

## Removal of Trace Elements in Waste Water by Alumina Nanoparticles from Coal Fly Ash

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### ABSTRACT

Coal burning produces fly ash, also known as flue-ash. It is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Fly ash is generally captured by electrostatic precipitators. In the present study, coal fly ash samples were collected from Tigypt Power Plant located in Piinlaung Township of Taungyi District in Shan State, Myanmar. It aimed to synthesize alumina nanoparticles from coal fly ash by using alkali lime sintering method and to apply it for waste water treatment. Alumina nanoparticles were obtained from leaching, pre-desilication, leaching, desilication, carbonation, and calcination steps, sand were found to agree with the aluminum nitrate using lactic acid as a standard reference. Using Debye Scherrer equation, the average crystallite size of alumina nanoparticles from chemical source and coal fly ash were found to be 47.83 nm and 63.55 nm, respectively. According to Lattice parameter values, the crystal structure of the obtained alumina nanoparticles was observed to be hexagonal. Using field emission scanning electron microscope, the morphology of alumina nanoparticles from chemical source and coal fly ash were found to be spherical in shape. Fly ash can be used as soil amendment to improve soils physical and chemical properties, to reduce pest damage on crops. Use of fly ash instead of lime in utilization of agriculture can reduce CO<sub>2</sub> emission and also reduce global warming. Using the alumina nanoparticles, removal of trace elements (copper, lead, nickel, zinc and cadmium) from waste water obtained from Textile Mill No (6) Branch, Heavy Industrial, No. (3), Ministry of Industry, Sagaing City, Sagaing Region was performed.

**KEYWORDS:** *alumina, Coal fly ash, Debye Scherrer, FE SEM, XRD*

### 1 INTRODUCTION

Fly ash represents the finest fraction of the non-combustible residue from coal burning. Fly ash particles are generally spherical in shape and range in size from 0.5  $\mu\text{m}$  to 300  $\mu\text{m}$  (Visa et al., 2014). The

major constituents of most of the fly ashes are silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (FeO) and calcium oxide (CaO) (Huang et al., 2011). The other minor constituent of the fly ash is MgO, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub>, MnO, TiO<sub>2</sub> and unburnt carbon) (Shoumkova et al., 2008). Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of a coal-fired power plant. This ash is a fine material that possesses good pozzolanic property. Any coal based thermal power station may have the following four kinds of ash: fly ash, bottom ash, pond ash, and mound ash (Kumar and Jha., 1991). There is a wide range of variation in the principal constituents-silica (25- 60%), alumina (10-30%) and iron oxide (5-25%). When the sum of these three principal constituents is 70% or more and the reactive calcium oxide is less than 10%, technically the fly ash is considered as siliceous fly ash (class F fly ash). This fly ash type is produced by burning of anthracite or bituminous coal and possesses pozzolanic property (Shoumkova et al., 2008). On the other hand, if the sum of these three constituents is equal or more than 50% and the reactive calcium oxide is not less than 10%, fly ash is considered as calcareous (class C fly ash). This type of fly ash is commonly produced by burning of lignite or sub-bituminous coal and possesses both pozzolanic and hydraulic properties (Kumar and Jha., 1991). The use of fly ash is very effective in the improvement of water quality in polluted lakes, which can reduce inorganic phosphorous, suspended matter, water color and organic concentrations (Amitava et al., 2011). Application of fly ash in clay soil significantly reduced the bulk density, and improved the soil structure, which in turn improves porosity, workability, root penetration and moisture retention capacity of the soil (Kishor et al., 2010). Fly ash can be used chemical fertilizers as a good nutrient supplement for degraded soils to some extent. Fly ash addition increases plant growth and nutrient uptake. Fly ash can also be used as insecticide and decrease the metal mobility and availability in soil to improve soil texture, to reduce bulk density of soil, to improve water holding capacity and soil aeration, percolation and water retention in the treated zone (Kishor et al., 2010).

Manufactured nanoparticles of aluminum oxide (nano-alumina) have been widely used in the environment. However, their potential toxicity provides a growing concern for human health because aluminum

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(a relatively stable in the form of alumina or aluminum oxide) can enter the body through drinking water, food intake, inhalation, and skin contact (Hongbin, 2011). Also, specific medical interventions, such as dialysis or certain aluminum-containing drugs, may lead to aluminum accumulation in the tissues (Hongbin, 2010). Fly ash can be applied in construction industry, ceramic industry environmental protection, and catalysis, zeolite synthesis and valuable metal recovery (Kumar, 1991). It can be found in China, India, U.S and EU countries. The aim of the present study was to prepare, characterize, and apply the alumina nanoparticles for waste water treatment.

## 2 MATERIALS AND METHODS

### Chemicals

Aluminum nitrate [British Drug House (BDH) Chemicals., Ltd., England], lactic acid (BDH) and polyvinylpyrrolidone (PVP) from (BDH), sodium hydroxide (BDH), calcium hydroxide (BDH) and deionized water were used in this study.

### Sample collection of coal fly ash

Coal fly ash samples were collected in Tigyit Power Plant from South-west Shan State in Myanmar (Fig. 1). The samples were collected at evening time. Non-magnetic portion of the coal fly ash samples was obtained by using magnetic separation machine. The coal fly ash samples were sieved to get the 200-mesh size (74  $\mu\text{m}$ ) after separation. This power plant is the only operating coal fired power station in Myanmar.

### Sampling of coal fly ash by coning and quartering method

A total of 10 kg per bag were collected for sampling. Sampling was done by placing the well mixed material into a flat cone and dividing it into quarters. Opposite quarters were rejected and the remaining half portion again treated as mentioned above, and rolling the sample back and forth on a paper. Each of four corners of the paper was kept for better mixing. The sample was treated again by coning and quartering for five times until desired amount of the representative sample was obtained. The representative sample was ground by mortar and pestle to the size of 200 mesh (74  $\mu\text{m}$ ) (Campos, 2017).

### Preparation and characterization of alumina nanoparticles from coal fly ash

Technologies of alumina extraction from coal fly ash can be classified into acidic, alkali and acid alkali methods. Among these methods, alkaline leaching sintering method was used to obtain alumina nanoparticles (Cheng, 2011). A 100 g of coal fly ash with 150 mL of 4 M sodium hydroxide solution were leached in a beaker (500 mL, Pyrex) as a leaching step (Mongia *et al.*, 2010). The mixed solution was heated at 100°C in an oven in a covered 500 mL beaker for 3 hours to dissolve silica. The solution was filtered with a Whatman No. 1 filter paper into a beaker. It was

carefully wiped and rinsed with distilled water to avoid the loss of residues. The residue on the filter paper was washed with 100 mL hot deionized water several times and dried in an oven at 105°C for 3 hours. The dried leached ash was placed into a muffle furnace (LEF-1035, DAIHAN LABTECH Group, Korea) at 1000°C for 3 hours. An amount of 70 g leached ashes was mixed with 94 g lime stone and 42 g soda ash. The mixture was placed into a muffle furnace at 1000°C for three hours to produce clinker. Sodium hydroxide solution (5 %) was added into the clinker (1:3). The mixed solution was heated at 90°C in a covered 500 mL beaker for 30 minutes with constant stirring to dissolve the silica and to produce sodium aluminate solution. The solution was filtered with a Whatman No. 1 filter paper and washed with hot distilled water. The sodium aluminate solution was desiccated by adding saturated lime milk at 1000°C for 1 hour (Audrone *et al.*, 2012). The sodium aluminate was obtained by desiccation. Then, the aluminum hydroxide was prepared by passing carbon dioxide into the sodium aluminate solution for carbonation decomposition (Fig. 1). Alumina nanoparticles were obtained by sintering aluminum hydroxide at 1000°C for 3 hours (Rodica *et al.*, 2011). Characterization of alumina nanoparticles from coal fly ash samples was carried out by (X-ray diffractometer, XRD, Rigaku-D-max 2200, Japan) and Field Emission Scanning Electron Microscope (EVO 60, Brand: Carl ZEISS, Germany).



Figure 1. a) Map of Myanmar and b) Tigyit power plant in Shan State

### Preparation and characterization of alumina nanoparticles from aluminum nitrate

A mixture of 10 g of aluminum nitrate, 3 g of lactic acid, and 50 mL of double distilled water was made, and was heated at 80°C with constant stirring in a covered beaker for three hours. Meanwhile, a 1.5 g of PVP was added into 30 mL double distilled water and stirred with a glass rod. The two solutions were later mixed and heated in a water bath for 1 hour. Then, the precursor solution was added in petri-dish and placed in an oven at 60 °C for two days. Crystalline nature of alumina nanoparticles was not found clearly at 800° and 900° C, but was observed at 1000° C. The particles obtained were calcined at 1000 °C for three hours in a muffle furnace. Finally, alumina nanoparticles were obtained (Rogojan *et al.*, 2011). Characterization of

alumina nanoparticles from aluminum nitrate was measured by XRD (Rigaku-D-max 2200, Japan) and FE-SEM (EVO 60, Brand: Carl ZEISS, Germany). The SEM was used to indicate the morphology and particle size of the sample.

#### Sample collection of waste water samples

Two different waste water samples were collected from a Textile Mill No. (6) Branch, Heavy Industrial, Ministry of Industry, Sangaing City, Sangaing Region.

#### Effect of time on the removal of Cu, Cd, Pb, Zn and Ni by alumina nanoparticles

FE-SEM measurement was carried out to analyze the structure and morphology of synthesized samples. FE-

beaker. The metal concentrations of Cu, Cd, Ni, Zn and Pb in the water filtrate samples were determined using atomic adsorption spectrophotometer (AAS Analyst 200, USA) before and after the addition of the prepared alumina nanoparticles (0.1 g) and stirring for 4 hours at room temperature. Removal of Cu, Zn, Ni, Pb, and Cd metal ions was measured at 324.8, 213.9, 232, 283 and 228.8 nm wavelengths, respectively (Visa and Chelara, 2014).

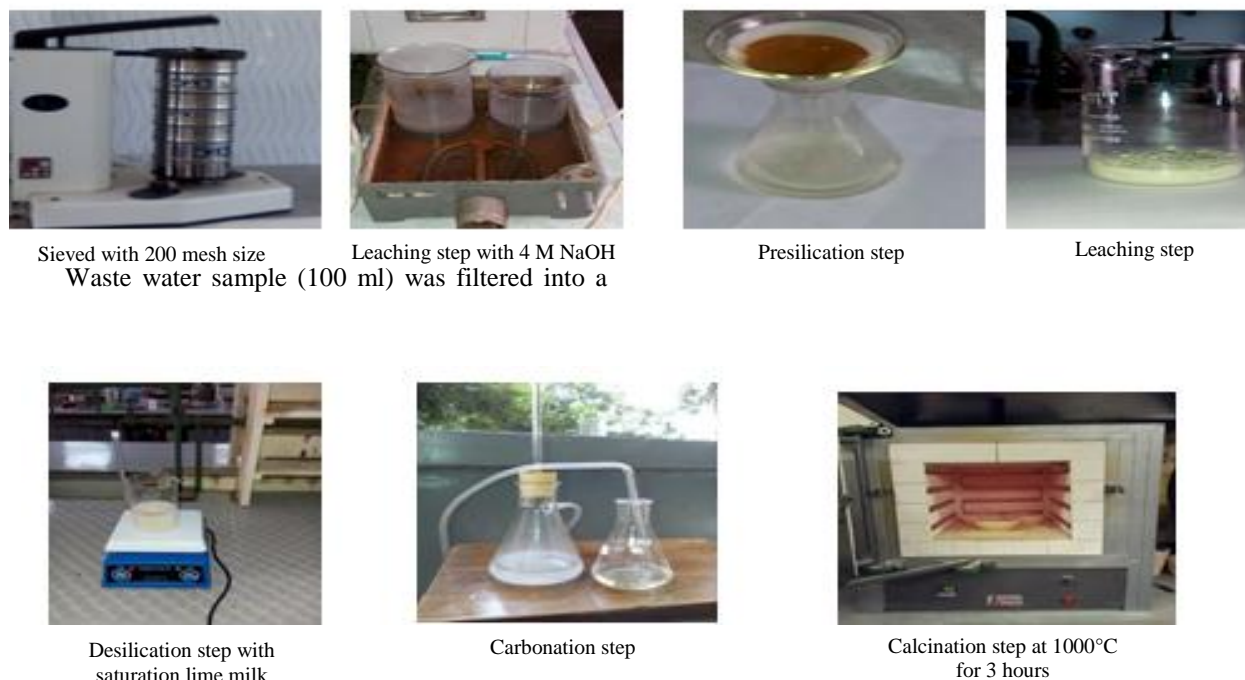


Figure 2. Procedure of alumina nanoparticles from coal fly ash by alkaline sintering method.

### 3 RESULTS AND DISCUSSION

#### Analysis of alumina nanoparticles from coal fly ash and aluminum nitrate by XRD

X-ray diffraction studies have widely applied in nanoparticle research to characterize their morphological features such as crystal structure, crystallite size, and lattice constants. Results revealed that the dominant diffraction peaks are located at  $25.71^\circ$ ,  $35.26^\circ$ ,  $43.44^\circ$ ,  $52.50^\circ$ , and  $57.58^\circ$ , which corresponds to the Miller indices (012), (104), (113), (024), and (116) planes, respectively, suggesting the formation of alumina nanoparticles. The diffraction peaks of alumina were matched with standard PDF data 80-0826 and 73-112 corundum  $Al_2O_3$  standard. The average crystallite size of alumina nanoparticles was calculated and found to be 65 nm by Debye Scherer equation. Results further revealed that the crystal structure of alumina nanoparticles found to be hexagonal according to lattice parameters ( $a = b = 4.75$

$\text{\AA}$ , and  $c = 12.8632 \text{\AA}$ ) and the average crystallite size of alumina nanoparticles from aluminum nitrate was observed to be 47 nm according to XRD data. XRD diffractogram of alumina nanoparticles from aluminum nitrate is shown in Figures 3 & 4. The XRD diffractogram reveals diffraction peaks of (012), (104), (110), (113), (024), (116), (214), and (300) correspond to  $2\theta$  values  $25.7^\circ$ ,  $35.2^\circ$ ,  $43.44^\circ$ ,  $52.5^\circ$ ,  $57.5^\circ$  respectively (Table 1 and 2). Alumina nanoparticles from aluminum nitrate are hexagonal according to lattice parameters  $a = 4.771 \text{\AA}$  and  $c = 12.7454 \text{\AA}$  (Table 1 and 2). Eight characteristic peaks of alumina nanoparticles obtained from coal fly ash at  $1000^\circ \text{C}$  for three hours are similar and exhibit diffraction pattern of alumina nanoparticles from aluminum nitrate. Alumina nanoparticles from aluminum nitrate need to use polymer solution for spinnability. When the content of polymer solution increases, the spinnability also increases for nanoparticles preparation. The spinnability of the solution is determined by the content of lactic

acid or spinning additive. Therefore, alumina nanoparticles from coal fly ash by alkaline leaching sintering method is simple and eco-friendly compared with sol gel and co-precipitation methods (Rajaeiyan *et*

*al.*, 2013). The simplest and most widely used method for estimating the average crystallite size is from the full width at half maximum (FWHM) of a diffraction peak using the Debye Scherrer Equation as follow:

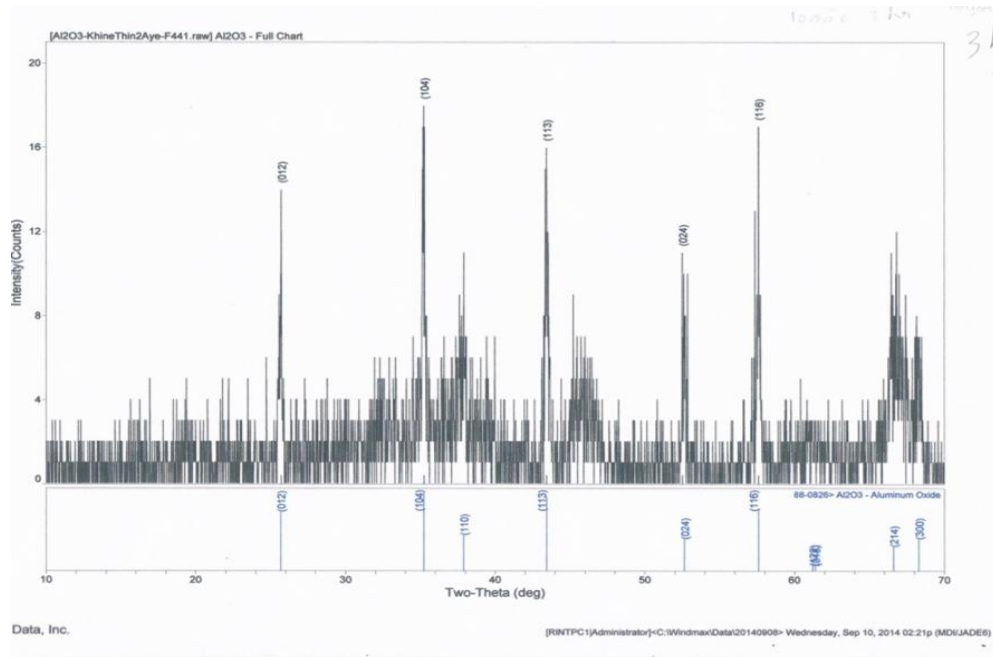


Figure 3. XRD diffractogram of alumina nanoparticles from coal fly ash

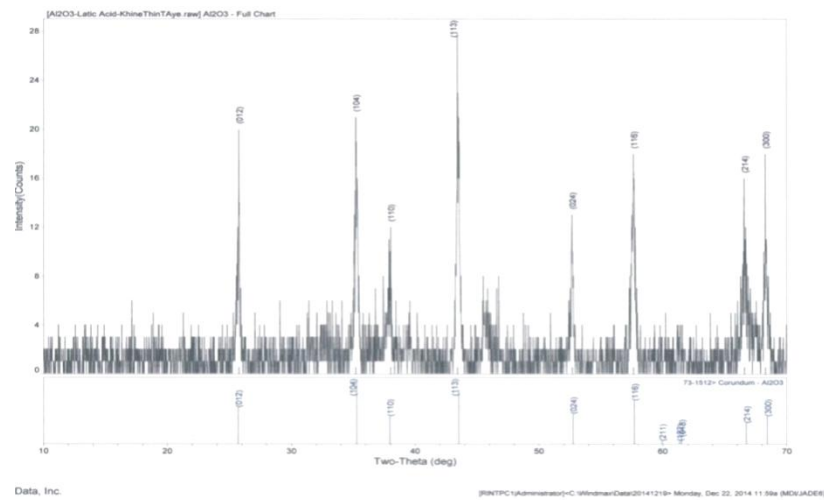


Figure 4. XRD diffractogram of alumina nanoparticles from aluminum nitrate

Table 1. XRD data of alumina nanoparticles from coal fly ash

No	2 Theta	D(A°)	(hkl)	Height (%)	Area(%)	FWHM
1	25.717	3.4613	(012)	77.8	72.7	0.163
2	35.264	2.5430	(104)	100.0	54.1	0.113
3	43.442	2.0813	(113)	88.9	100.0	0.195
4	52.505	1.7414	(024)	61.1	45.3	0.133
5	57.582	1.5994	(116)	94.4	54.1	0.105

Debye Scherrer Equation:

$$t = \frac{0.9\lambda}{B\cos\theta}$$

$t = 65.55\text{nm}$

$t$  = Average crystallite size in nm or ( $\text{\AA}$ )

$\Lambda$  = Wavelength ( $\text{\AA}$ ) or nm

$\theta$  = Diffraction angle of the peak

$\beta$  = Observed FWHM (in radians)

Table 2. Average lattice constant values of alumina nanoparticles from coal fly ash from XRD data

No	2-Theta	D( $\text{\AA}$ )	hkl	A axis	b-axis	c- axis
1	25.17	3.4613	012	4.7240	4.7240	12.9856
2	35.264	2.5430	104	4.7240	4.7240	12.9856
3	43.442	2.0813	113	4.8203	4.8203	12.3833
4	52.505	1.7414	024	4.7792	4.7792	12.8928
5	57.582	1.5994	116	4.7112	4.7112	13.0685

Average lattice constants = 4.7519

12.8632

**FE-SEM characteristics of alumina nanoparticles from coal fly ash and aluminum nitrate**

The morphology and particles size of alumina nanoparticles after the calcination temperature at  $1000^\circ\text{C}$  were investigated by FE-SEM. Alumina nanoparticles from coal fly ash resulted in a better adsorbent for the adsorption of pollutants from wastewaters. The morphological features of alumina nanoparticles from coal fly ash and aluminum nitrate are spherical shape with smooth and regular surfaces and showed well as nano size at different magnifications (2.74 KX, and 8.42 KX). Figure 5 (a) and (b) show the particle analysis of the fly ash which having less than  $100\ \mu\text{m}$ . Results revealed that the size range of the particles is very wide i.e.  $1\ \mu\text{m}$  to  $5\ \mu\text{m}$ . From the results, it is concluded that some of the particles are within 100 nano range (Raghavendra *et al.*, 2014).

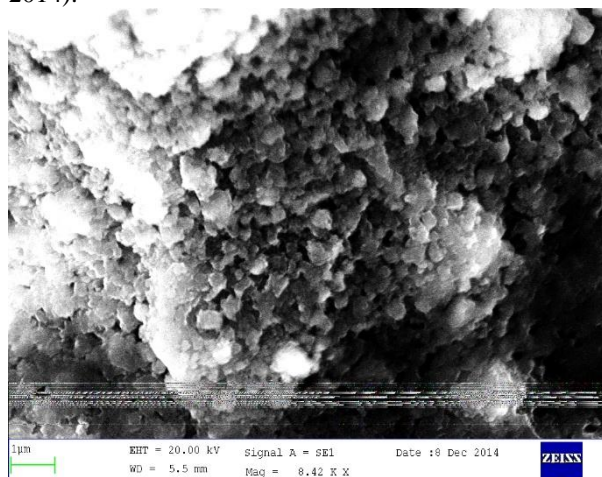


Figure 5. (a) Field emission scanning microscope image of alumina nanoparticles from coal fly ash

**Removal of Cu, Cd, Pb, Zn and Ni in textile waste water samples by alumina nanoparticles**

Before treatment, Cu, Ni, Zn and Cd contents in the waste water samples were observed to be 0.167, 0.2, 18.05, and 0.24 ppm, respectively. Lead was not found in the samples. After treatment with alumina nanoparticles, Cu, Ni, Zn and Cd were found to be 0.0015 ppm, 0.005 ppm, 1.05 ppm, and 0.018 ppm, respectively (Fig. 6). Results showed that the removal percentages of Cu, Ni, Zn and Cd contents were 99%, 98%, 94%, and 93%, respectively. It was observed that

the removal efficiency of trace metals in waste water on alumina nanoparticles from coal fly ash is better than that of 88% of Cu, 86% of Ni, 83% of Zn and 75% of Cd in waste water on alumina nanoparticles from aluminum nitrate. This is due to the effective catalytic action of alumina nanoparticles from coal fly ash is better than alumina nanoparticles from aluminum nitrate for the degradation of trace elements in waste water samples (Ayanda *et al.*, 2012).

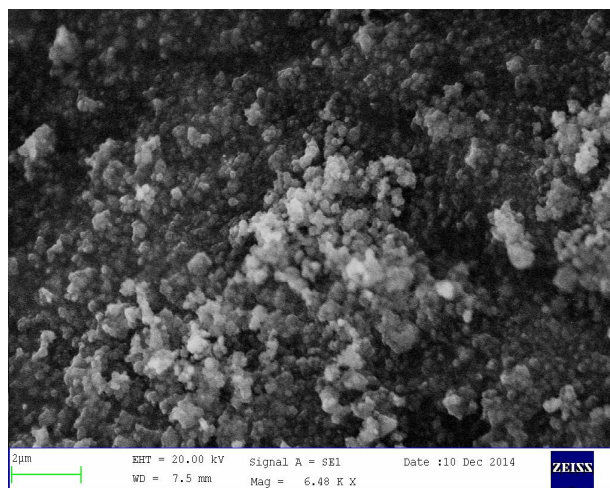


Figure 5. (b) Field emission scanning microscope image of alumina nanoparticles from aluminum nitrate with lactic acid

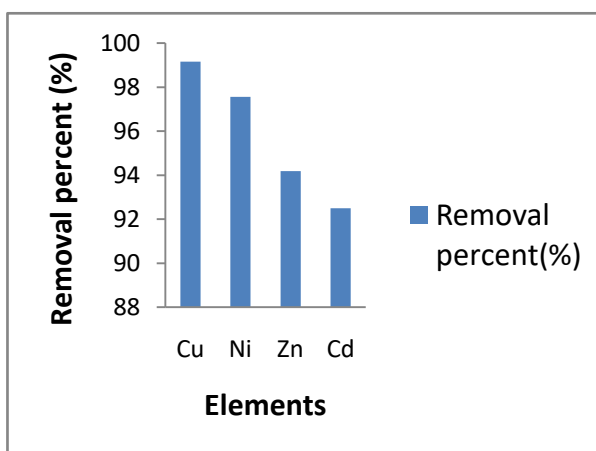


Figure 6. Removal percents of Cu, Ni, Zn and Cd in waste water samples with alumina nanoparticles from coal fly ash

#### 4 CONCLUSION

Removal of trace elements (Pb, Cd, Zn Ni and Cu) by alumina nanoparticles from coal fly ash was investigated in this study. The highest removal percent of copper was observed compared with the other elements in the waste water samples. This work focuses on the preparation, characterization of alumina nanoparticles from coal fly ash by alkaline sintering method that simple nontoxic and friendly technique and applied it for waste water treatment.

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