water and can be used economically as an alternative low cost adsorbent.

References

[1] J.E. Kotoski, Phosphorus mini fact and analysis sheet, Spring Harbor Environmental Magnet Middle School, Madison, WI, 1997.

[2] N. Bektas, H. Akbulut, H. Inan, A. Dimoglo, Removal of phosphate from aqueous solutions by electro-coagulation, J. Hazard. Mater., 106 (2004) 101–105.

[3] M. Ahmaruzzaman, A review on the utilization of fly ash, Progr, Energy Comb. Sci., 33 (2010) 327–363.

[4] J. Yan, D.W. Kirk, C.Q. Jia, X. Liu, Sorption of aqueous phosphorus onto bituminous and lignitous coal ashes, J. Hazard. Mater., 148 (2007) 395–401.

[5] K. Xu, T. Deng, J. Liu, W. Peng, Study on the phosphate removal from aqueous solution using modified fly ash, Fuel, 193 (2010) 123–133.

[6] Li. Feihu, Wu. Wenhao, Li. Renying, Fu. Xiaoru, Adsorption of phosphate by acid-modified fly ash and palygorskite in aqueous solution: Experimental and modeling, Appl. Clay Sci., 132–133 (2016) 343–352.

[7] S.G. Lu, S.Q. Bai, L. Zhu, H.D. Shan, Removal mechanism of phosphate from aqueous solution by fly ash, J. Hazard. Mater., 161 (2009) 95–101.

[8] P. Pengthamkeerati, T. Satapanajaru, P. Chularuengoaksorn, Chemical modification of coal fly ash for the removal of phosphate from aqueous solution, Fuel, 87 (2008) 2469–2476.

[9] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloids Surfaces A: Physicochem. Eng. Asp., 264 (2005) 17–28.

[10] H.M.F Freundlich, Over the adsorption in solution, J. Phys. Chem., 57 (1906) 385–470.

[11] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[12] A. Ugurlu, B. Salman, Phosphorus removal by fly ash, Environ. Int., 24 (1998) 911–918.

[13] J. Chen, H. Kong, D. Wu, X. Chen, D. Zhang, Z. Sun, Phosphate immobilization from aqueous solution by fly ashes in relation to their composition, J. Hazard. Mater., 139 (2007) 293–300.

[14] Ho. Yuh-shan, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics, 59 (2004) 171–177.

[15] P. Senthil Kumar, K. Kirthika, Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder, J. Eng. Sci. Tech., 4 (2009) 351–363.