

PHOSPHATE ION REMOVAL FROM MODEL SOLUTION USING ACID TREATED COAL FLY ASH

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Abstract

This research was aimed to examine the adsorption behaviour of phosphate ion on modified coal fly ash under different operating conditions to determine the optimum condition to remove phosphate ion. The coal fly ash was treated with hydrochloric acid and optimal conditions were found to be 2 M HCl solution, the ratio of coal fly ash and acid solution is 1:2 (w/v) and for 2 h of acid treated time at ambient temperature. Batch adsorption experiments were performed to evaluate phosphate removal efficiency of acid treated coal fly ash. The effect of various adsorption parameters, *i.e.* pH, adsorption time, adsorbent dose and initial phosphate ion concentration using the acid treated coal fly ash was studied. The maximum removal percent of phosphate ion was achieved 94.03 % at an adsorbent acid treated coal fly ash loading weight of 0.1 g/100 mL, 1 mg L⁻¹ of initial concentration of phosphate solution, pH of 3 and 90 min of contact time at ambient temperature. Coal fly ash (CFA), acid treated coal fly ash (ACFA) and phosphate ion sorpted acid treated coal fly ash (PACFA) were characterized by using modern techniques such as SEM, EDXRF and XRD. According to widen applicability of the proposed method, it can be used for the removal of phosphate from eutrophicated surface water.

Keywords: Coal fly ash, acid treated coal fly ash, removal of phosphate ion

Introduction

Excess concentrations of phosphate ion in water cause eutrophication (Mikendova *et al.*, 2010). In advanced stages of eutrophication, dissolved oxygen can become depleted to dangerously low levels causing fish death when algae decay. It is not only destroys the aquatic life but also disrupts the balance of the aquatic ecosystem (Mustafa *et al.*, 2008). During the past decades, various techniques, including biological treatment and chemical precipitation have been reported for phosphate removal. Adsorption is one of the techniques, which is comparatively more useful and economical for such removal (Ragheb, 2013). Fly ash is actually captured from the chimneys of coal fired power plants. It contains various trace elements in various quantities and during combustion process of coal trace elements get associated on the surface of ash particles due to evaporation and condensation (Benito *et al.*, 2001). Recently, the treated coal fly ash has been used for the removal of phosphate ion.

Materials and Methods

Materials

The chemicals used were procured from British Drug House (BDH), England, Wako Co. Inc., Tokyo, Japan and Sigma Aldrich, USA. The apparatus are conventional lab ware, glassware and modern equipment.

Sampling and Preparation of Coal Fly Ash

Coal fly ash sample was collected from Tigyit power plant located in South-west Shan State in Myanmar (PYO, 2011). Coal fly ash sample was taken systematically from a large number of material bags. Sampling was carried out by cone and quartering method. Sample was

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homogenized into small particles using a grinding mill and then made to obtain 250 μm mesh size. The obtained coal fly ash sample was dried at 105 °C in an oven for an hour.

Preparation of Standard Potassium Dihydrogen Phosphate Stock Solution

Standard stock solution of potassium dihydrogen phosphate 10 mg L⁻¹ was firstly prepared by dissolving 0.0219 g of KH₂PO₄ in 500 mL of deionized water. In the preparation of series of phosphate solutions 2, 4, 6, 8, 10 and 12 mL of 10 mg L⁻¹ stock solution were diluted to 100 mL with deionized water to give 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mg L⁻¹ solution respectively.

Preparation of Reagent Solutions

Ammonium molybdate solution

Ammonium molybdate 4 g was dissolved in 100 mL of deionized water.

2.5 M sulphuric acid

Concentrated sulphuric acid 70 mL was added to the 500 mL volumetric flask and diluted with deionized water to the mark.

Potassium antimonyl tartrate

Potassium antimonyl tartrate 1.3715 g was dissolved in 500 mL of deionized water.

Stock reagent

A stock reagent was prepared by adding 15 mL of ammonium molybdate solution, 50 mL of 2.5 M sulphuric acid, 5 mL of potassium antimonyl tartrate solution.

0.1 M ascorbic acid solution

Ascorbic acid 0.88 g was dissolved in 50 mL of deionized water.

Mixed reagent

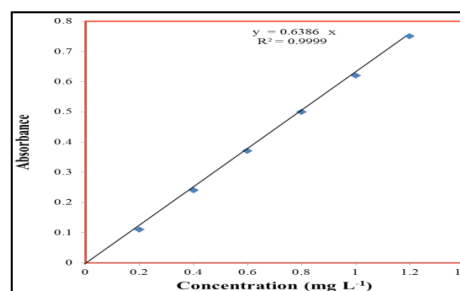
A mixed reagent was freshly prepared on the day of each analysis by adding 30 mL of ascorbic acid solution to 70 mL of stock reagent.

Calibration curve for phosphate solution

A spectrophotometer was used to measure the residual colour, remaining after adsorption. The residual colour index is expressed as absorbance. The primary stage of the work, include the construction of calibration curve by using absorbance and concentration of the phosphate solution. The calibration curve was used to evaluate the residual colour index (*i.e.* absorbance) against a series of standard phosphate concentrations (Arnold *et al.*, 1992). The stock solutions of phosphate in different concentrations range between 0.2 mg L⁻¹ to 1.2 mg L⁻¹ were chosen and dilution was made by using deionized water. A stock solution 50 mL was pipetted into a clean and dry beaker. Mixed reagent 8 mL was added and the solution was then allowed to stand for 10 min. A solution of the blue colour complex was formed. The absorbance of solution was measured by UV-visible spectrophotometer at 880 nm against a blank of distilled water. The data for plotting the calibration curve and plot are shown in Table 1 and Figure 1.

Table 1 Absorbance vs Concentration of Potassium Dihydrogen Phosphate Solution

Concentration (mg L ⁻¹)	Absorbance at 880 nm
0.2	0.11
0.4	0.24
0.6	0.37
0.8	0.50
1.0	0.62
1.2	0.75

**Figure 1** Calibration curve for potassium dihydrogen phosphate solution

Modification of Coal Fly Ash

The coal fly ash was subjected to the modification, because of its feasible grain composition. For the modification the solution of HCl in 1.0, 1.5, 2.0, 2.5 and 3.0 M concentrations was used. The mixture was treated at ambient temperature for 1 to 3 h. The fly ash was treated in HCl solutions in the ratio of 1:0.5, 1:1, 1:2, 1:3 and 1:4 (w/v) at ambient temperature. At the end of the treatment, the mixture was filtered and dried in the oven at 65 °C.

Phosphate Adsorption

0.08 g of each sample (acid treated coal fly ash) was added to 100 mL of KH₂PO₄ solutions in concentrations of 1 mg L⁻¹ at pH 3. The samples were equilibrated by continuous shaking on a rotating shaker 150 rpm at ambient temperature. The suspensions were then filtrated. The concentrations of phosphate ion were measured by standard spectrophotometric method with a UV-Visible spectrophotometer at 880 nm.

Percent Removal of Phosphate Ion by the Acid treated Coal Fly Ash

Percent removal of phosphate ion at different pH

The model solution of potassium dihydrogen phosphate 1 mg L⁻¹ was prepared and the pH was adjusted at 1, 2, 3, 4, 5, 6 and 7 by adding of 0.001 M and 1 M HCl. Each 100 mL of phosphate solution was separately mixed with 0.08 g of acid treated coal fly ash in the flasks. The flasks were shaken with electric shaker at room temperature for 1 h. At the end of the equilibrium time, each of the solution was filtered. A filtrate solution was measured by standard spectrophotometric method with a UV-Visible spectrophotometer at 880 nm.

Percent removal of phosphate ion at different contact times

The acid treated coal fly ash 0.08 g was placed into a 100 mL of phosphate solution 1 mg L⁻¹ at pH 3. The solutions were shaken by an electric shaker. After the contact times 20, 40, 60, 80, 100 and 120 min each solution was filtered. A filtrate solution was measured by standard spectrophotometric method with a UV-Visible spectrophotometer at 880 nm.

Percent removal of phosphate ion at different dosages of the acid treated coal fly ash

The accurately weighed acid treated coal fly ash in 0.04, 0.08, 0.12, 0.16, 0.20 and 0.24 g was taken into a conical flask. 100 mL of constant concentration of phosphate solution 1 mg L⁻¹, pH 3 was added to each of acid treated coal fly ash in separate conical flask and shaken by electric shaker at room temperature for 1 h. After this contact time, each of the solution was

filtered. A filtrate solution was measured by standard spectrophotometric method with a UV-Visible spectrophotometer at 880 nm.

Percent removal of phosphate ion at different initial concentrations of phosphate solutions

The model solutions of potassium dihydrogen phosphate 0.5 mg L^{-1} , 1.0 mg L^{-1} , 1.5 mg L^{-1} and 2.0 mg L^{-1} were prepared and the pH of the solutions was adjusted at 3 by adding 1 M HCl solution. Each 100 mL of phosphate solution was separately with mixed 0.1 g of acid treated coal fly ash in the flasks. The flasks were shaken with electric shaker at room temperature for 90 min. At the end of the equilibrium time, each of the solution was filtered. A filtrate solution was measured by standard spectrophotometric method with a UV-Visible spectrophotometer at 880 nm.

Characterization of Coal Fly Ash, Acid Treated Coal Fly Ash and Phosphate Ion Sorpted Acid Treated Coal Fly Ash

Coal fly ash, acid treated coal fly ash and phosphate ion sorpted acid treated coal fly ash were characterized by using modern instrumental techniques, such as SEM, EDXRF and XRD.

Results and Discussion

Modification of Coal Fly Ash

Effect of treated concentrations of HCl

Coal fly ash treated with a various HCl concentration showed different behaviors in the phosphate uptake. Coal fly ash treated with 1.0, 1.5, 2.5 and 3.0 M HCl showed even a lower phosphate removal percent than 2 M HCl (Figure 2). The best results were showed by the fly ash treated with 2 M HCl. The optimum condition of percent removal of phosphate ion was found to be 86.12 % by 2 M HCl treated coal fly ash while percent removal of phosphate ion by coal fly ash at pH 3 is 40.06 %.

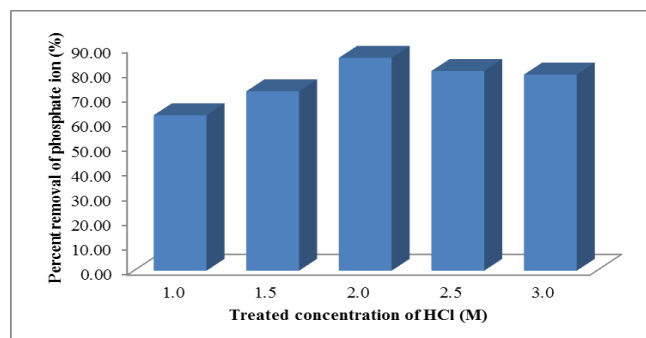


Figure 2 Effect of treated concentrations of HCl on the percent removal of phosphate ion by various HCl treated coal fly ash

Effect of treated time`

From the resulting data as treated time increases, the percent removal of phosphate ion also increases. Percent removal of phosphate ion at 2 h and 3 h treated time are nearly the same, therefore the optimum condition of treated time was 2 h. The results are shown in Figure 3.

Effect of ratio of coal fly ash and HCl concentration

The fly ash was treated in 2 M HCl solutions in the ratios of 1:0.5, 1:1, 1:2, 1:3 and 1:4 (w/v). The mixture was treated at ambient temperature for 2 h. From the resulting data,

optimum condition of ratio of coal fly ash and HCl concentration was found to be 1:2 (w/v). From the overall resulting data, optimum condition of the modification of coal fly ash was found to be 2 M HCl solution, in the ratio of 1:2 (w/v) and for 2 h of acid modification process. The results are shown in Figure 4.

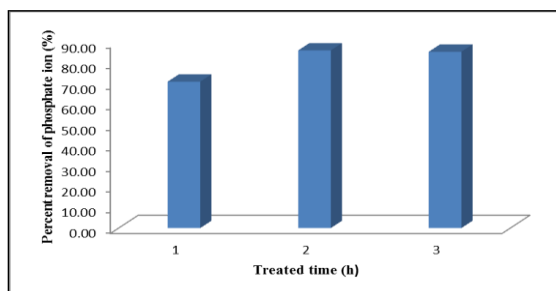


Figure 3 Effect of treated time on the percent removal of phosphate ion by 2 M HCl treated coal fly ash

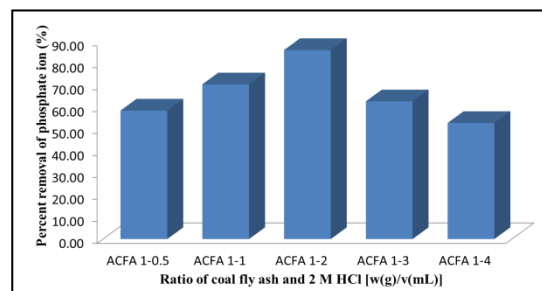


Figure 4 Effect of ratio of coal fly ash and 2 M HCl concentration on the percent removal of phosphate ion by acid treated coal fly ash

Percent Removal of Phosphate Ion by the Acid Treated Coal Fly Ash

Effect of pH

The dependence of removal of phosphate ion on pH of the aqueous dispersion for acid treated coal fly ash was studied and the results are shown in Figure 5. The percent removal of phosphate ion on acid treated coal fly ash was examined at various pH ranging from 1.0 to 7.0 with an initial phosphate ion concentration of 1 mg L⁻¹ at room temperature. From the resulting data, as pH increases, the percent removal was observed to increase until it reached to the optimum condition of pH 3. The maximum percent removal of phosphate ion in 1 mg L⁻¹ of initial concentration was 86.12 % by using dosage of acid treated coal fly ash 0.08 g/100 mL at pH 3 after 1 h contact time.

Effect of contact time

The effect of contact time on the percent removal of phosphate ion by using initial concentration of 1 mg L⁻¹ by acid treated coal fly ash was also studied and the results were shown in Figure 6. The percent removal of phosphate ion was measured by using 0.08 g/100 mL dosage of acid treated coal fly ash under pH 3 and ambient temperature at different contact times 20, 40, 60, 80, 100 and 120 min. Results showed that the extent of adsorption was observed to increase with contact time.

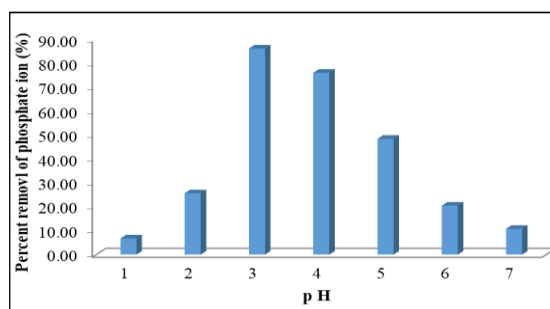


Figure 5 Effect of pH on the percent removal of phosphate ion by acid treated coal fly ash

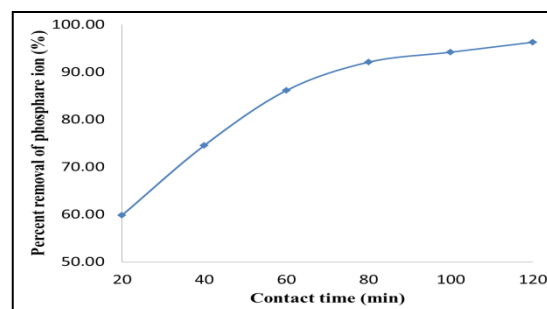


Figure 6 Effect of contact time on the percent removal of phosphate ion by acid treated coal fly ash

Effect of dosage of acid treated coal fly ash

The effect of acid treated coal fly ash dosage used for the percent removal of phosphate ion from a constant initial concentration 1 mg L^{-1} at pH 3 was also determined by using the amounts of sorbent in range from 0.04 g to 0.24 g in 100 mL potassium dihydrogen phosphate solution at contact time 1 h at ambient temperature. The corresponding resulting data in terms of percent removal with respect to sorbent dose are summarized in Figure 7. The percent removal of phosphate ion was increased by the increase of adsorbent dosage due to their increasing surface area.

Effect of initial concentration of phosphate ion

The effect of initial concentration of phosphate ion on the percent removal of phosphate ion by acid treated coal fly ash was studied at initial concentrations ranging from 0.5 mg L^{-1} , 1.0 mg L^{-1} , 1.5 mg L^{-1} and 2.0 mg L^{-1} by keeping all other parameters such as adsorbent dose 0.1 g/100 mL, pH 3 and contact time 90 min at ambient temperature. It was noticed that with increase in initial phosphate ion concentration, the percent removal of phosphate ion decreased. The maximum percent removal of phosphate ion was found to be 94.03 % by acid treated coal fly ash at 1 mg L^{-1} of initial concentration, 0.1 g/100 mL of dosage, pH 3 and 90 min of contact time at ambient temperature. The results are shown in Figure 8.

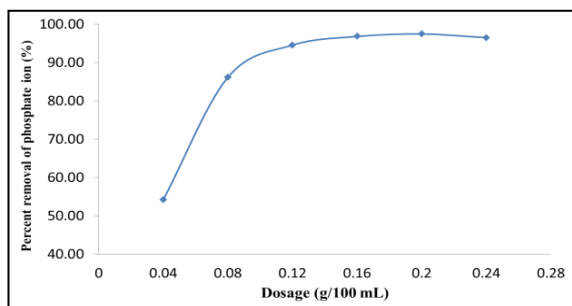


Figure 7 Effect of dosage on the percent removal of phosphate ion by acid treated coal fly ash

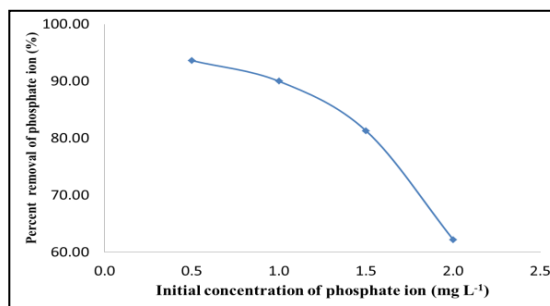


Figure 8 Effect of initial concentration of phosphate ion on the percent removal of phosphate ion by acid treated coal fly ash

Characterization of Coal Fly Ash, Acid Treated Coal Fly Ash and Phosphate Ion Sorpted Acid Treated Coal Fly Ash

SEM micrographs of the surface morphology of coal fly ash are given in Figure 9. It was found that coal fly ash showed the presence of different size of microparticles in the shape of smooth balls. SEM micrographs of the surface morphology of acid treated coal fly ash are given in Figure 10. It was found that acid treated coal fly ash showed only agglomerations of undefined shape. After acid treatment, the surface of fly ash particles is formed on the surface of a lot of grooves and holes, which can enhance the adsorption of the colloidal particles. SEM micrographs of the surface morphology of phosphate ion sorpted acid treated coal fly ash are given in Figure 11. It was found that phosphate ion sorpted acid treated coal fly ash showed that there were flocculant materials adhered to the particles or occurred separately.

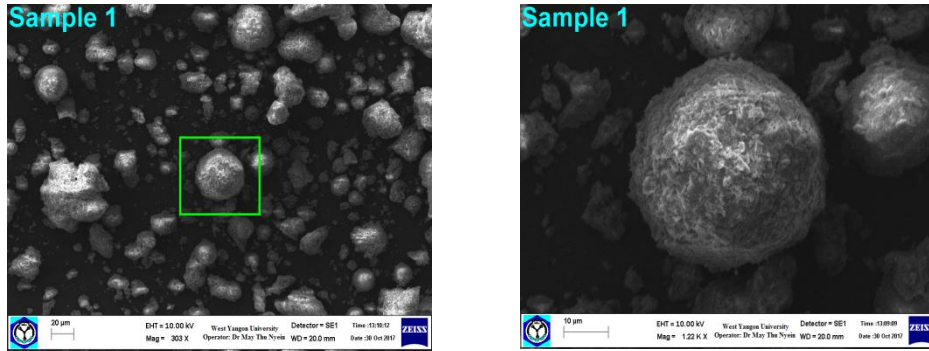


Figure 9 SEM micrographs of coal fly ash

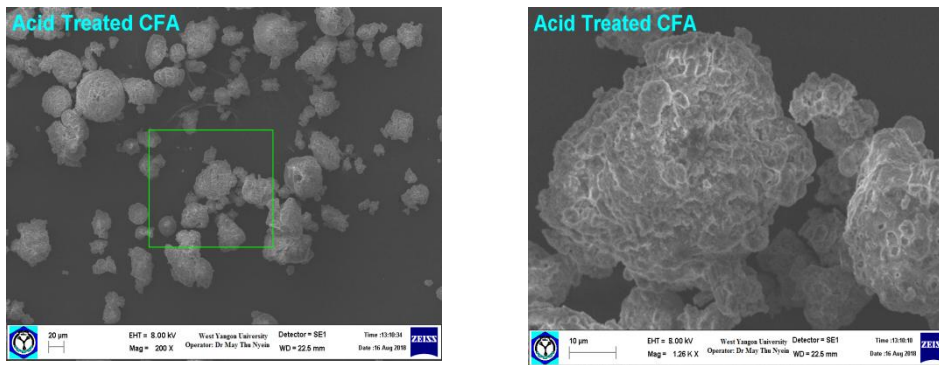


Figure 10 SEM micrographs of acid treated coal fly ash

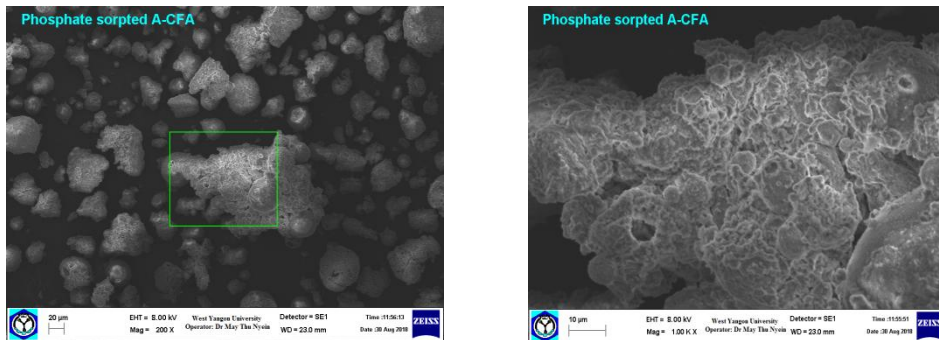


Figure 11 SEM micrographs of the phosphate ion sorpted acid treated coal fly ash

The relative abundance of metallic oxides in coal fly ash, acid treated coal fly ash and phosphate ion sorpted acid treated coal fly ash were examined by EDXRF technique. The chemical compositions of samples are shown in Table 2.

The highest amounts of SiO₂ (53.845 %), Al₂O₃ (21.330 %), CaO (17.632 %) and Fe₂O₃ (4.444 %) were found in the coal fly ash. Total relative abundance (%) of SiO₂+Al₂O₃+Fe₂O₃ is 79.619 %. Therefore this coal fly ash is class F and produced from burning of anthracite and bituminous coal.

The highest amounts of SiO₂ (47.697 %), Al₂O₃ (22.426 %), CaO (7.527 %) and Cl (10.398 %) were found in acid treated coal fly ash. After treating with HCl, it can be seen that Cl is one of the constituent in acid treated coal fly ash.

Table 2 Relative Abundance of Metallic Oxides in the Coal Fly Ash (CFA), Acid Treated Coal Fly Ash (ACFA) and Phosphate Ion Sorpted Acid Treated Coal Fly Ash (PACFA) by EDXRF

No	Metallic Oxides	Relative abundance (%)		
		CFA	ACFA	PACFA
1	SiO ₂	53.845	47.697	23.545
2	Al ₂ O ₃	21.330	22.426	5.276
3	CaO	17.623	7.527	2.525
4	Fe ₂ O ₃	4.444	6.364	1.147
5	TiO ₂	0.725	0.966	0.176
6	Cl	---	10.398	---
7	P ₂ O ₅	---	---	35.800

The highest amounts of P₂O₅ (35.800 %), SiO₂ (23.545 %), Al₂O₃ (5.276 %) and CaO (2.525 %) were found in phosphate ion sorpted acid treated coal fly ash. After sorption with model solution, it can be seen that P₂O₅ is one of the constituent in phosphate ion sorpted acid treated coal fly ash. The oxides of Al and Fe are significantly decreased in phosphate ion sorpted acid treated coal fly ash. This is due to the binding of phosphate ion with aluminum and iron resulting in the formation of metal phosphates.

In this research, XRD measurement was carried out on coal fly ash. The resultant XRD diffractogram is shown in Figure 12. According to XRD diffractogram, presence of strong intensity peaks of quartz (SiO₂) with Miller indices (101) and (100) were observed at 2θ values of 26.433° and 20.666° respectively. And then presence of aluminum oxide (Al₂O₃) with Miller indices (201) and (400) were observed at 2θ values of 24.814° and 30.967° respectively. The phase analysis of coal fly ash indicated the presence of quartz (SiO₂), aluminum oxide (Al₂O₃), hematite (Fe₂O₃) and lime (CaO). These findings confirmed that the coal fly ash mainly consists of quartz (SiO₂) and aluminum oxide (Al₂O₃). Average crystallite size of coal fly ash was calculated and found to be 24.04 nm by Debye Scherrer equation. The crystal structure of coal fly ash was found to be hexagonal according to lattice parameters (a = b = 6.9803 Å and c = 5.4938 Å).

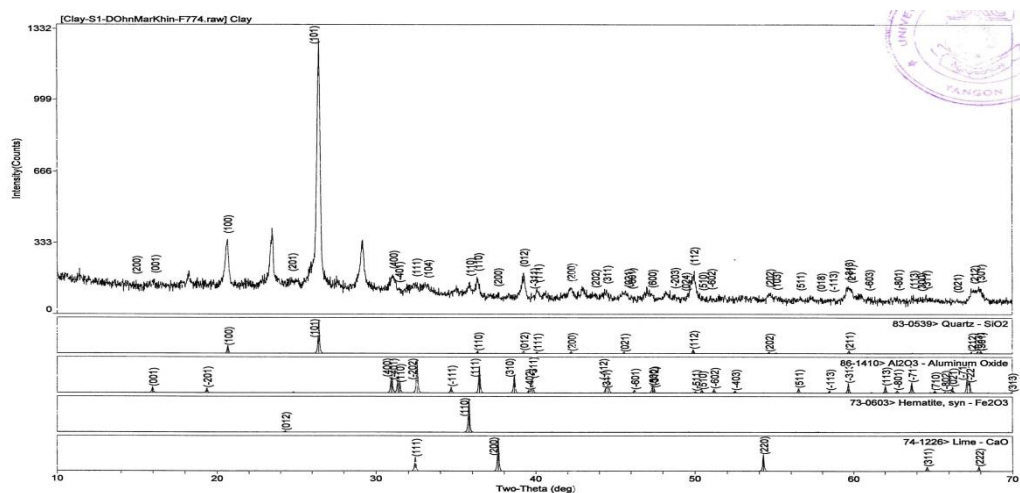


Figure 12 XRD diffractogram of coal fly ash

In this research, XRD measurement was carried out on acid treated coal fly ash. The resultant XRD diffractogram is shown in Figure 13. According to the XRD diffractogram, the presence of strong intensity peak of aluminum oxychloride (AlOCl) with Miller indices (111) was observed at 2θ values of 26.426° . The phase analysis of acid treated coal fly ash showed aluminum oxychloride (AlOCl), quartz (SiO_2), aluminum oxide (Al_2O_3), hematite (Fe_2O_3) and lime (CaO). These findings confirmed that the acid treated coal fly ash mainly consists of aluminum oxychloride (AlOCl). The presence of AlOCl was a result of the reaction of Al_2O_3 and acid soluble, aluminum containing compounds with hydrochloric acid. Average crystallite size of acid treated coal fly ash was calculated and found to be 26.51 nm by Debye Scherrer equation. The crystal structure of acid treated coal fly ash was found to be hexagonal according to lattice parameters ($a = b = 8.4307 \text{ \AA}$ and $c = 4.5657 \text{ \AA}$).

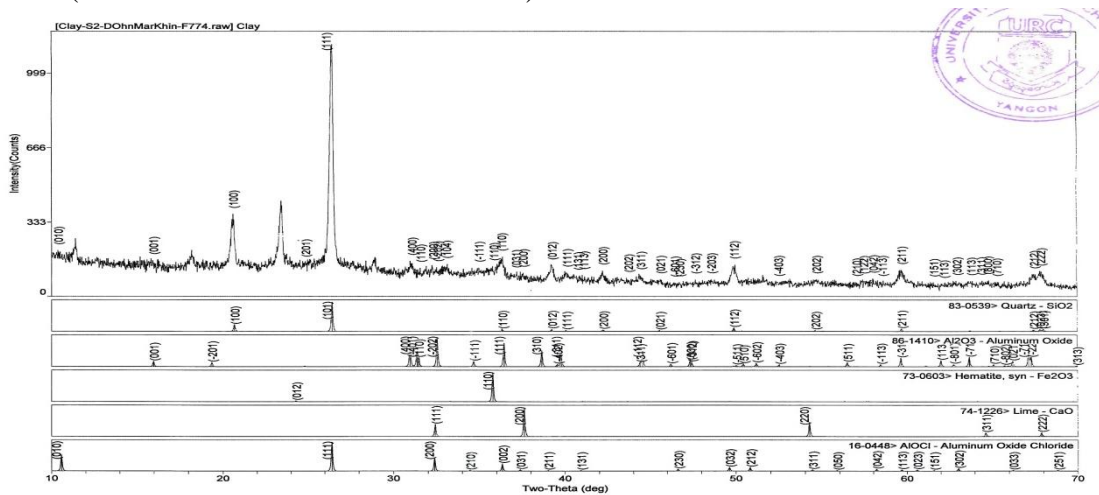


Figure 13 XRD diffractogram of acid treated coal fly ash

In this research, XRD measurement was carried out on phosphate ion sorpted acid treated coal fly ash. The resulting data are presented in Figure 14. According to XRD diffractogram, presence of strong intensity peak of aluminum phosphate (AlPO_4) with Miller indices (012) was observed at 2θ values of 26.414° . And then presence of iron phosphate $\text{Fe}(\text{PO}_4)$ with Miller indices (101) was observed at 2θ values of 21.873° . Average crystallite size of phosphate ion sorpted acid treated coal fly ash was calculated and found to be 31.82 nm by Debye Scherrer equation. The crystal structure of phosphate ion sorpted acid treated coal fly ash was found to be hexagonal according to lattice parameters ($a = b = 8.4403 \text{ \AA}$ and $c = 4.7976 \text{ \AA}$).

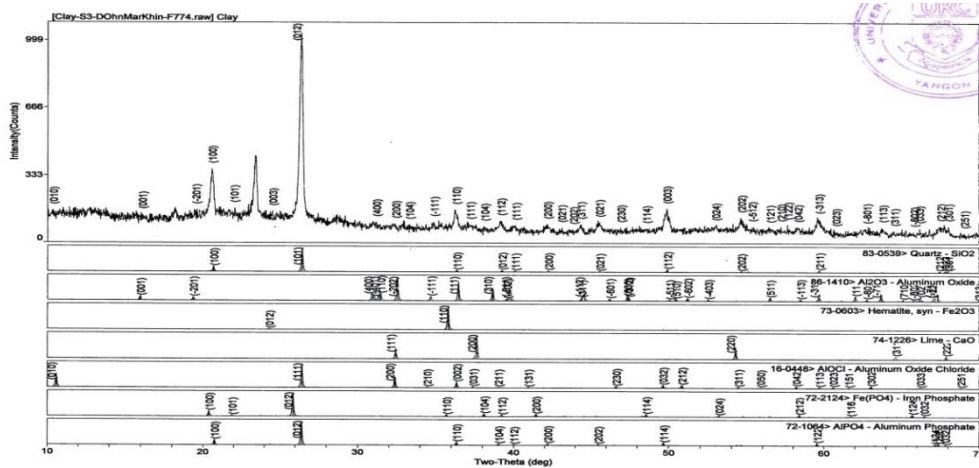


Figure 14 XRD diffractogram of the phosphate ion sorpted acid treated coal fly ash

Conclusion

In this research, adsorption method was used to remove the phosphate ion from the model solution by using acid treated coal fly ash as a sorbent. Modified acid treated coal fly ash is effective adsorbents as compared to coal fly ash collected from Tigyit power plant located in South-west Shan State in Myanmar for the removal of phosphate ion from aqueous solution. The sorption behaviors of the maximum percent removal of phosphate ion were found to be 94.03 % by acid treated coal fly ash at 1 mg L⁻¹ of initial concentration, 0.1 g/100 mL of dosage, pH 3 and 90 min of contact time at ambient temperature.

Coal fly ash, acid treated coal fly ash and phosphate ion sorpted acid treated coal fly ash were characterized by using modern instrumental techniques, such as SEM, EDXRF and XRD. SEM analysis showed the presence of different size of microparticles in the shape of smooth balls found in the coal fly ash. Acid treated coal fly ash showed only agglomerations of undefined shape and flocculant materials adhered to the particles or occurred separately in phosphate ion sorpted acid treated coal fly ash. EDXRF analysis showed that total relative abundance (%) of SiO₂+Al₂O₃+Fe₂O₃ is 79.619 %. Therefore, this coal fly ash is class F and produced from burning of anthracite and bituminous coal. XRD analysis also confirmed that the coal fly ash mainly consists of quartz (SiO₂) and aluminum oxide (Al₂O₃). XRD analysis confirmed that the acid treated coal fly ash mainly consists of aluminum oxychloride (AlOCl). The presence of aluminum oxychloride was a result of the reaction of Al₂O₃ and acid soluble, aluminum containing compounds with hydrochloric acid. According to XRD diffractogram, presence of strong intensity peak of aluminum phosphate (AlPO₄) was observed. These findings confirmed that the phosphate ion sorpted acid treated coal fly ash mainly consists of aluminum phosphate (AlPO₄).

It can be inferred from this research work that acid treated coal fly ash may be used as an effective sorbent to remove phosphate ions from eutrophicated surface water. Therefore, the outcome of this research work would lead to a cleaner and healthier environment.

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