Studies on Adsorbption Behaviour of Heavy Metals on Mixture of fly ash and Sand for Their Removal of Heavy Metals from Textile Effluent

MOHAMMAD SAJID ANSARI[1], AZIZUL HASAN ANSARI[1], BHAT BILAL BASHIR[1] and ABDUL AZIZ ANSARI[2]

Abstract

Because of sharply develop of textile dyeing industries across the world, there is widely used of heavy metals in textile dyeing industry which cause significant effects on environments. Various adsorbents have been used to remove heavy metal ions from textile waste effluent. Rice husk, sand, clays, baggase, tea waste, fly ash etc are among the common adsorbents used, mixture of sand and fly ash in acidic medium is a good adsorbent to remove the heavy metal ions from textile effluent(dyeing and finishing process waste water). The Adsorption is an effective and successful technique for removal of heavy metals from effluent received from textile dyeing industries. This work introduces the feasibility of using mixture of sand and fly ash in presence of hydrochloric acid. The adsorbent order of metal uptake capacities in $\mu mol\ g^{-1}$ for extraction of five metals ions from aqueous solution using adsorption techniques is Cu(II)>Pb(II)>Cr(II)>Zn(II)>Co(II). In this study, adsorbents sand and coal fly ash, available as natural resources in all areas of our country are examined as viable materials for treatment of Cu,Pb,Cr,Zn & Co containing in textile dyeing and finishing process effluent at controlled pH. The results obtained from this study revealed a relative ability of mixture of sand and fly ash in presence of hydrochloric acid and totally depends on pH,concentration of solution, adsorbent dose, size of the particles of adsorbent, temperature and time.

Key words: Sand,Fly Ash,pH,Adsorption, Heavy Metal Ions Removal, Textile Effluent,

Introduction

Heavy metals are toxic to both human and other living forms, the contribution of heavy metals and their ions to water pollution is a very serious problem with their accumulation

overtime causing damage to kidney, liver and reproductive system in addition to cancer[1] heavy metals are any elements in the d block of periodic table, or transition metals, waste water containing heavy metal ion mainly originated from textile dyeing & their finishing industries, chemical processing industries and metal processing industries. They precipitate into soil, underground water and surface water. Unlike Organic contaminants, heavy metals do not normally undergo biological decay and are thus considered a challenge for remediation. Many government have enacted laws to hinder discharging heavy metals into water bodies and using toxic substances such as lead[2]. Toxic metals such as Cd, Co,Zn, Cr, Pb, and Cu find their ways to the industries as textile dyeing, finishing, chemical processing industries, Adsorption with activated carbon is widely applied for removal of heavy metals at trace levels[3].

Heavy metal commonly found in area where industrial effluents are being discharged into natural waters.The harmful effects of such metals on living being are well known. Removal of heavy metals from industrial waste water has become a very important environmental issue.The purpose of adsorption is considered one of the most suitable methods of removal contaminants from water and a number of low cost adsorbents have been reported for removal of heavy metals(ions)from aqueous solutions[4].

In recent years considerable attention has been devoted to the low cost natural resources rather than synthetic or higher cost materials. Some investigators have used carbonacesous precursors like saw dust, sand, buffing dust,date pits,egg shell,cruid oil,almond shell, wool waste, coal ash, coconut shell, coir pit etc. for removal of heavy metal ions from textile waste water. Some of the low cost adsorbents for removal of heavy metals like waste tea leaves,agricultural by products such as almond shell, olive stones, and peach stones, biomass sediments of river, bed sediments of river Ganga, were used for removal of heavy metals.

Recently interest in low cost ,high surface areas materials, especially metal oxides such as iron oxides, aluminium oxides and silica, with their unique applications,in adsorption and chemical catalysis, has been growing. Numereous researchers have been used iron oxide as an adsorbent to treat heavy metals and organic compounds from the textile effluent, A low cost adsorbent was developed during treatment of bauxite by Bayer's process termed as plant sand generated in aluminium refineries for removal of Pb(II), Cd(II), and Zn(II) ions from aqueous solution at NALCO-India[5]

Chitosan, a type of biopolymer, is a good adsorbent to remove various kinds of anionic and cationic dyes as well as heavy metal ions. Chemical modifications that lead to the formation of chitosan derivatives, grafting chitosan and chitosan composites have gained much attention, extensively studied and widely reported in the literatures.[6]

Like many developing countries, Rwanda faces environmental challenges of wastewater management particularly industrial wastewater. This issue seems to be a subject which has not yet received adequate attention during the evolution of industries. Indeed very little investment has been made in the past on

effluent treatment, experiences from previous studies show that low cost agro residues have the capacity to purify waste water containing heavy metals. The researchers investigate the applicability of adsorptive treatment using available agroresidue,carbonized and activated rice husk for the removal of selected heavy metals from industrial wastewater.[7]

Activated charcoal is very efficient in removal of heavy metal ions,but is readily soluble under very low and high pH conditions (Hang,1989), Peat moss was used for removal of mercury,copper,cadmium, (Couple 1976), and nickel (Ho 1995),Claympers delessertti (moss) was used for the adsoption fo copper from aqueous solution (lee 1989), Also lead,zinc and cadmium were adsorbed on waste tea leaves (Tee 1988), The adsorbent discussed above show different efficiencies for different metals.In addition to above adsorbents, soil and clay also shows remarkable potential towards the removal of heavy metal ions from waste water(Murray,1994; Evangelou,1998).

In recent study,the removal performance and the selectivity sequence of mixed metal ions (Co^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+}) in aqueous solution were investigated by adsorption process on pure and chamfered-edge zeolite 4A prepared from coal fly ash (CFA) commercial grade zeolite 4A and the residual products recycled from CFA. The pure zeolite 4A (prepared from CFA) was synthesized under a novel temperature step-change method with reduced synthesis time. Batch method was employed to study the influential parameters such as initial metal ions concentration, adsorbent dose, contact time and initial pH of the solution on the adsorption process.[8-32]

This has encouraged research into using low-cost adsorbent materials to purify water contaminated with metals. Coal fly ash was formed by combustion of coal in coal fired power station as a waste product. The generation rate of coal fly ash for the whole world is approximately 500 million tons per year and is predicted to increase Efficient disposal of coal fly ash is a worldwide issue because of its massive volume and harmful effects on the environment[8].

In this research, sand & fly coal ash in presence of hydrochloric acid used as an adsorbent for removal of heavy metal ions, The sand is easily available with the cheap cost and fly ash is available free of cost and present days, the power generation plant which used coal as a fuel generated fly ash as a waste product and only its uses for land filling and cement manufacturing plant. There are several studies in sand and coal fly ash but use of these adsorbent as a mixture of sand and fly ash gives better results of heavy metal adsorption as compared to previous studies.

India is a big factory for generating of fly ash from its 90 thermal power plant which is run on coal fuel and generate 66.49 million tone and only 36.26million tone ash utilized (only 54.53%); Orissa, Chattisgarh and Uttarpradesh is only approx 15% utilized ash of total generation of ash in their plant(Central electricity authority,New Delhi, 2012)[9]

Materials and Methods

Equipment :

The concentration of heavy metal ions was evaluated by using atomic absoption

spectrometer(GBC 906AA). The equilibrium studies were carried out in a temperature controlled hot air oven (Double walled electric Oven BP-1-9). The pH measurements were done by using a pH meter (Orion 420A, thermoelectric Corporation.).

Chemicals :

All the chemicals used were of analytical grade and dilutions were made by using double distilled water. The following metal solutions were used for carrying out the adsorption studies.

a) Copper Standard solution 1000 PPM (Reageon Qualigens)
b) Lead Standard solution 1000 PPM (Reageon Qualigens)
c) Chromium Standard solution 1000 PPM (Reageon Qualigens)
d) Zinc Standard solution 1000 PPM (Reageon Qualigens)
d) Cobalt Standard solution 1000 PPM (Reageon Qualigens)
e) Sodium Hydroxide(Analytical grade-Qualigens)
f) Hydrochloric Acid (Analytical grade-Qualigens)

Simulated dilute solution of copper, lead, chromium, zinc and cobalt were prepared in distilled water by adding few drops of HCl (5% Hydrochloric acid for pH adjust upto 6.0 to avoid metal ions precipitation) to solutions containing 10, 20, 30, 40 and 50 mg/l of the metal ions solutions.
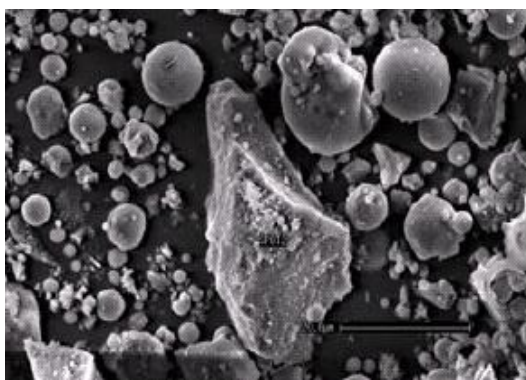
Chemical Treatment of Fly Ash:

The fly ash sample was collected from NTPC-Dadri, Dist Gautambudh Nagar. The fly ash sample was washed in ultrapure water by stirring, at room temperature for 48 hours,to remove the soluble compounds K_2O, Na_2O, MgO and CaO. After stirring filter the solution, the filtrate solution had constant pH (9.8) and conductivity (2.25mS) and dried by keeping in hot air oven at 105^oC for 24 hours. Subsiquently, it was sieved to 0.61 to 1.2 mm particles size using laboratory sieve[10-16].
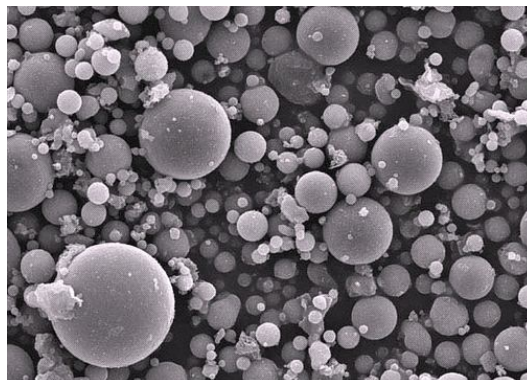
The oven dried sample (10.0 g) was filled in a glass column (size 2x50 cm fitted with glass wool plug) and treated with 5% HCl solution. The HCl solution was passed through the glass column 3-5 times at a flow rate of 5 ml per minute. Then it was kept in contact with the acid solution in the glass column for 24 hours at room temperature (25 ± 1 ^oC). The sample was then washed by passing distilled water through the column several times till the pH of the eluent became neutral and all the colored impurities were removed. The treated adsorbent material was taken out from the column and again dried by keeping in hot air oven at $105\pm$ ^oC for 24 hours and cooled at room temperature[15-30].

Picture of bulk fly ash

Uneven size particles of fly ash   1.2 mm sieved particles of fly ash
Picture of coal fly ash(magnified)

Chemical Treatment of sand:

Sand sample was procured from the Hindon river bank-Ghaziabad. The sand sample was washed with distilled water and filtered and dried by keeping in hot air oven at 105°C for 24 hours. Subsequently, it was sieved to 0.61 to 1.2 mm particles size using laboratory sieve.
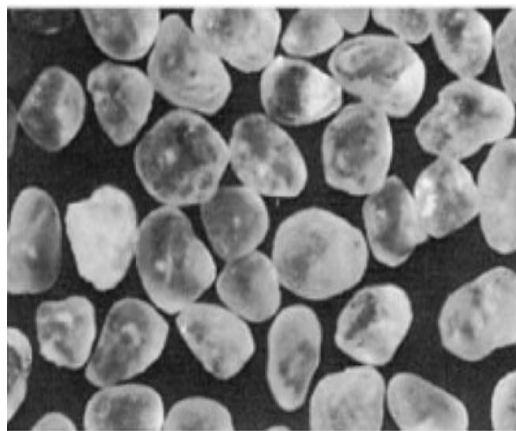
Impregnation of sand:

100 g of washed and over dried sand were pored in a conical flask and filled with one liter sodium hydroxide (96% by weight), the mixture stirred for 24 hours at room temperature and washed with distilled water and dried by keeping in hot air at. 105°C for 24 hours. The oven dried sample (10.0 g) was filled in a glass column (size 2x50 cm fitted with glass wool plug) and treated with 5% HCl solution. The HCl solution was passed through the glass column 3-5 times at a flow rate of 5 ml per minute. Then it was kept in contact with the acid solution in the glass column for 24 hours at room temperature (25±1 °C). The sample was then washed by passing distilled water through the column several times till the pH of the eluent became neutral and all the colored impurities were removed. The treated adsorbent material was taken out from the column and again dried by keeping in hot air oven at 105±°C for 24 hours and cooled at room temperature[26-32].

River bank containing sand

Untreated sand   Impregnated sand
A microscopic views(1.2mm sizes particles) of river sand of India

Preparation of adsorbent (Mixture):

　　5.5g of treated Fly Ash sample and 4.5g of treated sand sample mixed together and weight of 10 gm for each investigation.

Characterization of Adsorbents Material :

The adsorbent material was characterized by studying the following properties.

S.No.	Parameters	Coal fly Ash	Sand	Mixed adsorbent
1	Color	Grey	Grey black	Grey
2	Particle size	0.65-1.2 mm	0.65-1.2 mm	0.65-1.2 mm
3	Moisture	3.0%	1.94%	2.47%
4	Volatile matter	14.9%	8.7%	11.8%
5	Fixed carbon	82.1%	89.36	85.73%
6	Water regain	70%	40%	55%

1. Moisture Content :

　　The adsorbent material (1g) taken in a crucible and placed in an electric hot-air oven at at 105± ºC for 24hour. It was then cooled in a dessicator for half an hour and weighed. The percentage of moisture present in the material was then calculated by using the following equation-

% Moisture = (Loss in weight of adsorbent /

Weight of air dried adsorbent taken) x 100

The results are summarized in Table-1

2. *Volatile Matter :*

The crucible with moisture free adsorbent obtained after determination of moisture was covered with a lid and placed in an electric muffle furnace, heated at $900\pm5^{o}C$ for fifteen minutes. It was then taken out, cooled in a dessicator and weighed. The percentage of volatile matter was then calculated by using the following equation.

% Volatile matter = (Loss in weight of adsorbent / Weight of oven dried adsorbent taken) x 100
The results are summarized in Table-1

3. *Fixed Carbon :*

The fixed carbon content was calculated from the results of moisture content, volatile matter and ash content by using the following equation.

% Fixed carbon = 100 – (% Moisture + % Volatile matter + % Ash)

The results are summarized in Table-1

4. *Water Regain :*

The adsorbent material (1 g) was taken in a 100 ml beaker containing 50 ml distilled water and left for 24 hours with intermittent shaking for soaking. After 24 hours the supernatant water was decanted and the adsorbent material was gently squeezed between blotting papers to remove the excess of water and weighed immediately. The percentage of water regained by the material was then calculated by using the following equation-

% Water regain= (Gain in weight of adsorbent/ Weight of dried adsorbent taken) x 100

The results are summarized in Table-1

5. *Stability in Acidic Solutions :*

The stability of the material in dilute acid solutions was studied by keeping the adsorbent material (0.5 g) in different conical flasks containing 50 ml of 1%, 5% and 10% various of acid solutions (Nitric acid, Sulfuric acid, Acetic acid and hydrochloric acid). The contents were shaken well and left for 24 hours at room temperature ($25\pm^{o}C$). Then the adsorbent material was separated from the acid solutions by filtration and washed well with distilled water till a neutral pH was achieved. The separated materials were dried in hot air oven at $105\pm$ ^{o}C for 24 hours. Then they were cooled in dessicator for half an hour weighed. The percentage of loss in weight of the materials were then calculated by using the following equation.

% Weight Loss = (Loss in weight of adsorbent/ Weight of dried adsorbent taken) x 100
The results are summarized in Table-2 and plotted in Figure 1.

6. *Stability in Alkaline Solutions :*

The stability of the material in dilute alkaline solutions was studied by keeping the adsorbent material (0.5 g) in different conical flasks containing 50 ml of 1%, 5% and 10%

various of alkali solutions (Potassium hydroxide, Sodium hydroxide and Sodium carbonate). The contents were shaken well and left for 24 hours at room temperature (25± °C). Then the adsorbent material was separated from the acid solutions by filtration and washed well with distilled water till a neutral pH was achieved. The separated materials were dried in hot air oven at 105± °C for 24 hours. Then they were cooled in dessicator for half an hour weighed. The percentage of loss in weight of the materials were then calculated by using the following equation.

% Weight Loss = (Loss in weight of adsorbent/ Weight of dried adsorbent taken) x 100

The results are summarized in Table-3 and plotted in Figure 2.

7. Adsorption Capacity for heavy metals:

The adsorption capacity of the material for different metals (Copper, Lead, Chromium, Zinc and Cobalt) was determined by batch process. A known amount of the adsorbent was equilibrated with different metal ions solutions in stoperred conical flasks. The pH of the solutions was adjusted to 6.0 ± 0.1 with dilute hydrochloric acid solutions, wherever required. Then the supernatant liquid was separated from the adsorbent by filtration and absorbance of the filtrate was measured using a GBC906AA, Atotmic Absorption spectro-photometer. The wavelength values for the metal ions studied are summarized below.

S. No.	Name of metal ions	Detection Wave length(in nm)
1	Copper	240.7
2	Lead	217 & 283.3
3	Chromium	357.9
4	Zinc	213.9
5	Cobalt	240.7

The percentage of metal ions adsorbed by the adsorbent was then calculated by using the following equation.

% metal ions adsorption $= (Ao - Ae) \times 100/ Ao$

Where

A_o = Initial concentration of metal ions added

A_e = Concentration of metal ions left after equilibration

The results are summarized in Table-4 and plotted in Figure 3.

Optimization of Process Parameters :

The adsorbent material was selective for copper, lead, chromium, zinc and cobalt. Therefore, optimization of process parameters was done by equilibrating the metal ions solution with the adsorbent (mixture) in stoppered conical flasks. The concentration of the metal ions in the supernatant liquid before and after equilibration was determined by atomic absorption spectroscopy measurements of wavelength (in nm). The process parameters were optimized by studying the effect of following parameters

on metal ions adsorption.

The effect of particle size of adsorbent material was studied by equilibrating the adsorbent material having different particle sizes (mesh sizes 0-65,66-125 and 125-250) with 250 ml of 30 ppm metal ions solution. The results are summarized in Table-5

The effect of weight of adsorbent material on metal ions adsorption was studied by equilibrating different amount of adsorbent material ranging from 1.0 g to 10.0 g of adsorbent(mixture) with 250 ml of metal ions solutions. The results are summarized in Table-6 and plotted in Figure 4.

The effect of equilibration time and temperature on the adsorption behavior was studied by equilibrating 10.0 g of adsorbent with 250 ml of 30 ppm metal ions solution at three different temperatures (30, 45 and 60 ºC) in a conical flask for different time intervals. The results are summarized in Table-7 and plotted in Figure 5.

The effect of temperature and metal ions concentration on the adsorption phenomenon was studied by equilibrating 10.0 g of adsorbent with 250 ml of different concentrations (10 to 100 ppm) of metal ions solution at different temperatures (30, 45 and 60 ºC) in a conical flask. The results are summarized in Table-8 and plotted in Figure 6.

The effect of pH of the metal ions solution on adsorption behavior was studied by equilibrating 10.0 g of the adsorbent with metal ions solutions (30 ppm) having pH values ranging from 1-14. The results are summarized in Table 9 and plotted in Figure 7.

Regeneration of the Adsorbent and its Reuse:

The exhausted adsorbent material was regenerated by passing 7 % HCl solution through the adsorption column till all the adsorbed metal ions was removed from the adsorbent. The adsorbent was then thoroughly washed with distilled water till the effluent was having a neutral pH.The mixture of sand and fly ash can be segregated based on differences in their density[20-32].

Though it absorbed very less amount of heavy metals and it becomes saturated with adsorbed metals, it can be disposed off by employing it as a component of concrete used in various construction purposes.

Results & Discussion

(1) FLY ASH:

Fly ash is a cheap, eco-friendly and bio degradable material, so it can be effectively used for removal of heavy metals from waste water. It may be classified as follows-

a.Chemical properties of fly Ash

S.No.	Compound	Percentage (%)
1	SiO_2	51.98
2	Al_2O_3	28.55
3	Fe_2O_3	4.91
4	CaO	8.67
5	MgO	1.54
6	Na_2O	0.24
7	K_2O	1.80
8	SO_3	1.47
9	Loss of ignition	2.31
10	Cl^-	0.0053
11	Free Lime	0.64

b.Physical Properties of Fly Ash:

S.No	Parameters	5-15mm size grain	0-5mm size grain
1	Color	Grey	Grey
2	Specific gravity(Saturated surface dry)	2.61	2.0
3	Water absorption (%)	0.61	1.64
4	Melting Point	1400°C	1370°C

2. SAND:

a. Chemical properties of sand :

S.No.	Compound	Percentage (%)
1	SiO_2	97.18
2	Al_2O_3	1.16
3	Fe_2O_3	0.85
4	Silica(free)	0.4
5	TiO_2	0.2
6	Miscellaneous minerals	0.21

b. Physical Properties of Sand:

S.No	Parameters	Results
1	Color	Grey black
2	Specific gravity (Saturated surface dry)	2.72
3	Water absorption (%)	0.51
4	pH	5.5 to 7.0
5	Melting Point	1710°C

3. Characteristics of adsorbent (Mixture):

The analysis of adsorbent revealed that that it had small amount of moisture content, volatile matter and high temperature melting point in Table 1. Hence the material could be dried easily even at room temperature due low percentage of moisture content. This resulted in saving the electrical cost during the drying process. The table also shows that the adsorbent material had a high percentage of fixed carbon, which suggests that the material may be effectively used as an adsorbent like activated carbon which is the most commonly used adsorbent material. The material also had a very high water regaining capacity, which may be very useful in preparation of adsorption column. Low water regain may cause problem in column operations by floating on the surface. Due to larger specific area of the adsorbent which adsorbed the metal ions in a larger quantity and increase the overall adsorption efficiency of the solution[7-19].

Mixing of fly ash into sand sample is due to reduce the cost of the treatment and make the removal of heavy metal process ecofriendly by utilize the unused fly ash which is generating from power plant.

Table 1. General characteristics of the adsorbent

Loss on ignition	Volatile matter	Specific surface	Carbon	Water Solubility
2.47%	11.8%	250-350m$_2$/kg	85.73%	Less than 2%

Chemical Stability :

Table-2 and Fig.1 show that the adsorbent material shows moderate stability in dilute hydrochloric acid (1 %,) and acetic acid (1 %, 5 %, 10 %). However, it suffers significant weight loss in sulfuric acid and nitric acid even at low concentration (1 % acid solution). These results suggest that the material may be used for removal of the heavy metal ions from slightly acidic solutions containing hydrochloric acid and acetic acid.

Table 2. Weight loss of adsorbent in various acid solutions

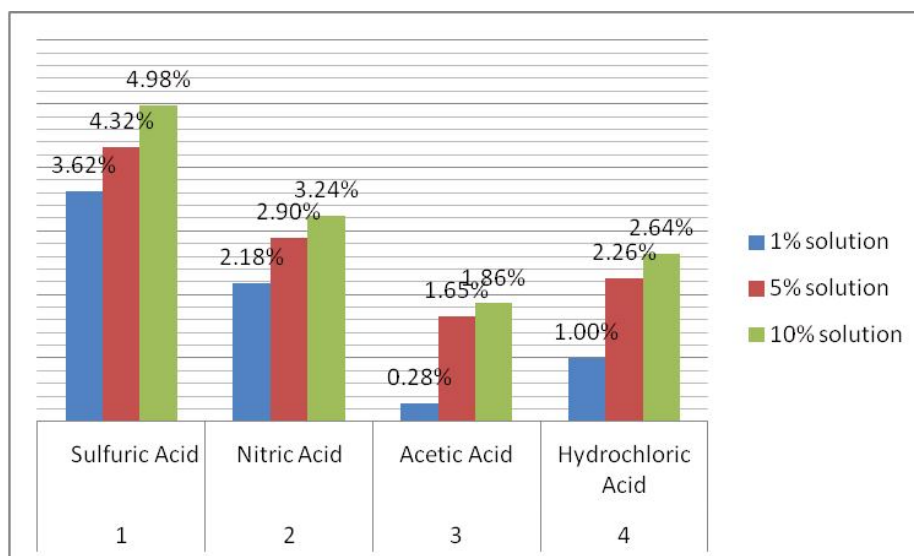| S. No.	Name of Acid	Weight loss at various concentrations of acids		
		1% solution	5% solution	10% solution
1	Sulfuric Acid	3.62%	4.32%	4.98%
2	Nitric Acid	2.18%	2.90%	3.24%
3	Acetic Acid	0.28%	1.65%	1.86%
4	Hydrochloric Acid	1.0%	2.26%	2.64%

Figure-1. Weight loss of adsorbent in various acid solutions

Table-3 and Figure-2 show that the adsorbent is reasonably stable in solutions containing potassium hydroxide and sodium carbonate. However, it is highly unstable in solutions containing sodium hydroxide, These results suggest that the material may be used for metal ions removal from solutions containing potassium hydroxide and sodium carbonate. But, its use should be avoided for metal ions removal from solutions containing sodium hydroxide.

Table 3. Weight loss of adsorbent in various alkali solutions

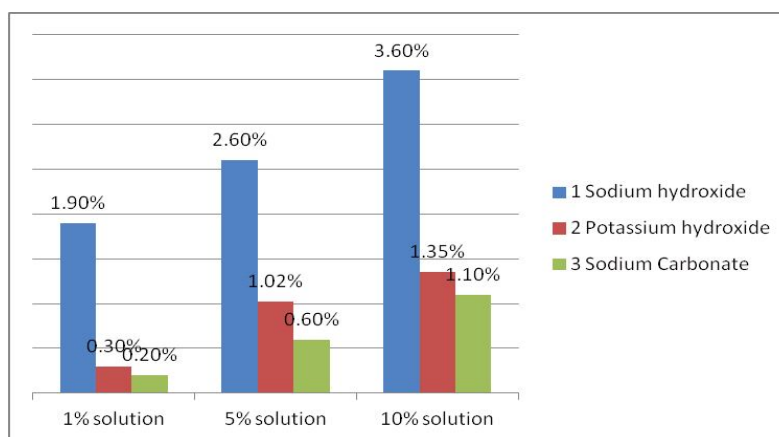| S. No.	Name of Alkali	Weight loss at various concentrations of alkali		
		1% solution	5% solution	10% solution
1	Sodium hydroxide	1.9%	2.6%	3.6%
2	Potassium hydroxide	0.3%	1.02%	1.35%
3	Sodium Carbonate	0.2%	0.6%	1.1%

Figure-2. Weight loss of adsorbent in various alkali solutions

Adsorption Capacity for Different metal ion

Table-4 and Figure-3 show that the material adsorbs a range of metal ions. The % adsorption for various metal ions varied from 10.0% to 90.0 % at different concentration levels (250 ml solution taken for each study) from 10 ppm to 50 ppm solutions. The highest adsorption was observed for Copper at a concentration level of 30-50 ppm and at 30 ppm other metal ions(lead,chromium,zinc and cobalt) shows excellent absorption efficiency, it also noted that adsorption efficiencies of mercury, iron, arsenic, magnese and cadmium is almost negligible or not detected. This suggests that the copper, lead, chromium, zinc and cobalt metals are selective for further studies and good adsorption efficiencies of all selected metals exhibits at 30 ppm metal ion concentration. Therefore, 30 ppm metal ions concentration was chosen for further studies.

Table 4. % Adsorption for different metal ions

S. No.	Name of metal	% Heavy metal adsorption on adsorbent(10 g mixture) at various metal ions concentration levels				
		10 ppm	20 ppm	30 ppm	40 ppm	50 ppm
1	Copper	10.0	41.0	89.0	89.0	90.0
2	Lead	26.0	32.0	78.0	78.1	77.3
3	Chromium	15.4	36.5	75.3	74.5	69.5
4	Zinc	18.3	39.0	69.0	72.0	71.0
5	Cobalt	15.0	36.0	68.0	67.2	61.0
6	Mercury	N.D.	N.D.	N.D.	N.D.	N.D.*
7	Iron	N.D.	N.D.	N.D.	N.D.	N.D.
8	Arsenic	N.D.	N.D.	N.D.	N.D.	N.D.
9	Magnese	N.D.	N.D.	N.D.	N.D.	N.D.
10	Cadmium	N.D.	N.D.	N.D.	N.D.	N.D.

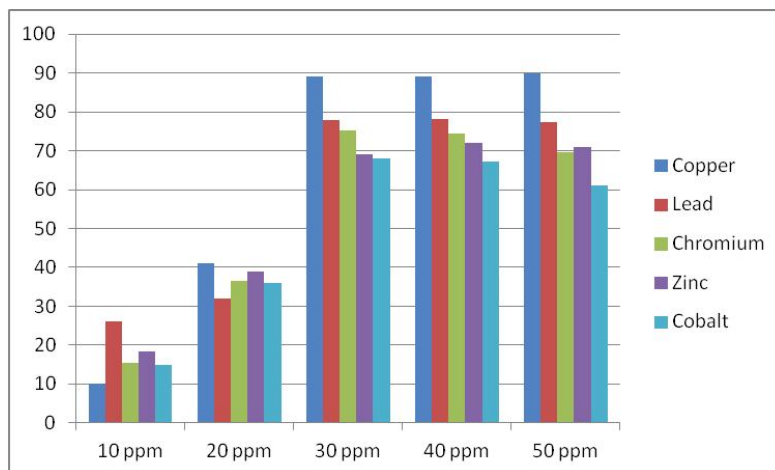Where as ND* indicates not detected.

Figure 3. % Adsorption for different metal ions

In order to understand the above metal trend of absorption on mixture of sand and fly ash may be helpful. Silica (SiO2) has a structure compounds of infinite three dimensional framework of tetrahedron (Murray, 1994). Each silicon atom forms single bonds with four oxygen atoms at the four corners of a tetrahedron.Like silica, aluminium oxide (Al_2O_3) and Ferric oxide$(Fe_2O_3)$are also framework of silicates.

A surface functional group in silicates

plays a significant roles in the adsorption process. It is a plane of oxygen atoms bound to the silica tetrahedral layer and hydroxyl groups that are associated with the edge of the silicates structural units (Donald, 1998). There functional groups provide surface sites for the chemisorption of transition and heavy metals (Murray, 1994).

Optimization of Process Parameters :

The process parameters were optimized by studying the effect of various parameters on metal ions adsorption such as particle size of adsorbent, quantity of adsorbent, equilibration time, temperature, pH and concentration of the metal ions solution etc.

1. Effect of Particle Size of Adsorbent :

Table 5 shows that the adsorption of metal ions by the adsorbent material decreased with an increase in particle size of the

adsorbent. The adsorbent with smallest particle size (0-65 micron & 66-120 micron) resulted in maximum adsorption of the metal ions (74%). This is because small particle size makes available a large surface area (adsorption sites) available for the adsorption of the metal ions[27-32].

2. Effect of Quantity of Adsorbent :

Table-6 and Figure-4 show that the adsorption of the metal ions increased with the quantity of adsorbent from 1.0 g to 10.0 g, after that there was no significant change in metal ions adsorption from solutions of 30 ppm metal ions concentrations. This suggests that there was no increase in metal ions adsorption after the equilibrium is achieved even if we increase the dose of adsorbent. These results confirm that the optimum quantity of adsorbent required for effective removal of metal ions from 250 ml of 30 ppm metal ions solution was 10.0 g.

Table-5. Effects of particle size of adsorbent(mixture) on metal ions adsorption

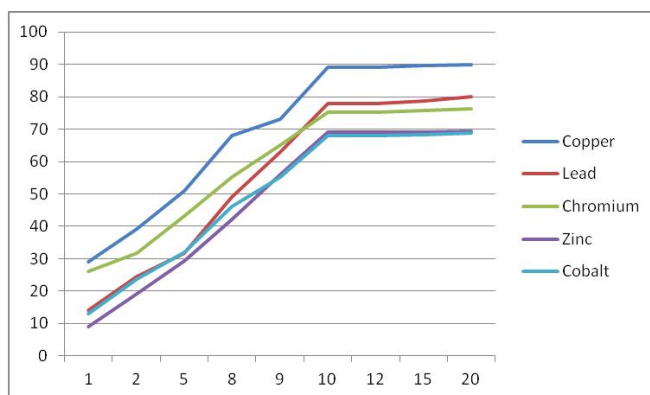| S. No.	Name of Adsorbent	% metal ions adsorption by adsorbent having different particle sizes		
		0-65 Micron	66-125 Micron	126-250 Micron
1	Adsorbent sample	74%	74%	51%

Figure 4. Effect of quantity weight in gram of adsorbent on metal ions adsorption

Table 6. Effect of quantity of adsorbent on metal ions adsorption

S. No.	Weight of adsorbent (in gram)	% adsorbent adsorption from 30 ppm solutions of different heavy metal ions				
		Copper	Lead	Chromium	Zinc	Cobalt
1	1.0	29.0	14.0	26.0	9.0	12.9
2	2.0	39.2	24.5	31.7	19.1	23.6
3	5.0	51.0	31.8	43.1	29.3	32.1
4	8.0	68.0	49.0	55.2	42.0	46.1
5	9.0	73.2	62.9	65.0	56.1	55.2
6	10.0	89.0	78.0	75.3	69.0	68.0
7	12.0	89.0	78.0	75.3	69.0	68.0
8	15.0	89.6	78.8	75.7	69.1	68.2
9	20.0	90.0	80.0	76.3	69.3	68.9

Note: The mixture of treated sand and treated fly ash has given best results of absorbency at the ratio 55 g ash and 45 g sand per 100 g of adsorbent (mixer).

Effect of Equilibration Time :

The effect of equilibration time on metal ions adsorption was studied at different temperatures. Table-7 and Figure-5 show that there was only a gradual increase in metal ions adsorption with increase in equilibration time at all the three temperatures. After 5 hours this increase in metal ions adsorption became insignificant, therefore 5 hours was taken as the optimum equilibration time to avoid unnecessary wastage of time. These results suggest that the attainment of equilibrium is very slow. Therefore, for batch experiments 24 hours may be allowed to achieve maximum adsorption. Here only the results in table 7 & figure 5 are given only for copper metal ions adsorption for reference purpose.

The results of metal ions adsorption at 60°C for 30 ppm solutions for 24 hours are given below:

S. No.	Particulars	Results of % adsorption at 60°C for 30 ppm solutions for 24 hours.
1	Copper	89.0
2	Lead	78.0
3	Chromium	75.3
4	Zinc	69.0
5	Cobalt	68.0

Effect of Equilibrium Temperature and metal ions Concentration :

The effect of temperature on metal ions adsorption was studied for various metal ions concentrations by equilibrating for 24 hours. The results shows that the metal ions adsorption increases with an increase in

Mohammad Sajid Ansari, *et al.*

Table 7. Effect of equilibration time on copper metal ion adsorption:

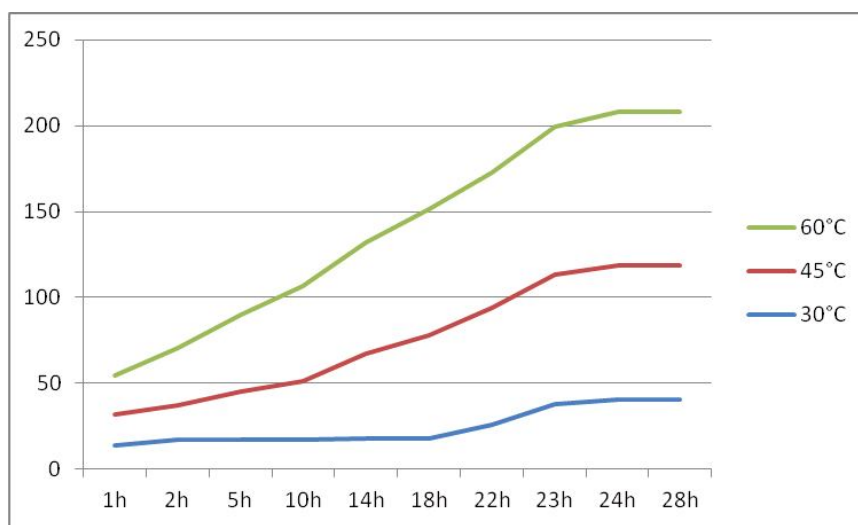| S. No.	Time in hour	% copper metal ions adsorption at different temperatures		
		30°C	**45°C**	**60°C**
1	1	14.2	18.0	22.1
2	2	16.9	20.2	33.6
3	5	17.0	24.1	39.7
4	10	22.0	34.3	55.2
5	14	23.1	49.0	65.2
6	18	24.1	60.1	73.3
7	22	26.0	68.0	79.0
8	23	38.0	75.0	86.2
9	24	40.9	78.0	89.0
10	28	40.7	78.1	89.0

Figure-5. Effect of equilibration time on copper metal ions adsorption

temperature from 30 ºC to 60 ºC at low level of metal ions concentrations (10-40 ppm). However, the effect of temperature on metal ion adsorption was not so prominent from solutions having more than 40 ppm metal ion concentration. This is due to complete attainment of equilibrium at low temperature when the metal ions concentration is high. Here only results of copper metal are displayed for study purpose.

The results of metal ions adsorption at 60°C for 30 ppm solutions are given below:

S.No.	Particulars	Results of % adsorption at 60°C for 30 ppm solutions
1	Copper	89.0
2	Lead	78.0
3	Cromium	75.3
4	Zinc	69.0
5	Cobalt	68.0

Table 8. Copper metal ions adsorption at different temperatures

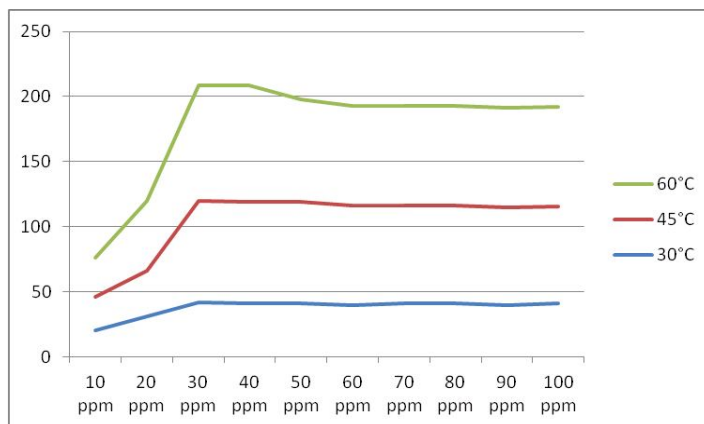| S. No.	Concentration of metal ions solution	% copper metal ions adsorption at different temperatures		
		30°C	**45°C**	**60°C**
1	10 ppm	19.0	25.0	4.4
2	20 ppm	30.0	36.0	52.9
3	30 ppm	40.9	78.0	89.0
4	40 ppm	41.3	78.0	89.0
5	50 ppm	41.2	78.0	78.5
6	60 ppm	40.0	76.2	76.9
7	70 ppm	40.8	75.7	76.4
8	80 ppm	40.8	75.6	76.4
9	90 ppm	40.0	75.1	76.0
10	100 ppm	40.8	75.0	76.3

Figure 6. Copper metal ions adsorption at different temperatures

Effect of pH of metal ions adsorption at adsorbent for 30 ppm Concentration :

Table 9 and Figure 7 shows that pH of the metal ions solution was an important parameter that controls the adsorption process. The metal ions adsorption was maximum at slightly acidic pH at 6.0 for all the metal ions concentrations and it gradually decreased when the metal ions solution was made more acidic and basic. The maximum adsorption 89.0% was observed for copper at ~ pH 6.0 from metal ions solution having 30 ppm concentration. The minimum adsorption (1% or ND) was observed at pH 1.0 and 14 from the same metal ions solution. This decrease in adsorption may be attributed to weakening of electrostatic force of attraction between the oppositely charged adsorbate (metal ions) and adsorbent (sand and ash particles) in the more acidic metal ions solutions[14-30].

Table 9. Heavy metal Adsorption from Solutions having Different pH Values

| S. No.	pH of heavy metal Solution	% Heavy metal Adsorption at different pH of solution				
		Copper (30 ppm)	Lead (30 ppm)	Chromium (30 ppm)	Zinc (30 ppm)	Cobalt (30 ppm)
1	1.0	5.0	ND	5.5	2.2	1.4
2	2.0	10.0	12.0	12.0	18.0	11.0
3	3.0	25.0	19.0	21.0	35.0	18.0
4	4.0	30.0	41.0	43.2	39.0	30.1
5	5.0	61.0	58.0	53.0	45.8	50.9
6	6.0	89.0	78.0	75.3	69.0	68.0
7	7.0	71.0	65.0	62.3	59.0	60.1
8	8.0	71.0	64.0	61.3	59.0	60.1
9	9.0	67.0	61.0	51.3	30.0	51.1
10	10.0	41.0	55.3	43.0	29.1	42.2
11	11.0	33.6	43.5	38.1	28.0	39.0
12	12.0	23.0	32.2	21.0	20.0	21.0
13	13.0	12.0	21.0	10.0	11.0	10.0
14	14.0	2.1	1.0	3.8	2.8	2.0
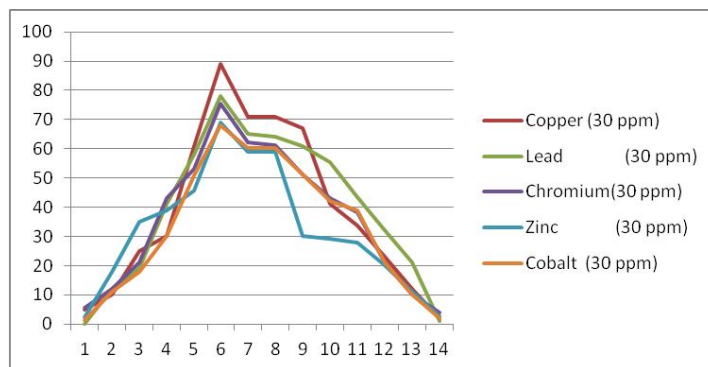
Figure 7: Effect of pH on Adsorption Behavior

Regeneration of the Adsorbent and its Reuse :

The exhausted adsorbent material could be regenerated by desorption of adsorbed metal ions from the adsorbent by treating it with 7 % HCl solution. This suggests the adsorbent material could be reused for removal of the metal ions from aqueous solutions. The recovered metal ions containing adsorbent during the regeneration process may be reused for removal of heavy metals after treatment.

Another reuse of the exhausted adsorbent is its reuse as a source of energy. It may be used as fuel after drying along with the conventional fuels and other potential organic matter. After burning, the ashes may be safely stored and used as additional raw materials for processing of some composite materials[30].

Conclusion

In this study, the efficiency of treated fly ash and impregnated sand was investigated. Based on the batch adsoption,it was found that impregnation ratio of treated sand with treated fly ash strongly affected the adsorption ability of the mixture(adsorbent) for removal of heavy metals.

Finally it may be concluded that mixture of fly ash and sand at the ratio of 55:45 is a potential adsorbent for the removal of heavy metal ions copper, lead, chromium, zinc and cobalt particularly from aqueous media. The optimum conditions for the removal of heavy metals using mixture of fly ash and sand are 10 g of adsorbent, 30 ppm metal ions concentration, 60 °C temperature, 24 hours contact time and 6.0 pH of the heavy metal containing solution.

In the view of that low cost & unused fly ash can be utilize with the low cost sand as an adsorbent for removal of heavy metals.

References

1. Removal of heavy metals,http://www. lenntech.com/ processes/heavy/ heavy_metals_removal.htm (2014).

2. Abdel-Shafy, H.I. and Raouf. O. Aly (2007). "Wastewater reuse-risk assessment, decision making and environmental security". Springer Netherlands, 375-382.

3. G.Annadurai, R.S. Juang, and D.J. Lee (2002), adsoption of heavy metals from waste water using banana and orange peels, *Water science and technology*, Vol 47, No. 1, pp. 185-190, IWA publishing (2002).

4. M. Ali Awan, Removal of heavy metals through adsorption using sand, *Journal of environmental science,* Vol. *15*, No. *3,* p. 413-416 (2003).

5. M. Mohapatra, S. Khatun and S. Anand (2009), Adsoption behaviour of Pb(II), Cd(II), and Zn(II) on NALCO plant sand, *Indian Journal of Chemical technology,* Vol. *16*, July, pp.291-300 (2009).

6. Meng-Wei Wan*, Chi-Chuan Kan, (1997) Adosrption of coppler(II) by Chitosan Immobilized on sand, *Chia-Nan, Annual Bulletin* Vol. 33, PP. 96-106 (2007).

7. I. Nhapi, N. Banadda, R. Murenzi, C. B. Sekomo and U.G Wali (2011), Removal of Heavy Metals from Industrial Wastewater Using Rice Husks, *The open environemental engineering journal, 4,* p. 170-180 (2011).

8. K.S. Hui, C.Y.H. Chao and S.C. Kot, (2005), Removal of mixed heavy metal

ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *Journal of hazardous materials* B127, pp.89-101 (2005).

9. Central electricity authority, New Delhi, Report on Fly ash generation at coal/lignite based thermal power stations and its utilisation in the country, 1st half of the year 2011-12 (2012).

10. M. J. Iqbal and M. N. Ashiq, *Journal of Hazardous Materials, 139(1),* 57 (2007).

11. T. M. Elmorsi, Y. M. Riyad Zeinhom, H. Mohamed, and HassanM. Bary, *Journal Hazardous Materials, 174(1-3),* 352 (2010).

12. Semsi Yazici,Effects of fly ash finess on mechanical properties of concrete, Sadhana, Vol. 37, Part 3, June 2012, pp. 389-403, Indian academy Science. (2012).

13. Harsh Vardhan,A note of physical characteristics of river sand, Defence science organisation,New Delhi,April 18, 1952 (FNI).

14. Elzbieta Sobiecka, Fly ash vetrifications as effective pshyco chimical waste stabilisation method, Institute of general food chemistry, Technical university of Lodz, 90-924, Lodz (Biotechnol food Science 75(2)35-38 (2011).

15. Diamond J.M., Bower W., Guber D., 1993, Use of manmade impoundment in mitigating acid mine drainage in the north branch Potomac River (J). *Environ Management, 17,* 225-238.

16. R Jiraratananon, A. Sungpet, and P. Luangsowan, *Desalination,* 130, 177 (2000).

17. Donald L. S., Environmental physical chemistry (M). San Diego, Acedamic press (1998).

18. Evangelou V. P., Environmental soil and water chemistry{M}.USA,John Wiley & Sons, Inc (1998).

19. Jaffar M., Experimental physical chemistry [M]. Pakistan university grant commission, pp. 232-238 (1983).

20. Murray B. M., Environmental chemistry of soil[M]USA, oxford university press (1994).

21. Vallejo B. *et al*., Cement for stabilisation of industrial residues containing heavy metals [J]. *J Environ Monit, 1(6),* 563-568 (1998).

22. Maria Cristina Silva, Juliana Arriel Torres, Lívian Ribeiro Vasconcelos de Sá, Pricila *Journal of Molecular Catalysis B:* Enzymatic, Volume *89,* May 2013, Pages 122–129.

23. Tee T. W., Khan R. M., Removal of lead, cadmium and zinc by waste tea leaves[J] *Environ Tech Lett, 9,* 1223-1232 (1998).

24. C. Kersch, MJE Van Roosmalen, 2000. Exptration of heavy metals from fly ash and sand with leigands and supercritical carbon di oxide, laboratory of process equipment, Delft university of technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands.

25. Mohammad Anuar Kamaruddin,influence of impregnation ratio on chemically modified silica sand for heavy metals removal from stailized landfill leachate, IJEP, Malasia (2012).

26. M.J. Santosh Yabe and E. De Oliveira, Heavy metals removal in industrial effluents by sequential adsorbent treatment, *Advance in environemental research, 7,* 263-272 (2003).

27. D.L. Jones, K.L. Badawy A.M. Gamel, I.H. Zidan and A.R. Mowafy,purification of wet process phosphoric acid by decreasing iron and uranium using sand,

Journal of environmental sciences(China), *15,* 413-416 (2003).

28. Rao, M., Parwate, A.V., Bhole, A.G., Removal of Cr6+ and Ni2+ from aqueous solution using bagasse and fly ash, Waste Wanagement, Vol. 22, p. 821-830 (2002).

29. Mylsamy Shanker, *World Journal of Applied Environmental Chemistry,* Volume 1, Issue *1,* 22-29

30. R.C. Vaishya, and S.K. Gupta, Arsenic removal from groundwater by iron impregnated sand, *Journal of environmental engineering, 129,* 89-92 (2003).

31. S. Trabelsi, N. Oturan, plasma chemical oxidation of phthalic anhydride,application to treatment of Tunisian landfill leachate, (2010).

32. A. Halin, H.A. Aziz, M.A.M. Johari and K.S. Ariffin, Comparison study of ammonia and COD adsorption on zeolite,activated carbon and composite materials in landfill leachate treatment, *Desalination, 262,* 31-35 (2010).