

SOME APPLICATIONS OF ALUMINA NANOPARTICLES FROM COAL FLY ASH

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Abstract

In the present research, coal fly ash samples were collected in Tigypt coal-fired Power Plant from Southwest Shan State in Myanmar. Alumina nanoparticles was synthesized from coal flyash by using alkali lime sintering method. Alumina nanoparticles were obtained by using six steps leaching , pre-desilication, desilication, carbonation, and calcination at 1000° C for 3 h. Among these three metal ions, removal percent of copper was the highest. Adsorption properties of alumina nanoparticles from coal fly ash was studied. Catalytic degradation properties of prepared alumina nanoparticles from coal fly ash was applied to remove some heavy metalions from wastewater samples collected from textile workshop in Inn Lay Lake, Southern Shan State. Copper, zinc and cadmium contents in waste water sample were found to be 0.12 ,0.15 and 0.17 ppm before treatment. After treatment with alumina nanoparticles for 2 h, cadmium, zinc and copper contents were found to be 0.0054,0.009 and 0.060 ppm. Antimicrobial activity of alumina nanoparticles from coal fly ash were performed against six microbial strains *Bacillus subtilis*(N.C.T.C- 8236), *Staphylococcus aureus*(N.C.P.C- 6371), *Pseudomonas aeruginosa* (1679), *Bacillus pumilus* (N.C. I.B-8982), *Candida albicans*, and *E coli* (N.C.I.B-8134). Maximum inhibition zones of alumina nanoparticles from coal fly ash were measured by agar well diffusion method. The highest antimicrobial activities of coal fly ash was observed in *Candida albicans* strain and the maximum inhibition zone of alumina nanoparticles from coal fly ash was found to be 50 nm. Gas sensor applications of alumina nanoparticles were investigated by using ammonia gas to observe the response of gas to the sensing properties .

Key words : fly ash, alumina, antimicrobial activity, adsorption, gas sensor

Introduction

Formation of Fly Ash and Classification of Coal Fly Ash

Fly ash, also known as flue-ash, is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases. Ash which does not rise is termed bottom ash (Goswami *et al.*, 2013). Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys of coal-fired power plant,

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and together with bottom ash removed from the bottom of the furnace is in this case jointly known as coal ash. There is wide range of variation in the principal constituents-silica (25- 60%), alumina (10-30%) and ferric oxide (5-25%). When the sum of these three principal constituents is 70% or more and reactive calcium oxide is less than 10%-technically the fly ash is considered as siliceous fly ash or class F fly ash. If the sum of these three constituent is equal or more than 50% and reactive calcium oxide is not less than 10%, fly ash will be considered as calcareous also called as class C fly ash. (Kumar and Tha, 1991).

Nanoparticles in Waste Water Treatment

Four classes of nanoscale materials that are being evaluated as functional materials for water purification: (1) dendrimers (2) metal-containing nanoparticlees (3) zeolites and (4) carbonaceous nanomaterials. These have a broad range of physicochemical properties that make them particular attractive as separation and reactive media for water purification (Veeradate *et al.*,2011).

Aim and objectives

The main aim of this work was to prepare alumina nanoparticles from coal fly ash by using alkaline leaching sintering method. The objectives were: to characterize alumina nanoparticles by using XRD, FT IR, SEM, and FE SEM techniques and to carry out some applications (. adsorption properties, antimicrobial activity and gas sensor applications of prepared alumina nanoparticles from coal fly ash .

Materials and Methods



Figure1. Tigyit power plant

Sample collection

Coal fly ash samples were collected from Tigyit Coal-fired Power Plant (Figure 1) in South-west Shan State, Myanmar. Wastewater samples were collected from Textile workshops in Inn Lay, Southern Shan State.

Chemicals

Zinc sulphate heptahydrate, cadmium sulphate octahydrate, copper (II) sulphate pentahydrate (BDH), and sodium hydroxides (BDH) were used.

Apparatus

Atomic Absorption Spectrophotometry (AA-6300, Shimadzu, Japan), measuring flask (100 mL), beakers (100 mL and 250 mL), a magnetic stirrer, a centrifuge, a pH meter and an oven, Petri-dishes, test tubes, a hot plate, a constant temperature bath, an autoclave, a hot air sterilizer, an incubator, an electronic balance, spirit burner, pipettes (0.1, 1 and 10 mL), 100 mL and 50 mL measuring cylinders, a glass rod, 250 mL conical flasks, 250 mL volumetric flasks, and aluminium foil were used.

Preparation of Alumina Nanoparticles from Coal Fly Ash

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 first step. The mixed solution were heated at 100 °C in a covered 500 mL beaker for 3 hours to dissolve silica. Then the solution was filtered with 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 distilled water several times and dried in an oven at 105 °C for 3 hours. The dried leached ash was placed into a muffle furnace at 1000 °C for 3 hours. A 70 g leached ashes were mixed with 94 g lime stone and 42 g soda ash. The mixture sample was placed into a muffle furnace at 1000 °C for 3 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 Whatman No. 1 filter paper and washed with hot distilled water. The sodium aluminate solution were deeply

desilicated by adding saturated lime milk at 1000 °C for 1 hour. The sodium aluminate were obtained by desilication. Then, the aluminium hydroxide were prepared by passing carbon dioxide into the sodium aluminate solution for carbonation decomposition. Alumina nanoparticles were obtained by sintering aluminum hydroxide at 1000 °C for 3 h (Cheng , 2012).

Effect of pH and time on metal removal of coal fly ash on Adsorption Experiments

Procedure

Each 100 ppm of copper (II) sulphate pentahydrate crystals (0.195) g, cadmium sulphate octahydrate crystals (0.157) g, and zinc sulphate heptahydrate crystals (0.22) g were used as model solutions. Prepared alumina nanoparticles from coal fly ash samples (0.1g each) were placed in separate beaker and then 50 mL of Zn (II) ions (100 ppm) were added and stirred at 250 rpm for 1h. This step was carried out at different pH of 3, 5 and 7. Sodium hydroxide solution (0.1N) and hydrochloric acid solution (0.1 N) were used for pH adjustment. Final concentrations of Zn (II) ions were analyzed by atomic absorption spectroscopy. Similarly, the above procedure was carried out for 2 h, 3 h and 4h. Similar experiment was conducted using cadmium (II) ion and Cu (II) ion solutions with the concentration of 100 ppm each (Mongia *et al.*, 2010).

Determination of Removal Percent of Dye in Textile Waste Water Samples Using Prepared Alumina Nanoparticles from Coal Fly Ash and Aluminium Nitrate

The dye in textile waste water effluent samples were collected from Textile Industry in Inn Lay, Southern Shan State in Myanmar. A 100 mL of water sample was filtered into a beaker. The Cd, Zn and Cu contents in filtrate water sample were measured by atomic absorption spectrophotometer, 50 mL of waste water samples were taken out and centrifuged for 15 min. To the above nanopaticles from coal fly ash was added and stirred for 1 hour at room temperature. The concentration of Cu , Zn and Cd in supernatant solutions was determined by AAS (Hongbin *et al.*,2011).

Determination of Antimicrobial Activities of Alumina Nanoparticles and from Coal Fly Ash and Aluminium Nitrate

Antimicrobial activities of alumina nanoparticles from coal fly ash and aluminium nitrate were determined by agar well diffusion method. *In vitro* screening of antimicrobial activities of alumina nanoparticles from coal fly ash samples were carried out against six kinds of microorganisms at Central Research and Development Center (CRDC), Ministry of Industry, Yangon, Myanmar. Microorganisms used were *Bacillus subtilis* (N.C.T.C-8236), *Bacillus pumilus* (N.C.I.B-8982), *Candia albicans*, *Staphylococcus aureus* (N.C.P.C-6371), *Pseudomonas aeruginosa* (N.C.T.C-6749) and *Escherichia coli* (N.C.I.B-8134). Bacteria spore suspension 0.1 g was inoculated into sterile petri-dish including nutrient agar and autoclaved for 25 min at 121 °C. It was cooled at 60 °C. These nutrient agar were made by 10 mm diameter cork borer. Alumina nanoparticles from coal fly ash (0.1 g) was added to these agar and incubated at 37 °C for 24 h. The maximum inhibition zone was measured. Standard (0.1 g/ 10 mL) amoxicillin antibiotic was used as control (Amitava *et al.*, 2011).

Fabrication of Gas Sensing Devices and Gas Sensor Testing System

Alumina nanoparticles (0.5g) are mixed with 5% polyvinyl acetate binder well and pasted on the interdigitated electrodes (IDEs). Alumina coated electrodes were dried at 150⁰C for 2 h . The gas sensor testing system was designed to test sensor by a static environment method and fixed volume (1.18L).The multimeter of type U 1232 A True RMS with Keysight Handheld Meter logger Software is used to record the variation of the sensor resistance exposed to predetermined air gas mixing ratio(Figure 2).



Figure 2. Gas sensor testing system

Results and Discussion

Application in Removal Efficiencies of Alumina Nanoparticles from Coal Fly Ash on Textile Waste Water Samples

It was found that copper, zinc and cadmium contents in waste water sample were observed to be 0.12, 0.15, 0.17 ppm before treatment. After treatment with alumina nanoparticles for 2 h, Cu, Zn and Cd contents were found to be respectively 0.0054, 0.009 and 0.060 ppm (Figure 3 and Table 1). And thus that the removal percentages of copper, zinc and cadmium were calculated to be 95.50%, 94% and 67.70% respectively (Figure 4).

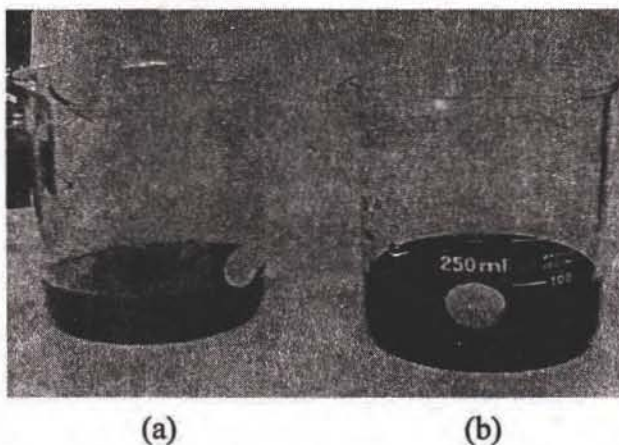


Figure 3. Photographs of waste water samples by using alumina nanoparticles from coal fly ash

- (a) = After treatment with prepared alumina nanoparticles in Black Silk solutions
- (b) = Before treatment with prepared alumina nanoparticles

Table 1. Residual Concentration of Cu, Zn and Cd in Waste Water Samples by using alumina nanoparticles

No.	Metals	Before treatment (ppm)	After treatment (ppm)	Removal (%)
1	Cu	0.12	0.0054	95.50
2	Zn	0.15	0.009	94.00
3	Cd	0.17	0.060	67.70

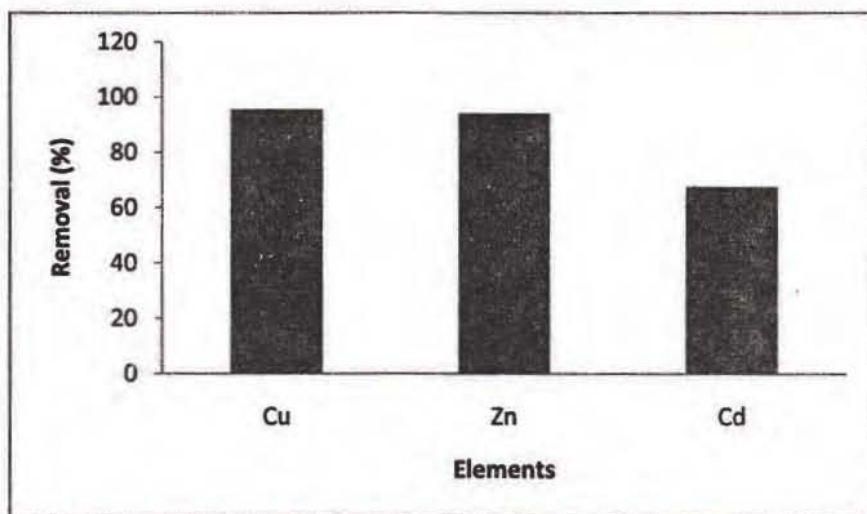


Figure 4. Removal percentages of copper, zinc and cadmium on alumina nanoparticles by AAS

Adsorption Properties of Prepared Alumina Nanoparticles on the Removal of Zn (II), Cd (II) and Cu (II) Ions

In this work, the effect of pH and time of coal fly ash on metal removal was investigated. Prepared alumina nanoparticles were used for the removal of Zn (II), Cd (II) and Cu (II) ions from aqueous solutions at different pH values and temperatures. By the increase of pH the removal efficiency of alumina nanoparticles from coal fly ash increased for elimination of Zn (II) ion. The removal percentages of Zn (II) at pH 3 were found less

effective than at pH 5 and 7. Among the three cations, the removal percentage of Cu (II) ion was found to be the highest at pH 7. It was found that the maximum adsorption of Cu (II) were observed followed by Zn (II) and Cd (II). Metal cations in aqueous solution are found in their hydrated forms. It was observed that the smaller hydrated diameter of Cu, (0.838 nm), the more adsorption properties was pronounced and higher than those of Zn (II) (0.860 nm) and Cd (II) (0.9852nm) (Nightingale,1959). Therefore it was found that the difficulty in the diffusion of large hydrated ions into small pores is a reason for the low adsorption of Zn (II) and Cd (II) ions (Tables 2,3 and 4) and (Figures 5, 6 and 7)

Table 2. Effects of pH and Time on the Removal of Zn (II) Ions

No	pH	Time (h)	Residual concentration of	Removal percent (%)
			Zn(II) Ion (ppm)	
1		1	2.90	97.09
2		2	2.80	97.19
3	3	3	2.75	97.25
4		4	2.55	97.45
1		1	2.38	97.62
2		2	2.25	97.75
3	5	3	2.15	97.85
4		4	2.10	97.89
1		1	2.01	97.99
2		2	1.98	98.02
3	7	3	1.81	98.19
4		4	1.68	98.31

Initial concentration of Zn (II) ions = 100 ppm

Table 3. Effects of pH and Time on the Removal of Cd (II) Ions

No	pH	Time (h)	Residual concentration of Cd (II) Ion (ppm)	Removal percent (%)
1		1	8.69	91.31
2		2	8.66	91.33
3	3	3	8.50	91.49
4		4	8.10	91.89
5		1	4.92	95.08
6		2	4.28	95.71
7	5	3	4.18	95.81
8		4	4.01	95.98
9		1	3.88	96.12
10		2	3.70	96.29
11	7	3	3.68	96.31
12		4	3.57	96.42

Initial concentration of Cd (II) ions=100 ppm

Table 4. Effects of pH and Time on the Removal of Cu (II) Ions

No	pH	Time (h)	Residual Concentration of Cu (II) Ion (ppm)	Removal percent (%)
1		1	3.23	96.76
2		2	3.01	96.98
3	3	3	3.15	96.85
4		4	3.08	96.92

No	pH	Time (h)	Residual Concentration of Cu (II) Ion (ppm)	Removal percent (%)
5		1	2.97	97.02
6		2	2.89	97.10
7	5	3	2.80	97.19
8		4	2.75	97.25
9		1	1.97	98.02
10		2	1.56	98.43
11	7	3	1.15	98.85
12		4	1.08	98.92

Initial concentration of Cu (II) ions=100 ppm

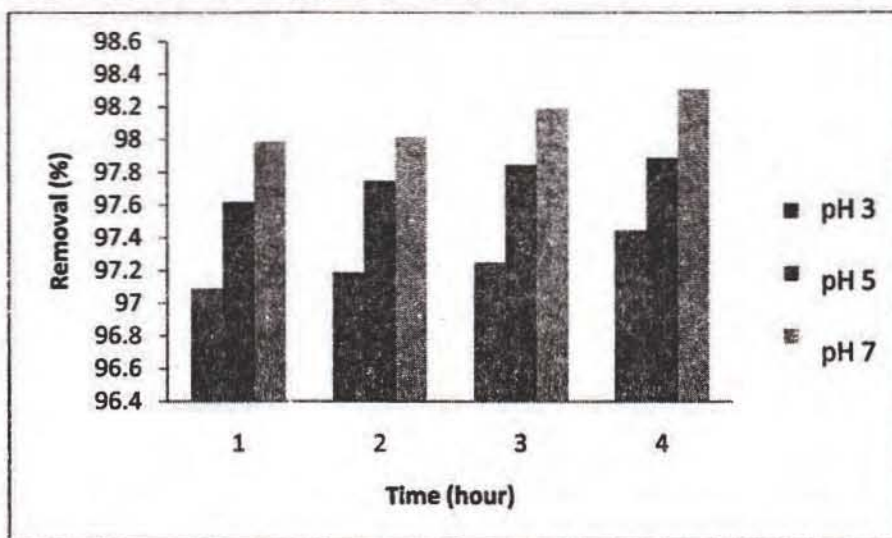


Figure 5. Zinc metal removal (%) on alumina nanoparticles

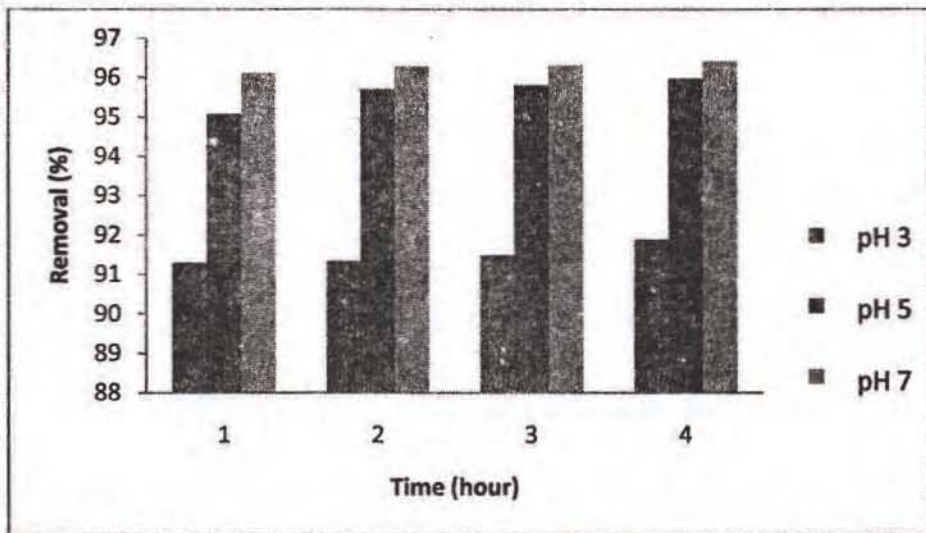


Figure 6. Cadmium metal removal (%) on alumina nanoparticles

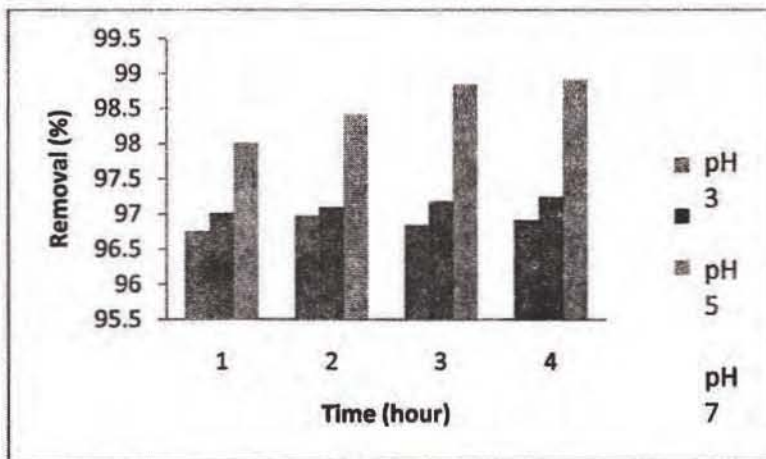


Figure 7. Copper metal removal (%) on alumina nanoparticles

Antimicrobial Activity of Prepared Alumina Nanoparticles from Coal Fly Ash and Aluminium Nitrate by Agar Well Diffusion Method

Antimicrobial activity of alumina nanoparticles by employing agar well diffusion method on six species of microorganisms such as *Bacillus subtilis*, *Staphylococcus aureus*, *Bacillus pumilus*, *Pseudomonas aeruginosa*, *Candida*

albicans and *Escherichia coli* was screened at Central Research and Development Center (CRDC) in Insein. Resultant inhibition zone diameters are described in Table 3. In this study, alumina nanoparticles showed remarkable antimicrobial activity against both gram-positive and gram-negative bacteria. As a result, the larger inhibition zone diameters, found the greater the antimicrobial activity. The inhibition zone of alumina nanoparticles against six species of microorganisms shows *Bacillus subtilis* (40 mm), *Staphylococcus aureus* (35 mm), *Pseudomonas aeruginosa* (30 mm), *B. pumilus* (40 mm), *Candida albicans* (50 mm) and *E. coli* (33 mm) respectively. Maximum inhibition zones of antimicrobial activity on alumina nanoparticles are shown in (Figures 8 and 9 and Table 5).

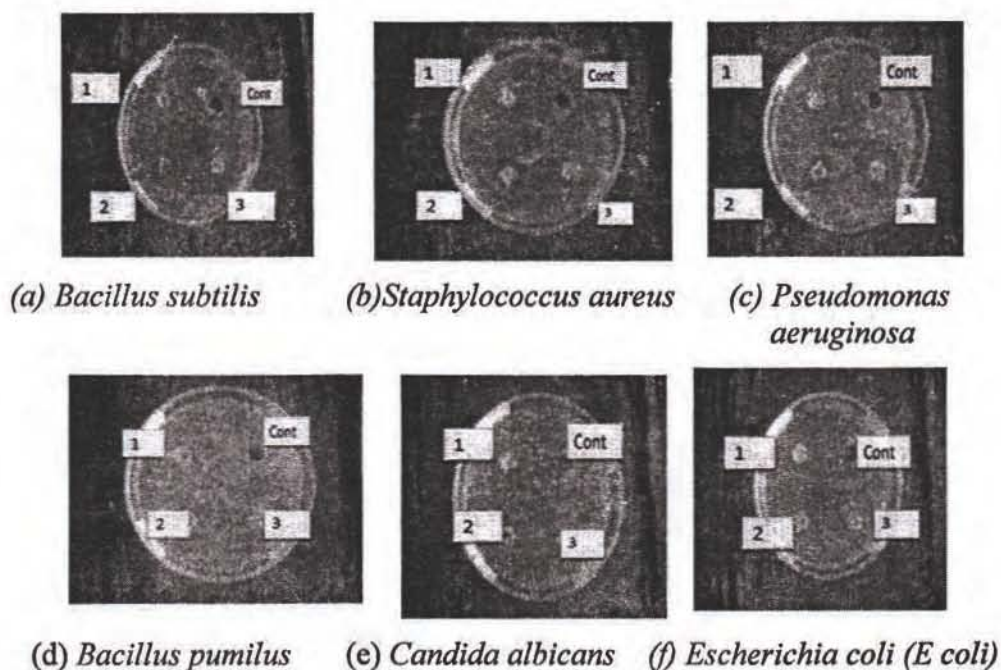


Figure 8. Inhibition zones of different microbial strains on alumina nanoparticles

Table 5. Determination of Inhibition Zones Produced by Alumina Nanoparticles from Coal Fly Ash

Sample	Organisms					
	<i>Bacillus subtilis</i> (mm)	<i>Staphylococcus aureus</i> (mm)	<i>Pseudomonas aeruginosa</i> (mm)	<i>Bacillus pumilus</i> (mm)	<i>Candida albicans</i> (mm)	<i>E.coli</i> (mm)
Alumina nanoparticles from aluminium nitrate	13 (+)	-	15 (++)	12 (+)	26 (+++)	-
Alumina nanoparticles from coal fly ash	40 (+)	35 (+++)	30 (+++)	40 (+++)	50 (+++)	33 (+++)
Control	10	10	10	10	10	10

Agar well- 10 mm

10 mm – 14 mm (+)

15 mm – 19 mm (++)

20 mm above (+++)

Organisms

- 1) *Bacillus subtilis* (N.C.T.C- 8236)
- 2) *Staphylococcus aureus* (N.C.P.C- 6371)
- 3) *Pseudomonas aeruginosa* (1679)
- 4) *Bacillus pumilus* (N.C. I.B-8982)
- 5) *Candida albicans*
- 6) *E coli* (N.C.I.B-8134)

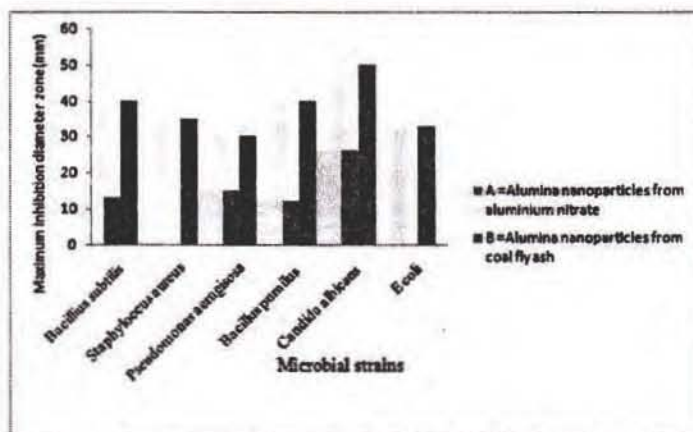


Figure 9. Maximum inhibition zone diameters of different microbial strains

Sensing Characteristics of Alumina for Ammonia Gas

Gas sensing properties of Al_2O_3 sensor were tested with ammonia gas. The response of alumina sensor is shown in Figure 10 (a), (b) and (c) by using 8.47 ppm, 16.94 ppm and 32.45 ppm respectively. According to experiment, the resistance of alumina sensor decreased when contacted with air ammonia gas mixture. The response and recovery times were about 220 s, 130 s for 8.47 ppm, 455 s and 200 s for 16.94 ppm and 560 s and 630 s for 32.45 ppm respectively.

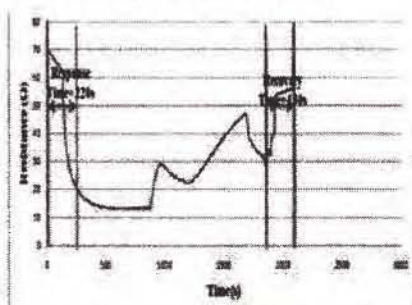


Figure 10 (a) Resistance Vs time for alumina sensor with 8.47 ppm ammonia at temperature 25°C

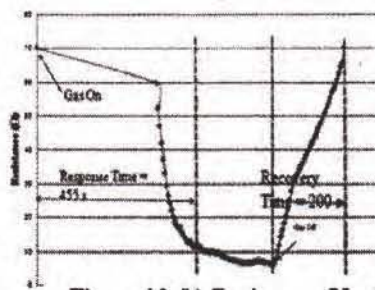


Figure 10 (b) Resistance Vs time for alumina sensor with 16.94 ppm ammonia at temperature 25°C

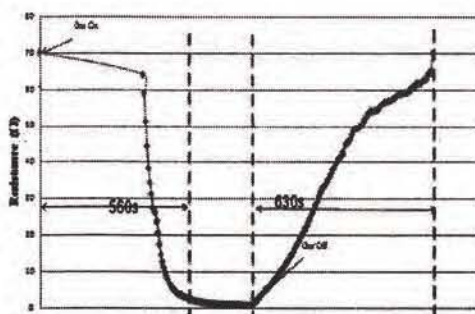


Figure 10 (c) Resistance Vs time for alumina sensor with 32.45 ppm ammonia at temperature 25°C

Conclusion

In this research, alumina nanoparticles synthesized from coal fly ash by using alkaline sintering method was obtained at 1000° C for 3 h. Waste water samples collected from textile workshop. Adsorption properties of alumina nanoparticles was found dependent on pH. The pH of the highest metal adsorption was found at pH 7. The highest adsorption of copper was found to be the highest on alumina nanoparticles compared with that of Zn and Cd. Application of alumina nanoparticles was carried out by using the waste water collected from textile workshop Inn Lay Lake, Southern Shan State. After treatment of alumina nanoparticles, it was found to decrease the metal concentrations and the highest removal percent of copper was 95.50 %, and the second removal percent of zinc was 94 % and the third removal percent of cadmium was 67.70 %. It was observed that the maximum antimicrobial activity of alumina nanoparticles was found on *Candida albicans* and its maximum inhibition zone diameters was shown to be 50 mm. It was found that Al₂O₃ sensor can detect as low as 8.47 ppm of ammonia gas.

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