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Adsorption of Cu (II) Ions from Aqueous Solution by Hydrochloric Acid, Hydrofluoric Acid Treated Lignite Fly Ash

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Abstract
The adsorption of toxic compounds from industrial wastewater is an effective method for both treating these effluents. In this context, the lignite fly ash was demineralised using concentrated HCl (FA-HCl) and HF (FA-DEM) and were used as adsorbents for Cu(II) ions from aqueous solutions. Batch experiments were carried out under various adsorbent dosages, pH, contact time and different metal ion concentrations. For FA-HCl, the adsorption percentage of Cu(II) ions was 76.92% and for FA-DEM, the adsorption percentage of Cu(II) ions was 48.23% achieved under the optimum conditions of adsorbent dosages, pH, temperature, the contact time and the influence of other metals. The adsorption of Cu(II) ions onto FA-HCl and FA-DEM followed the pseudo second order kinetics. The Langmuir isotherm model best represented the equilibrium data for both the adsorbents compared to other studied adsorbents. Influence of Ni(II) ions and Zn(II) ions on adsorption of Cu(II) ions on FA-HCl and FA-DEM in binary and tertiary systems showed certain decrease on adsorption of Cu(II) ions.

Key words: Fly ash, Adsorption, Kinetics, Isotherm.

I. Introduction

Many electroplating and printed circuit board factories discharge large amounts of poisonous heavy metals in their wastewater, with copper ions being one of the most common. These effluents must be decontaminated to avoid their toxicity and carcinogenicity [1, 2]. Copper is highly toxic because it is non-biodegradable and carcinogenic [3, 4].

World Health Organization (WHO) recommended a maximum acceptable concentration of Cu(II) in drinking water of 1.5 mg/ L [5]. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in liver and kidney [6]. A number of methods are available to reduce heavy metals in wastewater, including chemical precipitation, ion exchange, adsorption, reverse osmosis and so on [7-10], but the high costs of these methods restrict their applicability. The amount of coal waste (fly ash), released by factories and thermal power plants has been increasing throughout the world, and the disposal of the large amount of fly ash has become a serious environmental problem. The present day utilization of ash on worldwide basis varied widely from a minimum of 3% to a maximum of 57%, yet the world average only amounts to 16% of the total ash [11].

Considerable research is being conducted worldwide on the use of waste materials in order to avert an increasing toxic threat to the environment, or to streamline present waste disposal techniques by making them more affordable. It follows that an economically viable solution to this problem should include utilization of waste materials for new products rather than land disposal [12]. Despite a considerable portion of fly ash is used in relevant industry, such as construction or soil amendment, there is still a large portion that is directly disposed to the environment [13]. Such disposal is not economic and environmental sounds [14].

In this paper we report the efficiency of Cu(II) ions uptake on lignite fly ash modified by the treatment with 4M HCl (FA-HCl) and followed by the treatment with HF (FA-DEM). The adsorption kinetics and substrate capacity were discussed, and are correlated with surface structure (SEM and EDAX) by batch mode study.

II. Materials and methods

2.1. Modification of fly ash

The lignite fly ash in this study was supplied by Neyveli Lignite Corporation, Neyveli, Tamil Nadu, India. The sample was oven dried at 110°C before treatment. 200 gram of the raw fly ash was treated with 200 mL of 4M HCl and then kept in magnetic stir at 60°C for an hour. After the solution was allowed to settle for 12 hours and washed with distilled water again and again till the conductivity of the filtrate was below 200 µs. It was then filtered and dried in hot air oven at the temperature of 105°C. The dried acid treated fly ash (FA-HCl) was then powdered and one portion was used as an adsorbent and the other part was then treated with HF solutions [(40%), liquid/solid ratio 0.006dm^3/g] at 60°C for one hour over water bath. After treatment, filtered, washed, dried at 105°C and used for further studies.

2.2. Preparation of Adsorbate

Copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$), Zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$), Nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$), NaOH, HCl and HNO_3 were of analytical grade and were used without further purification. Stock solutions were prepared by dissolving 1 g of $ZnSO_4$ in one litre of water. Double distilled water was used throughout the study.

2.3. Characterization of Adsorbent

2.3.1. Determination of Iodine value of the adsorbents

Iodine solution with (A) and without sample (B) was titrated against sodium thiosulphate. Iodine value is expressed in mg/g.

$$Iodine\ value = C \times Conversion\ factor \quad (1)$$

where C = (B-A)

2.3.2. Surface acidity and basicity of the adsorbent

1. Acidity

To 0.2g of adsorbent, 25mL of 0.5M NaOH solution is taken in a conical flask, agitated it for 10 hours in a closed flask. Filtered and the filtrate is titrated with 0.05M HCl.

2. Basicity

To 0.2g of adsorbent, 25mL of 0.5M HCl solution is taken in a conical flask, agitated it for 10 hours in a closed flask. Filtered and the filtrate is titrated with 0.05M NaOH.

Acidity and basicity is expressed in m. mol./g.

2.3.3. X-Ray Diffraction studies (XRD)

The adsorbent can be crystallographically characterized by means of X-ray diffraction (XRD). The adsorbents were exposed to Cu Kα radiation (k = 1.54060 A°) with the 2h angle varying between 1° and 70°. The phases were identified by comparing the peak positions and intensities with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files.

2.3.4. Scanning electron microscopic studies (SEM) and Energy dispersive X-ray analysis (EDAX)

SEM analysis of the adsorbents studied, were obtained using JEOL Scanning electron micrograph, was used to characterize the surface morphology of porosity of the adsorbents. With SEM in combination with EDAX is also possible to find out which elements different part of a sample contain. It is used to make a quantitative chemical analysis of an unknown material. Inorganic elements can be analysed and it is possible to see how they are distributed in the material. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum [15]. It was done by using JED-2300 analysis station (JEOL).

2.4. Batch mode adsorption studies

Batch mode adsorption studies for individual samples were carried out to investigate the effect of different parameters such as adsorption dosage, adsorbate concentration; contact time and pH were studied. All the experiments were triplicated and only the mean values are reported. The maximum deviation observed was less than ±4 %.

A stock solution of Copper Sulphate (1000 ppm) were prepared and suitably diluted accordingly to the various initial concentrations. Adsorption studies were carried out at room temperature (27 ± 1°C). Batch adsorption studies carried out using 0.2 g of adsorbents for each bottle and to this, 50 mL of solution of required concentration and pH of the solutions and kept for shaking in a bench shaker at a fixed shaking speed of 120 rpm. The resulting mixture was filtered (Whatmann filter paper No.41) and the final concentration of Cu(II) ions in the filtrate determined by UV-2450 visible spectrophotometer at maximum absorbance of 324.75 nm respectively. From the initial and final concentration, percentage removal was calculated by using the following equation.

$$\%\ of\ Removal = \frac{(C_o - C_f) \times 100}{C_o} \qquad (2)$$

where, C_o - initial concentration of heavy metal ion in mgL^{-1}, C_f- final concentration of heavy metal ion in mgL^{-1}.

The amount of the heavy metal adsorbed at equilibrium onto adsorbent, q_e (mg/g), was calculated by using the following mass balance relationship;

$$q_e = \frac{v \times (C_0 - C_e)}{w} \qquad (3)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid-phase concentration of heavy metal ion solution, V the volume of the solution (L), and W is the weight of the adsorbent used (g).

2.4.1. Effect of pH

To determine the effect of pH on the adsorption of Cu(II) ion (50 mL) of the concentration 100 ppm were adjusted from 2 to 9 pH using 0.1M HCl and 0.1M NaOH and the initial concentrations of the Cu(II) ion solution were using UV-2450 visible spectrophotometer. To the above solution, 0.2 g of adsorbent was added and agitated at preset equilibrium time. After agitation, the solution was filtered and the final concentrations of the solutions were measured.

2.4.2. Desorption and recycling studies

Desorption studies were carried out for the heavy metal loaded adsorbents employing batch methods. After adsorption, the adsorbate - loaded adsorbents were separated from the solution by centrifugation and the supernatant was drained out. The heavy metal loaded adsorbent was given a gentle wash with double - distilled water to remove the unadsorbed heavy metal if present. The heavy metal loaded sample were agitated with distilled water by adjusting the initial pH values with 0.1M HCl or 0.1 M NaOH from a series of pH, from 2 to 9. The desorbed heavy metal ion in the solution was separated by centrifugation and analyzed as before. The percentage of desorption was calculated.

The adsorbent, which was desorbed by the above, said method, again used for adsorption. The adsorption ability on recycling for all the adsorbents was studied by applying batch mode method.

2.4.3. Effect of agitation time

For the determination of rate of Cu(II) ions adsorption by the studied adsorbent from 50 mL of 100 ppm Cu(II) ion solution, the filtrate was analysed for residual heavy metal concentration at different intervals of time. The pH, adsorbent dosage and adsorbate concentration was kept constant.

2.4.4. Effect of adsorbate concentration

The effect of adsorbate concentration was studied by varying the concentration of 50 mL of the heavy metal solution ranging from 25, 50, 75, 100, 125, 150, 175 and 200 ppm. The equilibrium time and the pH were kept constant depending on the heavy metal solution under consideration.

2.4.5. Effect of dose of adsorbent

The effect of adsorbent dosage i.e., the amount of the adsorbents on adsorption of heavy metals was studied at different dosage ranging from 0.2 g to 1 g/50 mL with 100 ppm. The equilibrium time and the pH were kept constant depending on the heavy metal under consideration.

2.5. Adsorption kinetic studies and isotherms.

2.5.1. Kinetic studies

The pH of the solution, whose concentration was 100 ppm, was adjusted to optimum pH by using 0.1M HCl and 0.1M NaOH. For the determination of rate of heavy metal adsorption by the studied adsorbent from 50 mL of 100 ppm heavy metal solution, the filtrate was analysed for residual heavy metal concentration at different intervals of time until the adsorption attains equilibrium. The pH, adsorbent dosage and adsorbate concentration was kept constant.

2.5.2. Adsorption isotherms

Equilibrium studies were undertaken to understand the behaviour of the adsorbent at equilibrium conditions. Equilibrium data are basic requirements for the design of adsorption systems and adsorption models were used for the mathematical description of the adsorption equilibrium of the metal ion on to the adsorbent. The results obtained on the adsorption of Cu(II) ions were analysed by the well-known models given by Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill isotherms. For the sorption isotherms, initial metal ion concentration was varied while the pH of solution and adsorbent weight in each sample held constant.

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites [16]. The linear form of Langmuir equation is derived as:

$$\frac{C_e}{q_e} = \frac{1}{Q_e K_L} + \frac{1}{Q_e} C_e \qquad (4)$$

where Q_e (mgg^{-1}) and K_L (dm^3g^{-1}) are Langmuir constants related to adsorption capacity and rate of adsorption.

Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [17]. The logarithmic form of the Freundlich isotherm is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (5)$$

where K_F (mgg^{-1}) (Lmg^{-1}) and 1/n are the Freundlich adsorption constant and a measure of adsorption intensity.

Tempkin assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) [18]. Tempkin isotherm has been used in the form of:

$$q_e = B \ln A + B \ln C_e \qquad (6)$$

where B=RT/b, b and A, R and T are the Tempkin constant related to heat of sorption (J/mol), equilibrium binding constant ($L.g^{-1}$), gas constant (8.314 $Jmol^{-1} K^{-1}$) and absolute temperature (K).

The D-R model was applied to estimate the porosity apparent free energy and the characteristics of adsorption [19- 21]. The D-R isotherm does not assume a homogeneous surface or constant adsorption potential. The D-R model has commonly been applied in the following Eq. (7)

$$q_e = Q_m \exp\left(-K\varepsilon^2\right) \qquad (7)$$

where K is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the Polanyi potential, calculated from Eq. (8)

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (8)$$

The slope of the plot of ln q_e versus ε^2 gives K (mol^2 $(kJ^2)^{-1}$) and the intercept yields the adsorption capacity, Q_m ($mg.g^{-1}$). The mean free energy of adsorption (E), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the K value using the following relation [22].

$$E = \frac{1}{\sqrt{2K}} \qquad (9)$$

The Harkins-Jura adsorption isotherm can be expressed as

$$\frac{1}{q_e^2} = \left(\frac{B_2}{A}\right) - \left(\frac{1}{A}\right) \log C_e \qquad (10)$$

where B_2 is the isotherm constant. $1/q_e^2$ was plotted vs log C_e. This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution [23].

The Frenkel-Halsey-Hill isotherm can be expressed as

$$\ln q_e = \frac{1}{n}\ln K - \frac{1}{n}\ln C_e \qquad (11)$$

ln q_e was plotted vs ln C_e. This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution of the adsorbent [24].

2.6. Common ion effect (Binary and tertiary system)

Sulphates of Zn(II), Cu(II) and Ni(II) were taken and the common ion effect on adsorption of Cu(II) ions (Binary and Tertiary systems) were also studied.

2.6.1. Binary system

The concentration of one studied metal ion solution was kept as 100 ppm. The concentration of other one studied metal ion concentration was varied as 10, 20, 30, and 40 ppm. 25 mL of each solution was placed in a bottle with the studied adsorbents and the pH was adjusted to optimum pH. After shaking for equilibrium time and the percentage adsorption was calculated. Percentage adsorption decreased due to the increase in concentration of sulphate ion concentration (Common ion) of the other heavy metal ion. The same procedure was repeated for other metal ion solution.

2.6.2. Tertiary system

The concentration of one studied heavy metal ion solution was kept as 100 ppm. The concentrations of other two studied metal ion solutions were varied as 10, 20, 30, and 40 ppm. Solutions of other two studied metal ion solution each 12.5 mL were added to the 25 mL of first metal solution in a bottle with the adsorbents and the pH was adjusted to optimum. After shaking for equilibrium time, the percentage of adsorption was calculated. Percentage adsorption decreased due to the increase in concentration of sulphate ion (Common ion) present in other heavy metal ion. The same procedure was repeated for other metal ions.

III. Results and discussion

3.1.1. Physiochemical characterization of FA-HCl and FA-DEM (Acidity, basicity and iodine value)

Physiochemical characteristics of the adsorbent were assessed and presented in the Table 1**.** The recorded values of iodine number, acidity and basicity FA-HCl and FA-DEM were given in the Table 1. The acidity, basicity and iodine value for the adsorbent FA-HCl, 2 m. moles, 1.92 m. moles and 317.04, and for the adsorbent FA-DEM, 4, 0.6 m. moles, 10.97 m. moles and 314.36 respectively. This variation in the physiochemical characteristics was due to the treatment of raw lignite fly ash with HCl (FA-HCl) and HCl followed by HF (FA-DEM) treatment. The pH_{zpc} of FA-HCl was less compared to FA-DEM. This shows that more negative surface was available for adsorption of Cu(II) ions on FA-HCl than FA-DEM. From the results shown in Table 1, also proves the higher adsorption of Cu(II) ions on FA-HCl than FA-DEM.

Table 1. Physiochemical characterization of the FA-HCl and FA-DEM

Adsorbent	pH_{ZPC}	Acidity(m. moles)	Basicity(m. moles)	Iodine value
FA- HCl	3.0	2	1.92	317.04
FA-DEM	4.0	0.6	10.97	314.36

3.1.2. X-Ray Diffraction studies (XRD)

The adsorbent can be crystallographically characterized by means of X-ray diffraction (XRD). The adsorbents were exposed to Cu K_α radiation (k = 1.5406 A°) with the 2θ angle varying between 1° and 90°.The presence of SiO_2 (ɣ-quartz) and Al_2O_3 was evident from the XRD patterns of the studied adsorbents FA-HCl and FA-DEM before (Fig. 1.a.) and after adsorption of Cu(II) ions (Fig. 1.b). The XRD spectra shows that the major components of fly ash are: Carbon (graphite), SiO_2 in various structures Cubic and rhombohedra) combined with Al_2O_3 as rhombo H, mullite ($3Al_2O_3$. SiO_5), along with ɣ-Al_2O_3. Hematite (Fe_2O_3) and CaO. Anatas TiO_2 was also present in trace. The peaks were slightly shifted to higher angles after adsorption of Cu(II) ions when compared to the XRD of FA-HCl and FA-DEM before adsorption.

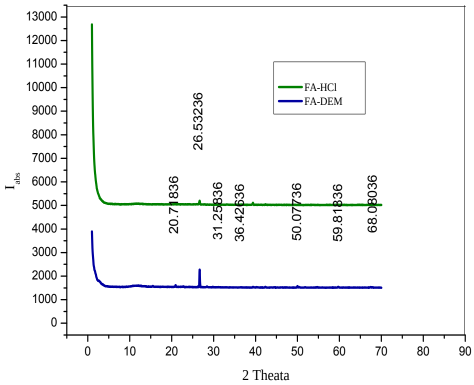


Fig. 1.a. XRD of FA-HCl and FA-DEM before adsorption

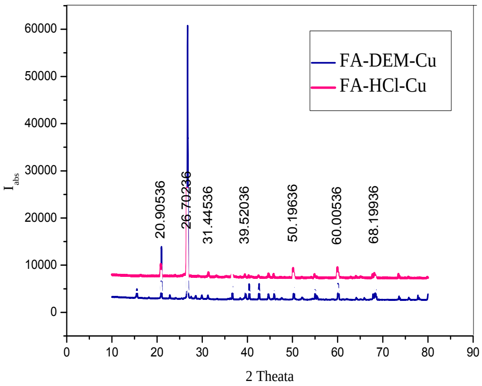
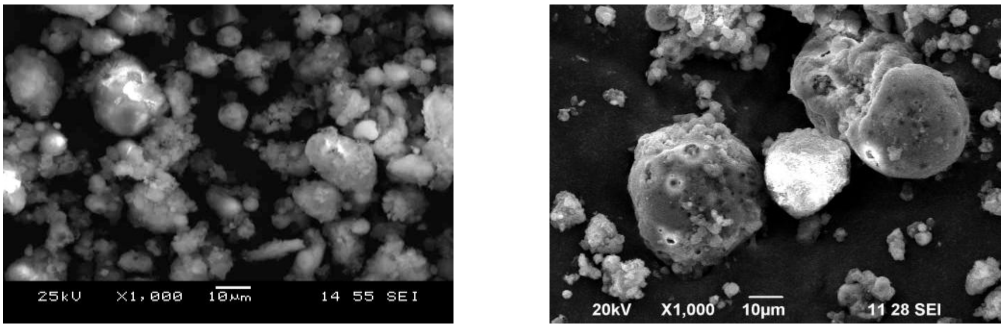


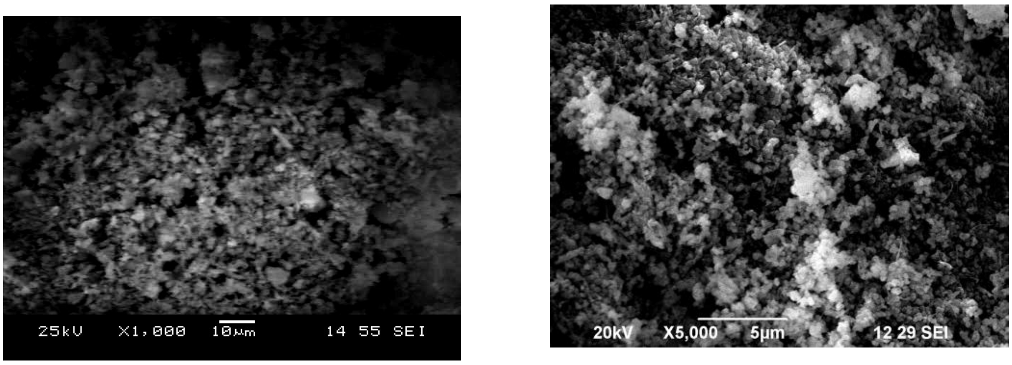
Fig. 1.b. XRD of FA-HCl and FA-DEM after adsorption of Cu(II) ions

3.1.3. Scanning electron microscopic studies (SEM)

The adsorbents FA-HCl and FA-DEM were subjected to SEM. Scanning electron microscopy was used to study the surface morphology and the pore size of the studied adsorbents. Fig. 2. shows the SEM micrographs of the studied adsorbents before and after adsorption. As can be seen from the fig. 2., size fractions. the adsorbents exhibit uneven and rough surface morphology. Fly ash is a heterogeneous material consisting largely of small spheres, formed by the condensation of aluminous and siliceous glass droplets in the air. Also found in fly ash samples are irregular, porous which are often concentrated in the larger



FA-HCl before adsorption **FA-HCl after adsorption of Cu(II) ions**



FA-HCl before adsorption **FA-HCl after adsorption of Cu(II) ions**

Fig. 2. SEM images of FA-HCl and FA-DEM before and after adsorption of Cu(II)ions

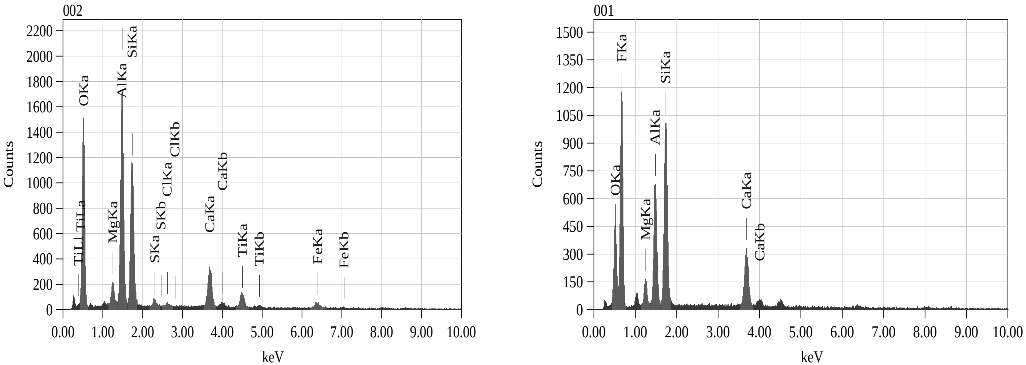
SEM image clearly shows that finer fly ash particles are primarily spherical, whereas the coarser particles are mainly composed of irregular and porous particles in these adsorbents. In order to understand the morphology of studied adsorbents, SEM analyses of fly ash samples before and after adsorption of Cu(II) ions were carried out and are shown in fig. 2. for FA-HCl and FA-DEM respectively.

The comparison of SEM picture between adsorbents shows that there are morphological changes in the adsorbents before adsorption and after adsorption. The chemically modified fly ash particles are covered by precipitates and complexes formed by the heavy metal ions.

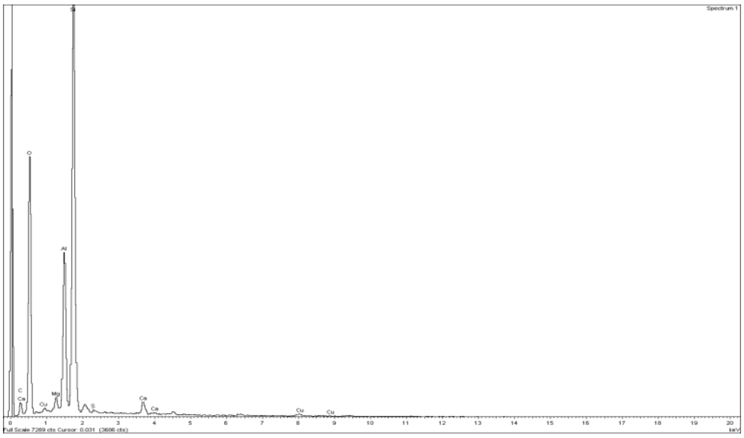
The various roughness appear due to a complex of factors, involving alkaline oxides leached by washing followed by the various treatment with HCl and HF lead to the formation of new structures, play an important role in the heavy metal adsorption; where the observed differences in the reflection of the images are due to the presence of heavy metals which was adsorbed.

3.1.4. Energy dispersive spectroscopy (EDX)

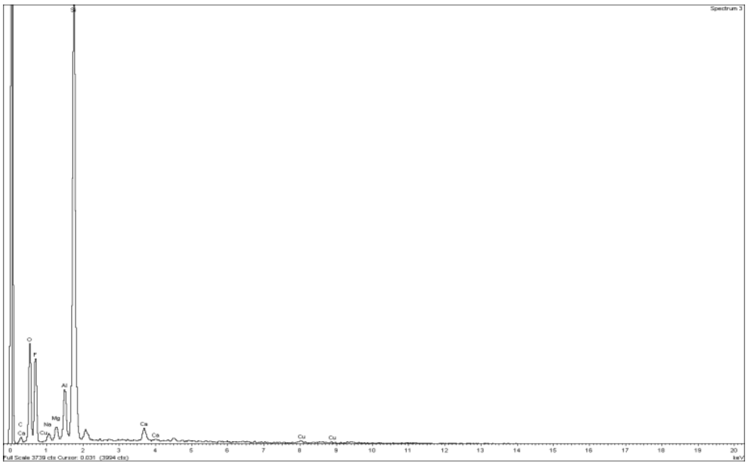
From the data obtained from EDX analysis (Table 2) the percentage of SiO_2 was reduced from 38.83 % (FA-HCl) to 31.86 % after treating FA-HCl with HF (FA-DEM). The Fe_2O_3 content was reduced from 2.16 % (FA-HCl) to 1.14 % after treating FA-HCl with HF. CaO content was 7.31% in FA-HCl and 10.9% in FA-DEM. SiO_2 and Fe_2O_3 content were reduced to certain extend, proves that demineralisation took place while treating fly ash with HCl and HF. From the spectrum (Fig. 3. before and after adsorption) Cu(II) ions on the keV scale in between 0 to 2 and 7 to 9 took place on FA-HCl and FA-DEM.



EDX spectrum of FA-HCl before adsorption **EDX spectrum of FA-DEM before adsorption**



EDX spectrum of FA-HCl after adsorption of Cu(II) ions



EDX spectrum of FA-DEM after adsorption of Cu(II) ion

Fig. 3. EDX spectrum of FA-HCl and FA-DEM before and after adsorption of Cu(II)ions

Table 2. Composition of FA-HCl and FA-DEM adsorbents before and after adsorption of Cu(II) ions

ZAF Method Standardless Quantitative Analysis(Oxide)					
FA-HCl			FA-DEM		
Compound	Before Cu(II) ion adsorption Mass %	After Cu(II) ion adsorption Mass %	Compound	Before Cu(II) ions adsorption Mass %	After Cu(II) ions adsorption Mass %
MgO	04.58	00.85	MgO	05.53	01.18
Al_2O_3	40.53	08.87	Al_2O_3	24.87	03.85
SiO_2	38.83	24.08	SiO_2	01.86	01.19
CaO	07.31	01.04	CaO	10.90	01.28
TiO_2	04.14	---	TiO_2	02.54	---
Fe_2O_3	---	00.21	Fe_2O_3	01.14	---
SO_3	02.16	---	SO_3	---	---
Cl	00.4	---	F	49.51	29.89
Na_2O	---	---	Na_2O	03.64	01.02
CuO	---	00.77	CuO	---	00.92

3.2. Effect of pH on adsorption of Cu(II) ions onto all the studied adsorbent

3.2.1. Effect of pH on adsorption of Cu(II) ions

Fig. 4. indicates that the pH of the solution (2.0-10.0) had a significant effect on the adsorption of Cu(II) ions onto FA-HCl and FA-DEM Adsorption of Cu(II) ions on FA-HCl and FA-DEM were 76.92 % at pH 4 and 48.23 % at pH 5 respectively. Although, Cu(II) ions were removed by precipitation rather adsorption above pH 6 [25]. Thus, we fixed the pH below 6 in this study. The precipitation of the heavy metal ions except copper was less than 20 % at pH below 8 indicating that the removal of the metals except copper was mainly accomplished by adsorption. Since the fly ash has a low ZPC, the surface of the fly ash was negatively charged under the pH investigated.

As pH increased from 4 to 8 can be expected that the fly ash surface becomes more negatively charged. Thus, more favourable electrostatic attraction forces enhanced cationic metal ion adsorption as pH increased. However, the dependence of heavy metal adsorption on pH was different for each metal [26]. The effect of pH on adsorption of copper onto FA-HCl and FA-DEM was shown in Fig. 4.

As pH increased from 3 to 8, it can be expected that the fly ash surface becomes more negatively charged. Thus, more favourable electrostatic attractive forces enhanced cationic metal ion adsorption as pH increased. The maximum removal of Cu(II) ions (76.92%) onto FA-HCl was observed compared to FA-DEM (48.23%).

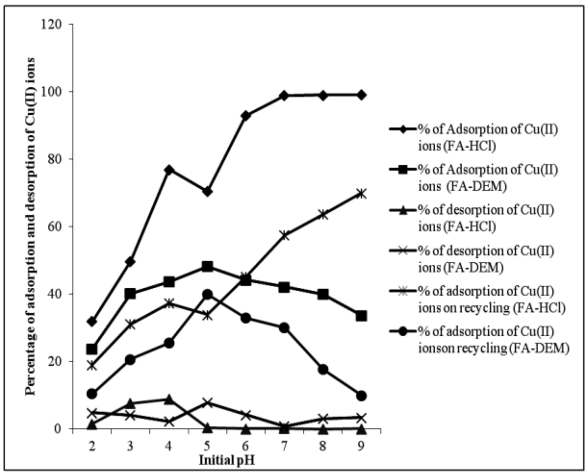


Fig. 4. Effect of pH on adsorption and desorption of Cu(II) ions onto FA-HCl and FA-DEM

3.2.2. Desorption of Cu(II) ions from the loaded adsorbents

In the wastewater treatment systems using adsorption process, the regeneration of the adsorbent or disposal of the loaded adsorbent are very important. Desorption studies were carried out for all the adsorbents by employing batch methods [27]. The results indicate that copper ions adsorbed on all the adsorbents can be recovered by distilled water, 0.1M HCl and 0.1M NaOH. For FA-HCl, it was 8.92 % at pH 4, and for FA-DEM was 7.77 % at pH 5 in batch modes. The batch mode desorption was clearly shown in the Fig. 4. From FA-HCl, maximum Cu(II) ions were removed compared to FA-DEM.

3.2.3. Adsorption of Cu(II) ions on recycling

The adsorbent which was desorbed by the above said method, used for adsorption again. The adsorption ability for FA-HCl and FA-DEM was studied by batch modes. It was found to increase as the pH of the Cu(II) ion solution increases, maximum adsorption percentage on recycling was reached at the pH 4 and it was 37.34% at pH 4 for FA-HCl and 40% at pH 5 for FA-DEM. These results were shown in Fig. 4. and showed that the adsorbent FA-HCl can be more efficient than FA-DEM. From the study of desorption and recycling capacities of the adsorbents, the cost of production of the adsorbents can be minimized and the production of waste material also reduced to certain extent.

3.3. Effect of contact time on adsorption of Cu(II) ions onto FA-HCl and FA-DEM

The randomness is increased during adsorption process, resulting in better contact between the adsorbate and adsorbent. Consequently, this led to the enhanced rate of adsorption. The amount of heavy metal ion adsorbed (mg/g) increased with increasing contact time and reached equilibrium after 75 minutes for FA-HCl and 70 minutes for FA-DEM for the adsorption of Cu(II) ions. Fig. 5.a shows the adsorption characteristics as a function of time. The kinetic experiments were performed by agitating the fly ash in bottles on shaking bath for 1.30 h at 30 °C. The pH was fixed as 4.0 for FA-HCl and pH 5.0 for FA-DEM, where the precipitations of copper metal were relatively low than of high pH. The metal concentrations were determined at varying intervals. As shown the rate of uptake of Cu(II) ions removal was 77.14% on FA-HCl in the first 75 minutes and 48.33 % on FA-DEM in the first 70 minutes. However, only 48.33% of copper was removed from the solution at equilibrium, indicating that less time for FA-DEM was needed to remove copper ions compared to FA-HCl.

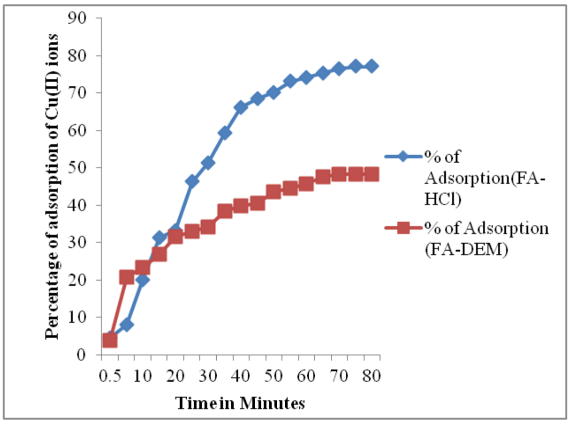


Fig. 5 a. Effect of adsorption of Cu(II) ions on FA-HCl and FA-DEM with contact time

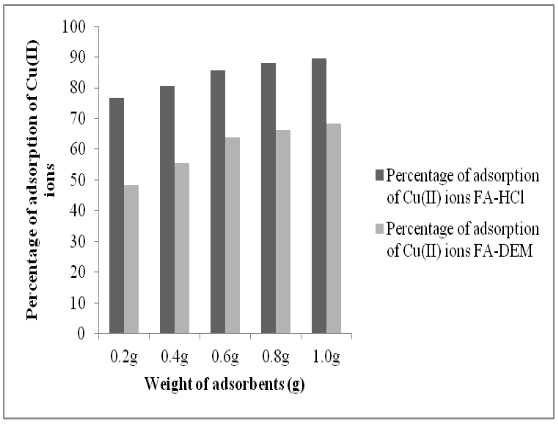


Fig. 5.b. Effect of varying dose of FA-HCl and FA-DEM on adsorption of Cu(II) ions

3.4. Effect of Cu(II) ion concentration on adsorption on all the adsorbents studied

The initial metal concentration provides an important driving force; hence a higher initial concentration of metal ions will increase the sorption rate. As the concentration of Cu(II) increased from 25 ppm to 200 ppm the percentage of adsorption decreased. The percentage of adsorption for FA-HCl was decreased from 87.01 % to 32.34 % and the percentage of adsorption for FA-DEM was decreased from 50.65 % to 29.04 %. This indicates a decrease in adsorption which is attributed the lack of active sites for the high initial concentration of Cu(II) ions.

3.5. Effect of Cu(II) ions on all the adsorbents on varying adsorbent dose

Fig. 5.b. indicates that the maximum adsorption capacities of FA-HCl and FA-DEM with increase in adsorbent dose. It was increased from 76.57% to 89.71% for FA-HCl at pH 4.0 and 48.42% to 68.49% for FA-DEM at pH 5.0 as the increase in the adsorption sites while increasing the dose from 0.2g to 1g for Cu(II) ion adsorption. This is because of the increase in adsorption sites as increase in adsorbent dose.

3.6. Adsorption isotherms

3.6.1. Langmuir adsorption isotherms

The adsorption of heavy metal ions in the concentration range of 25 mg/L to 200 mg/L and the data for Cu(II) ions were fitted to the Langmuir isotherm. A plot of C_e/q_e versus C_e gave a straight line, the slope and intercept of which correspond to Q and b respectively. The computed correlation co-efficient and the Langmuir constants are presented in Table 3 showed strong positive evidence on the adsorption of Cu(II) ions metal ion onto FA-HCl and FA-DEM were well fitted to Langmuir isotherm model. The applicability of the linear form of Langmuir model to, FA-HCl and FA-DEM was proved by the high correlation coefficients R^2>0.95. This suggests that the Langmuir isotherm provides a good model of the sorption system. The maximum monolayer capacity of Q_m obtained from the Langmuir is 8.4 mg g^{-1} ($Q_{m\ exp.}$= 3.01 mg g^{-1}) for FA-HCl and 6.95mg g^{-1} ($Q_{m\ exp.}$= 3.01 mg g^{-1}) for FA-DEM. These results show that for Cu(II) ion adsorption, the monolayer adsorption capacity (Q_m=8.4 g^{-1}) was high for FA-HCl compared to FA-DEM.

3.6.2. Freundlich Isotherm

It is another form of Langmuir approach for adsorption on amorphous surface. It assumes the heterogeneity of surface and the exponential distribution of active sites and their energies [17]. When log q_e was plotted against log C_e, a linear plot was obtained for each of the metal tested. The data for Freundlich isotherm are given in Table 3. The Freundlich constants 1/n and Kf were computed from the slope and intercept of the plot. The computed correlation coefficients and Freundlich constants for Cu(II) ions studied are presented in the Table 3. The R^2 values obtained for Langmuir equation for the metals studied are higher than those obtained for Freundlich equation. The constant 1/n and its fractional value ($0 < 1/n < 1$) show the adsorption intensity and its fractional value shows the heterogeneous nature of adsorbent.

Table 3. Isotherm parameters for the adsorption of Cu(II) ions onto FA-HCl and FA-DEM

Adsor-bent	Langmuir isotherm		Freundlich isotherm		Experimental Value	
	R^2	q_e	R^2	1/n	K_f	q_e
FA-HCl	0.9462	8.4	0.7925	0.24	34.91	16.22
FA-DEM	0.9735	6.954	0.7525	0.21	23.07	10.55

Adsor-bent	Tempkin isotherm			D-R Isotherm			Harkins Jura Isotherm				Frenkel Halsey isotherm		
	R^2	A	B	R^2	q_e	E (KJ)	R^2	q_e	A	B	R^2	1/n	N
FA-HCl	0.87	0.61	3.59	0.222	14.33	0.71	0.591	8.24	156.1	0.6	0.80	0.14	7.14
FA-DEM	0.796	0.42	2.36	0.266	9.68	0.24	0.666	6.32	100	0.7	0.77	0.23	4.35

Higher the fractional value, higher is the heterogeneity of the surface [28]. Smaller the values of 1/n, higher will be the affinity for metals. For the studied adsorbents FA-HCl and FA-DEM, the adsorption capacity from Freundlich isotherm computed for Cu, K_F was 34.91, and 23.07 respectively. For Cu, the 1/n value was 0.24 and 0.21for FA-HCl and FA-DEM respectively.

3.6.3. Tempkin isotherm for the adsorption of Cu(II) ions

Tempkin isotherm [18] is a modification of Langmuir isotherm which considers the effect of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggests that heat of adsorption decreases linearly with coverage.

The values which were calculated from the intercept and slope of the plot ln C_e versus q_e for Cu(II) ions onto FA-HCl and FA-DEM. The correlation coefficient and the values of Tempkin are given in Table 3. An examination of all the values shows that the R^2 Values of Cu(II) ions for adsorbents FA-HCl and FA-DEM were 0.8713 and 0.7960.

3.6.4. D-R isotherms

Dubnin Radushkevich isotherm model was applied to find out the sorption capacity. From the D-R plots, the correlation coefficients and the values of β and K values are computed from the slopes and intercepts of the plots obtained for Cu(II) ions onto the studied adsorbents FA-HCl and FA-DEM are given in Table 3. The constant β gives the mean free energy 'E' of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution.

The value of E for ion exchange mechanism should be in between 1.3 kJ mol^{-1} to 9.6 kJ mol^{-1}. The free energy (E) calculated for Cu(II) onto FA-HCl and FA-DEM were 0.41 kJ mol^{-1} and 0.11 kJ mol^{-1}. The correlation coefficients were lower than Langmuir and Freundlich isotherms for Cu(II) ions indicating that the D-R equation represents the poorer fit to experimental data than Langmuir and Freundlich equations.

3.6.5. Harkins Jura Isotherm for the adsorption of Zn(II), Cu(II) and Ni(II) ions onto all the studied adsorbents

Harkins Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore diffusion. From Harkins Jura plots of $1/q_e^2$ versus log C_e for the adsorbents FA-HCl for Cu(II) ions, The values of the constants A and B calculated from the slope and intercept are given in Table 3. The A and B value for FA-HCl were 156.1 and 0.6, and for FA-DEM, were 100 and 0.7 respectively. Harkins Jura isotherm represents the poorer fit to experimental data than Langmuir, Freundlich, Tempkin and D-R isotherm suggesting that there is no multilayer adsorption of Cu(II) ions onto the studied adsorbents from the R^2 values given in Table 3.

3.6.6. Frenkel Halsey Hill Isotherm for the adsorption of Zn(II), Cu(II) and Ni(II) ions onto all the studied adsorbents

Frenkel Halsey Hill isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution of the adsorbent. From Frenkel Halsey Hill plots of ln C_e versus log q_e, the values of 1/n calculated from the slope are given in Table 3. Then value shows the number of adsorption layers for the adsorption of Cu(II) ions onto the studied adsorbents. The values for the linearized plots were determined and also shown in Table 3. Frenkel Halsey Hill isotherm represents the poorer fit to experimental data than Langmuir, Freundlich, Tempkin and D-R isotherm suggesting that there is no multilayer adsorption of Cu(II) ions onto the studied adsorbents from the R^2 values given in Table 3. The n values for Cu(II) ions adsorption on FA-HCl and FA-DEM were 7.14 and 4.35 respectively. Tang *et al.* (2003) that when *n* fall in between 1.0 and 4 [29]. At higher coverage, i.e., $n > 2.0$, the adsorbed molecules form multi-layers and may be incorrect. The n values for the adsorption of

Cu(II) ions onto FA-HCl and FA-DEM fall in between 7.14 and 4.35 suggests that the adsorbed molecules may also form multi-layers. From the correlation coefficients obtained shown in Table 3 for the adsorption of Cu(II) ions adsorption obtained from Frenkel Halsey Hill linear plot also suggests the better fit to Frenkel Halsey Hill isotherm compared to Harkins Jura isotherm.

3.7. Adsorption kinetics for the adsorption of Cu(II) ions onto all the studied adsorbents

From the data obtained for Cu(II) ions from kinetic experiments, the linear regression coefficient (R^2) for pseudo first order equation was 0.855 for FA-HCl and 0.6914 for FA-DEM whereas the R^2 value for pseudo second order equation was 0.9853 for FA-HCl and 0.9834 for FA-DEM respectively. The R^2 value for pseudo second order equation was close to unity compared to pseudo first order R^2 value for all the studied adsorbents. From Table 4, the calculated adsorption maximum value ($q_{e,\ cal}$) was 29.28 for FA-HCl and 14.64 for FA-DEM for first order kinetics and the experimental q_e value was 13.18 for FA-HCl and 13.18 for FA-DEM. The calculated q_e value from second order kinetics was 18.25 for FA-HCl and 14.56 for FA-DEM, which was close to the experimental q_e value (Table 3). The calculated q_e values from second order kinetics also agree very well with the experimental data than pseudo first order kinetics. These indicate that the adsorption system studied belongs to the pseudo-second-order kinetic model.

The Elovich constants from the plot lnT vs q_t was given in Table 4. The initial adsorption rate (Table 4) B_E was 1.7 for FA-HCl and 9.3 for FA-DEM respectively. Desorption constant A_E was 0.2301 for than FA-HCl and 0.435 for FA-DEM. Desorption constant was very less for FA-HCl and FA-DEM than initial adsorption rate.

The possibility of intra particle model diffusion was explored by using the Weber and Morris intra particle diffusion model [30]. The values of q_t were found to be linearly correlated with values of $t^{1/2}$. The K_d values were calculated by using correlation analysis. K_d =2.55, C=1.816, R^2=0.9536 for FA-HCl and K_d =1.2426, C=1.609, R^2=0.9674 for FA-DEM were calculated from the plot respectively. The R^2 values were found to be close to unity for both FA-HCl & FA-DEM.

According to Ho *et al.*, 2003, if the intraparticle diffusion is sole rate limiting step, it is essential for the q_t vs $t^{1/2}$ plots (Table 4) to pass through the origin, which were not in this case, it may be concluded that the surface adsorption and intraparticle diffusion were concurrently operating during the Cu(II) ion and adsorbent interactions [31, 32].

The pseudo second-order kinetic model provides the best correlation for all of the adsorption process, whereas the intraparticle diffusion model fits the experimental data well for an initial period of the adsorption process only. Hence it was concluded that the intraparticle diffusion was found to be rate limiting, followed by the pseudo second-order kinetic model. Similar phenomena are also observed in adsorption of phenols on fly ash [33], in adsorption of lead (II) on cypress leaves [34] and in adsorption of chrome dye (OCRME) on mixed adsorbents-fly ash and coal [35].

Table 4 Kinetic parameters for the adsorption of Cu(II) ions

Adsorbents	Pseudo First order kinetics			Pseudo Second order kinetics			Elovich equation		Intraparticle diffusion	
	$q_{m,exp.}$ (mg/g)	$K_1 sec^{-1}$	$q_{e,\ cal.}$	$K_2(Lmole^{-1}\ sec^{-1})$	$q_{e,cal}$ (mg/g)	$h(mgg^{-1}min^{-1})$	A_E(mg/g min.)	B_E (g/min.)	K_d (mg/g.min½)	C
FA-HCl	20.28	0.065	13.18	0.060	18.25	19.95	0.2301	1.700	2.5500	1.8160
FA-DEM	14.64	0.060	13.18	0.077	14.56	14.56	0.4350	9.300	1.2426	1.6900

3.6. Common ion effect on adsorption of Cu(II) ions in presence of Zn(II) and Ni(II) ions onto all the studied adsorbents (Binary system and Tertiary system)

i. Influence of Zn(II) ions on adsorption of Cu(II) ions. (Binary system)

The metal ions with almost same ionic radius were taken and studied the influence of those metals on adsorption onto FA-HCl and FA-DEM. There was a competitive adsorption between those metals took place and the adsorption of Cu(II) ions were decreased to some extent. The concentration of Cu(II) ions solution was kept as 100 ppm.

The concentration of Zn(II) ion was varied as 10, 20, 30 and 40 ppm. Each solution was taken in the bottles and the pH was adjusted to optimum pH for each adsorbent and after shaking to attain equilibrium, the percentage of adsorption was calculated. The percentage of adsorption decreased from 76.92 % to 51.03 % for FA-HCl and 48.23 % to 32.41 % for FA-DEM (fig. 6.) respectively. This showed that there was a competitive adsorption taking place to certain extends between the Zn(II) and the Cu(II) ions and as the increase in concentration of sulphate ions in aqueous solution also reduces the percentage of adsorption due to common ion(sulphate ion).

i. Influence of Ni(II) ions on adsorption of Cu(II) ions. (Binary system)

The same procedure was repeated for Cu(II) ions in presence of Ni(II) ions. The adsorption percentage of Cu(II) ions was decreased from 76.92 % to 48.91 % for FA-HCl and 48.23 % to 26.21 % for FA-DEM in presence of Ni(II) ions. The percentage of adsorption of Cu(II) ions in presence of Ni(II) ions was also shown below in fig. 6.

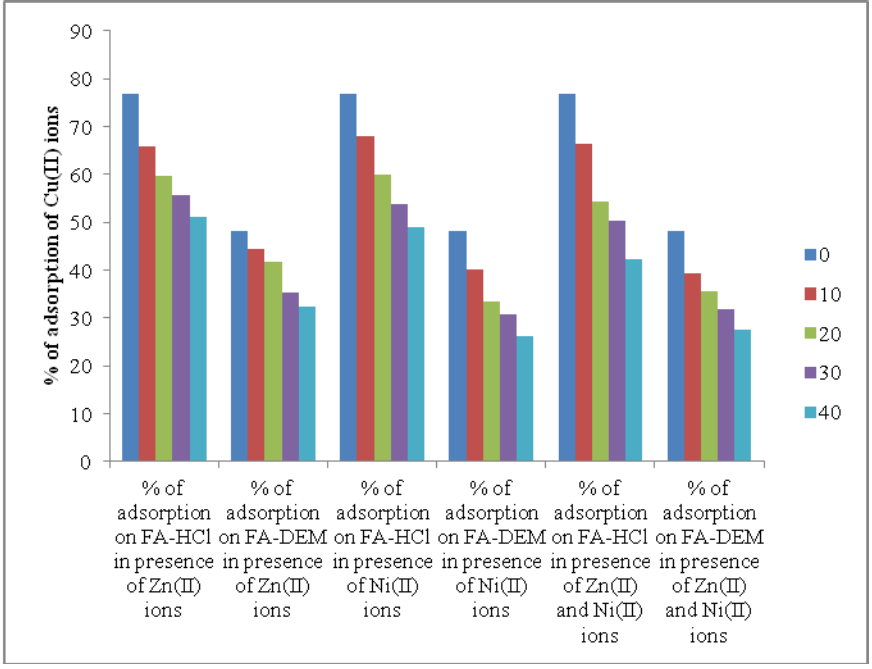


Fig. 6. Influence of Zn(II) and Ni(II) ions on adsorption of Cu(II) ions onto FA-HCl and FA-DEM

ii. Influence of Zn(II) ions and Ni(II) ions on adsorption of Cu(II) ions (Tertiary system)

The concentration of Cu(II) ion solution was kept as 100 ppm. The concentration of Zn(II) ion solutions and Ni(II) ion solutions were varied as 10, 20, 30 and 40 ppm. Each solution was taken in the bottles which were added to Cu(II) ion solution and the pH was adjusted to optimum pH FA-HCl and FA-DEM and after shaking to attain equilibrium, the percentage of adsorption of Cu(II) ion was calculated. The percentage of adsorption decreased from 76.92 % to 42.34 % for FA-HCl and 48.23 % to 27.48 % for FA-DEM as the concentration of Ni(II) ions and Zn(II) ions increased from 10 ppm to 40 ppm. This showed that there was a competitive adsorption taking place to certain extend between the Ni(II) ions, the Zn(II) ions and Cu(II) ions and also the increase in concentration of common ion (sulphate ion). The percentage of adsorption of Cu(II) ions in presence of other metals was decreased. It was clearly shown in fig. 6.

IV. Conclusion

Treating the fly ash with HCl (4M) solutions and HF, the surface is modified by dissolution and reprecipitation reactions. By dissolution of acid oxides, the specific surface area is enhanced and activated and the efficiency of heavy metal removal increases. The adsorption of Cu(II) ions is pH-dependent with maximum adsorption of 76.92% on FA-HCl occurring at pH 4 and 48.23% on FA-DEM occurring at pH 5. The adsorption data was well fitted by the Langmuir isotherm model which shows monolayer adsorption capacity of FA-HCl. Adsorption of Cu(II) ions onto FA-HCl obeyed pseudo second order kinetics. The adsorbed Cu(II) ions can be desorbed from the adsorbent using water. The percentage of adsorption of Cu(II) ions on FA-HCl and FA-DEM was slightly higher in single system than binary and tertiary system which shows the competitive adsorption between the metal ions and also due to common ion (Sulphate) effect. Comparing the adsorption capacity of FA-HCl and FA-DEM, the percentage of adsorption was higher for FA-HCl than FA-DEM. This may be due to the diminution of SiO_2 and Fe_2O_3 content in FA-DEM than in FA-HCl. The experimental result shows that this can be an up-scalable solution and represent a step in investigating the process of complex treatment of wastewater containing metal ions.

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