

ACID TREATED LIGNITE FIRED FLY ASH FOR THE REMOVAL OF Zn(II) IONS FROM AQUEOUS SOLUTION

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ABSTRACT:

This study investigated the adsorption capacity of lignite fly ash treated with HCl. For adsorption fly ash after treating with 4M hydrochloric acid (FA-HCl) was used as an adsorbent for removing Zn(II) ions from aqueous solution. Batch experiments were carried out under various adsorbent dosages, pH, contact time and different metal ion concentrations. For FA-HCl, the 63.14% removal of Zn(II) ion was achieved under the optimum conditions of adsorbent dosages of 4g/L, pH at 6, temperature at 303 K and the contact time of 1.15 hours, a removal of 63.14% of the Zn(II) was obtained. The adsorption of Zn(II) ions onto FA-HCl followed the pseudo second order kinetics. The equilibrium data were best represented by the Langmuir isotherm model.

Keywords: Fly ash, Zinc(II), Adsorption, Kinetics, Isotherm, Batch experiments.

[I] INTRODUCTION

The presence of heavy metals in natural water and subsurface aquifers represents a serious threat for human health. Heavy metals are present in wastewaters because of discharge by industry, for example electroplating, inorganic pigment manufacture, wood processing, photographic operations, and petroleum refining. Small amounts of some heavy organisms, but excessive levels of essential metals can be harmful to the organisms and cause serious health effects (cancer, liver damage, renal disorder, visceral cancers, insomnia, depression, lethargy, vomiting)[1]. Children, in particular, are at risk; consumption of food containing excessive amounts of heavy metals can result in reduction of growth and damage to the

nervous system and brain. To minimize human and environmental exposure to hazardous heavy metals the US Environmental Protection Agency (US EPA) established limits of cadmium, lead, and zinc that may be discharged into wastewater at 0.01, 0.006, and 0.80, respectively. Heavy metals can deactivate the active sludge (by poisoning the bacteria) in secondary treatment plants[2]; therefore, chemical treatment must be used to remove heavy metals before the biological step. Various physical and chemical methods are used for treating heavy metals from industrial wastewater, that include: adsorption, ion exchange, complication and membrane separation[3,4]. The method most common and

widely used for removing heavy metals from wastewater is chemical precipitation by use of caustic soda or lime [5]. This method is not expensive, but requires a large amount of chemicals and results in a large quantity of sludge that requires supplementary treatment. Replacing synthetic substrates with low-cost adsorbents has, therefore, been intensively studied, and there have been reports of the use of materials obtained from agriculture and from forest wastes, for example, bagasse fly ash[6], sugar beet pulp[7], activated carbon derived from bagasse[8], maple sawdust[9], clay[10,11], volcanic ash bone char[12], humus[13], or bituminous coal, for removal of heavy metals. Removal of heavy metals (cadmium, copper, zinc, and nickel) on scrap rubber, bituminous coal, peat[14], natural zeolite[15], alkali treated lignite fly ash[16] and alkali followed by methyl orange treated lignite fly ash[16] has also been reported.

Fly ash is an amorphous mixture of Ferro aluminosilicate minerals generated by combustion of ground or powdered coal[17]. Approximately 70 % of the combustion by-products is fly ash collected in electrostatic precipitators. This is the most difficult by-product to handle[18], and there is a need for environment-friendly uses of fly ash. Fly ash is mostly used as a substitute for Portland cement in the manufacture of roofing tiles and as structural fill, sheetrock, and agricultural fertilizer, and for soil amendment[19,20]. Chemically, 90–99 % of fly ash comprises Si, Al, Fe, Ca, Mg, Na, and K, with Si and Al being the major components. The mineralogical, physical, and chemical properties of fly ash depend on the nature of the parent coal[21,22]. The applications of fly ash depend on the presence of basic mineral elements resembling the earth's crust, which makes it an excellent substitute for natural materials. In this paper we report the efficiency of Zn(II) uptake on fly ash modified by treatment with HCl (4M HCl) (FA-HCl). The adsorption kinetics and substrate capacity were discussed,

and is correlated with surface structure (SEM and EDAX) by batch mode study.

[II] MATERIALS AND METHODS

2.1. Preparation of adsorbents

The fly ash used for this study was collected from the NLC Power Plant, Neyveli, Tamil Nadu, India. 150 gram of the raw fly ash was treated with 150 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 μ s. 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 used for further studies. The yield for FA-HCl was found to be 106 g.

2.2. Preparation of Adsorbate

Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), Nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), Copper sulphate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), NaOH, HCl and HNO_3 were of analytical grade and were used without further purification. Stock solutions were prepared by dissolving 1g of ZnSO_4 in one litre of water. Double distilled water was used throughout the study.

2.3. Characterization of adsorbent

2.3.1. Acidity and Basicity (Boehm titration)

Acidity and basicity were estimated by mixing 0.2 g of adsorbent (FA-HCl) with 20 mL of 0.1 M NaOH, 20 ml of 0.1 M Na_2CO_3 , 20 mL of 0.1 M NaHCO_3 in a closed flask separately, and agitating for 48 h at room temperature. Filtered and from that filtrate 5 mL was pipetted out and titrated with 0.1 M HCl[23].

2.3.2. Fourier transform infrared analysis

Functional groups in FA-HCl were examined by using the FTIR method of analysis. The FTIR spectrophotometer was based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum RX1 "Pelmer" version 5.3 Spectrophotometer in the spectral

range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

2.4. Adsorption and kinetic studies

A stock solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (1000mg/L) was prepared and suitably diluted accordingly to the various initial concentrations. Adsorption studies were carried out at room temperature ($28 \pm 5^\circ\text{C}$). Batch adsorption studies were carried out using 0.2g of adsorbent for each bottle, with 50 mL of solution of required concentration and pH of the solutions varied from 2 to 9 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 the metal ions in the filtrate determined by UV-2450 vis spectrophotometer at λ_{max} value of 213nm. The pH of the solution was adjusted using 0.1M HCl and 0.1M NaOH and buffer solution was used to maintain the exact pH. The experiments were carried out for various adsorbent dosages, different initial Zn(II) ions concentration, for various contact time and different initial pH of the solution. The Stock solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was prepared for the concentration of 1000 ppm and it was diluted to various required concentrations. From the initial and final concentration, percentage removal can be calculated by

$$\% \text{ of removal} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where, C_0 - initial concentration of Zn(II) ions in mg/L, C_f - final concentration of Zn(II) ions in mg/L. The data obtained in batch mode kinetics were used to calculate the equilibrium metal uptake capacity. It was also calculated for adsorptive quantity of Zn(II) ions by using the following expression:

$$q_e = \frac{v \times (C_0 - C_f)}{w} \quad (2)$$

where q_e is the equilibrium metal ion uptake capacity in mg/g, v is the sample volume in litre, C_0 the initial metal ion concentration in mg/L, C_e

the equilibrium metal ion concentration in mg/L and w is the dry weight of adsorbent in grams.

2.5. Adsorption isotherms

Equilibrium studies were undertaken to understand the behaviour of the adsorbent at an equilibrium condition. Equilibrium data are basic requirements for the design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the metal ion on to the adsorbent. The results obtained on the adsorption of Zn(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 the solution and adsorbent weight in each sample held constant. The sorption isotherms were realized with FA-HCl at solution pH 6.

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites[24]. The linear form of Langmuir equation is derived as:

$$\frac{C_e}{q_e} = \frac{1}{Q_e K_L} + \frac{1}{Q_e} C_e \quad (3)$$

where Q_e (mg/g) and K_L (dm^3/g) 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[25]. The well-known logarithmic form of the Freundlich isotherm is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F (mg/g) (l/mg) 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)[26]. The Tempkin isotherm has been used in the form of:

$$q_e = B \ln A + B \ln C_e \quad (5)$$

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), gas constant (8.314 J/mol K) and absolute temperature (K).

The D-R model was applied to estimate the porosity, apparent free energy and the characteristics of adsorption [27-29]. 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. (6) and its linear form can be shown in Eq. (7)

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (6)$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (7)$$

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

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

The slope of the plot of $\ln q_e$ versus ε^2 gives K ($\text{mol}^2/(\text{kJ}^2)$) and the intercept yields the adsorption capacity, Q_m (mg/g). 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[30].

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

The Harkin-Jura adsorption isotherm can be expressed as

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

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[31].

The Frenkel-Halsey-Hill isotherm can be expressed as

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

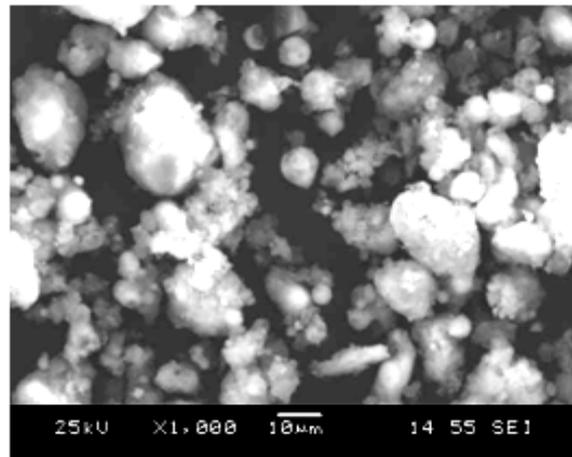
$\ln q_e$ was plotted vs. $\ln C_e$. This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution of the adsorbent[32].

[III] RESULTS

3.1. Characterization of the adsorbent

3.1.1 Scanning electron microscopic studies (SEM)

The Fig. 1.a., 1.b and Fig. 1.c clearly shows that the SEM was employed to observe the physical morphology of the Fly ash, FA-HCl at 1000 X magnification. The SEM images (Fig. 1.a) clearly shows that finer fly ash particles are primarily spherical, whereas the acid treated fly ash particles (Fig. 1.b) are mainly composed of irregular and porous particles in FA-HCl. Fig. 1.c shows the SEM image of FA-HCl after adsorption of Zn(II) ions at 10, 000X magnification in JEOL JED-2300 analysis station



1.a. SEM image of fly ash

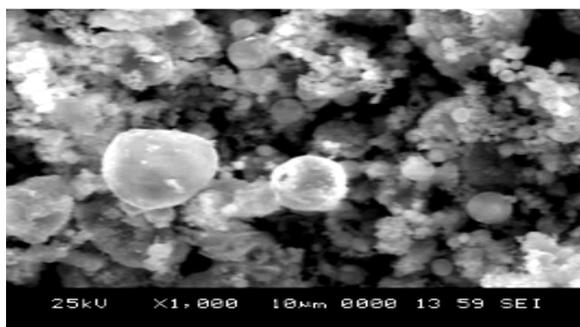


Fig. 1.b. SEM image of FA-HCl

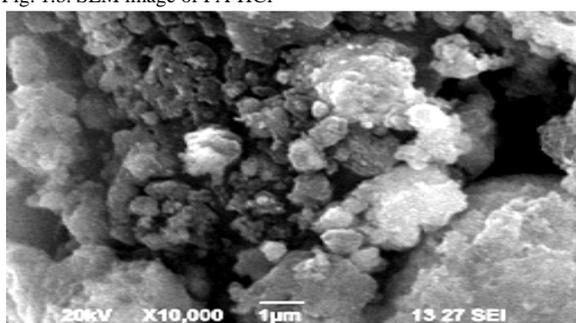


Fig. 1.c. SEM image of Zn(II) ions loaded FA-HCl after adsorption

3.1.2. Energy dispersive X-ray spectroscopic analysis (EDX)

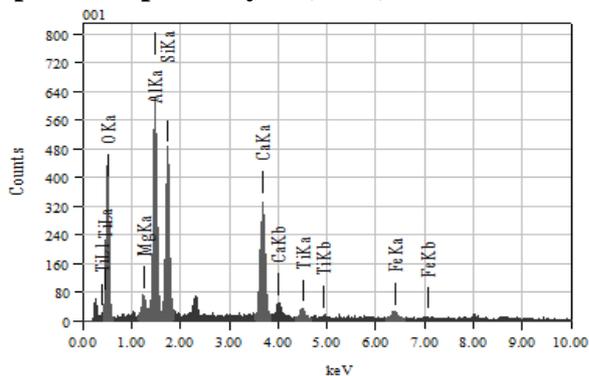


Fig. 2.a EDX spectrum of fly ash

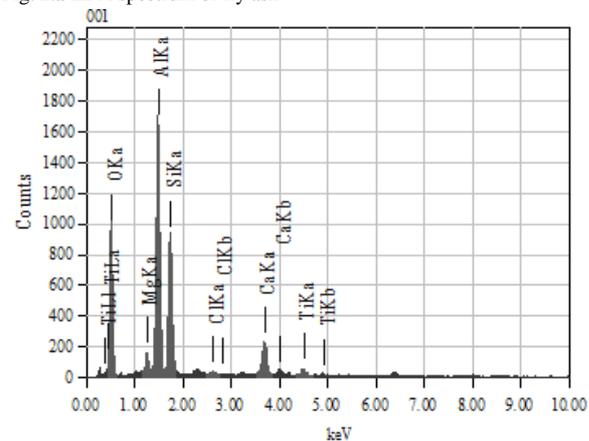


Fig. 2.b. EDX spectrum of FA-HCl

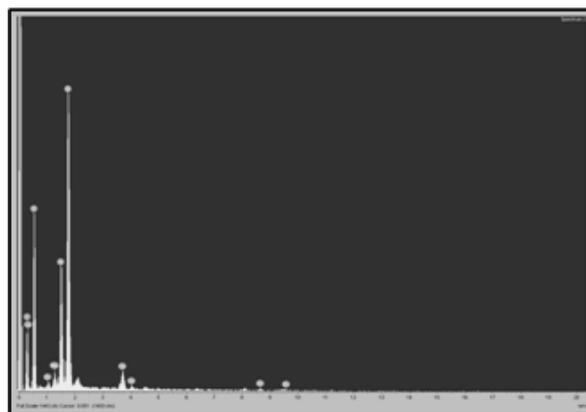


Fig. 2.c. EDX analysis of Zn(II) ions loaded FA-HCl

The components of fly ash was SiO₂ 38.1%, Al₂O₃ 36.36%, CaO 17.39%, MgO 3.28%, TiO₃ 2.55% and FeO 2.31%. The major components of FA-HCl was SiO₂ 40.41%, Al₂O₃ 47.63%, CaO 6.24%, MgO 3.84%, and TiO₂ 1.66%. The presence of the above mentioned elements in fly ash and FA-HCl are clearly shown in fig. 2.a, 2.b and 2.c SiO₂ and Al₂O₃ contents make up about 70% of the fly ash. FeO and CaO contents compose above 19% in fly ash whereas FeO was not found in FA-HCl and the amount of CaO was decreased to 6.24% in FA-HCl. From the EDX analysis, it was proved that the basic nature of fly ash was reduced by treating fly ash with 4M HCl.

3.1.3. FTIR spectroscopic studies

Surface functional groups were detected by Fourier transform infrared (FTIR) spectroscope from the scanning range(4000 cm⁻¹ - 400cm⁻¹) and elemental analysis was performed using an elemental analyse. FTIR spectra for FA-HCl before and after adsorption shows broad band between 3100 and 3700 cm⁻¹ in Fig. 3.a. and Fig. 3.b. respectively. This indicates the presence free and hydrogen bonded OH groups such as water either of clay minerals or phenolic groups on the adsorbent surface. This stretching is due to both the silanol groups (Si-OH) and adsorbed water[33,34]. The FTIR spectra of FA-HCl indicated weak and broadband in the region of 1600-1800 due to C=O group stretching bands from aldehydes and ketones. The band at 1636

cm^{-1} may be due to the conjugated hydrocarbon bonded carbonyl groups. The band at 1091 cm^{-1} may be due to vibrations of CO group lactones[35]. The FTIR of FA-HCl after adsorption of Zn(II) ions shifted the band from 1091 cm^{-1} to 1080 cm^{-1} . A doublet of Si-O stretching bands of quartz (802 cm^{-1} and 780 cm^{-1}). Additionally intense vibration at 572 cm^{-1} for FA-HCl is attributed to clay and silicate minerals[36]. Although some interference can be drawn about the surface functional groups from FTIR spectra, the weak and broad band's do not provide any authentic information about the nature of the surface oxides. The presence of polar groups on the surface is likely to give considerable cation exchange capacity to the adsorbents.

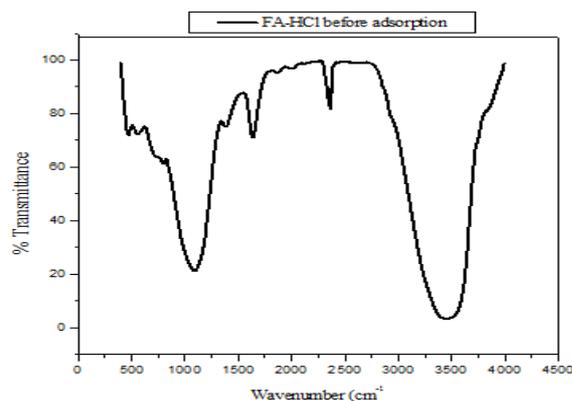


Fig. 3.a. FTIR spectrum of FA-HCl before adsorption

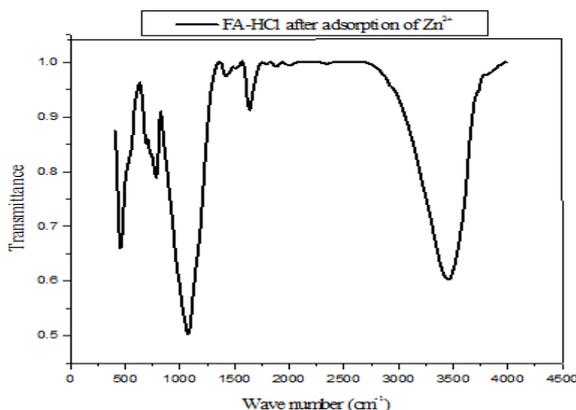


Fig. 3.b. FTIR spectrum of FA-HCl after adsorption of Zn(II) ions

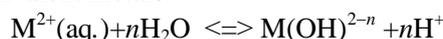
3.1.4. Acidity and basicity: (Boehm titration)

This titration shows the number of acidic, basic, phenolic, carboxyl and lactones sites. For FA-HCl,

the number of basic sites present was found to be 1.5625 mEq/g. L , the numbers of phenolic, carboxyl and lactones groups was found to be 3.33 mEq/g. L and the number of carboxyl groups present was found to be 1.722 mEq/gL . From the above result, there may be the possibility of ion exchange mechanism during the adsorption of Zn(II) ions process onto FA-HCl because the number of phenolic, carboxyl and lactones groups in FA-HCl[37-40].

3.2. Effect of pH on adsorption, desorption and recycling ability

The pH of the solution has a significant impact on the uptake of heavy metals. The pH_{zpc} of FA-HCl is 3. The solution pH is above than the pH_{zpc} of the adsorbent, the surface of the adsorbent is highly loaded with negatively charged ion. It favours the adsorption of metal cation onto the negative surface of the adsorbent due to the electrostatic attraction. Therefore, it can be expected that positively charged metal ions are likely to adsorb onto the negatively charged adsorbents at the pH above ZPC for FA-HCl[41]. Metal cations in aqueous solutions hydrolyse according to the generalized expression for divalent metals.



The silica in FA-HCl could adsorb either positive or negative contaminants depending on the pH of the solution. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid, which can react with water, forming silanol (SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charge. The pH_{zpc} of silica is generally in the neighbourhood of 2.0[42-44]. This indicates that the maximum Zn(II) ions adsorption capacity of FA-HCl can be attributed to the electrostatic interaction of the adsorbate with surface silica sites of the adsorbents [45-47].

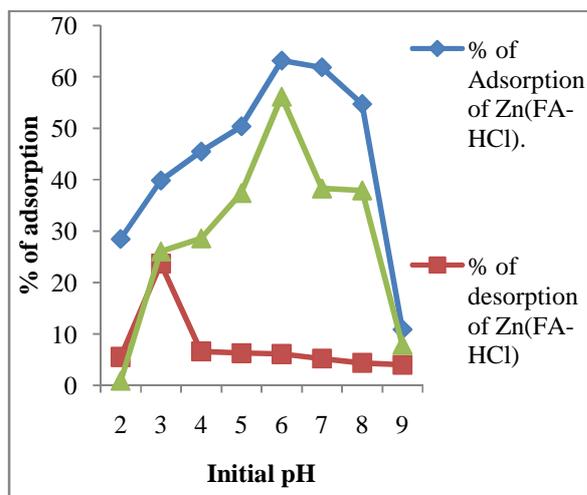


Fig. 4 Effect of pH on adsorption and desorption of Zn(II) ions onto FA-HCl; optimum conditions: Dose 0.2g/50 mL, Concentration: 0.1g/L

Fig. 4 indicates that the pH of the solution (2.0-9.0) had a significant effect on the adsorption of Zn(II) ions onto FA-HCl. At pH 6, the adsorptions of Zn(II) ions on FA-HCl were found to be 63.2%. Zn(II) ions were removed by precipitation not in adsorption if the solution pH is above pH 8 for FA-HCl. Thus, we fixed the pH 6 for Zn(II) adsorption onto FA-HCl in this study. As shown, 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 below pH 8. Since the FA-HCl has a low ZPC, the surface of the fly ash was negatively charged under the pH investigated. As pH increased from 3 to 9, 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. However, the dependence of heavy metal adsorption on pH was different for each metal. The effect of pH on adsorption desorption and recycling capacities of FA-HCl for Zn(II) ions removal in aqueous solution was given in the fig. 4. For FA-HCl, the adsorption capacity increases initially to 63.14% until the pH reaches 6 and after pH 6, it decreases.

In the wastewater treatment systems using adsorption process, the regeneration of the adsorbent and /or disposal of the loaded adsorbent are very important. Desorption studies were carried out for the adsorbents FA-HCl by employing batch methods shown in fig. 4. The maximum desorption of 23.67% took place in acidic medium at the pH 3 for FA-HCl. The results indicate that Zn(II) ions adsorbed onto FA-HCl can be recovered by distilled water. After desorption, the adsorbent were further used for adsorption process for the removal of Zn(II) ions. The percentage of removal of Zn(II) ions were found to be 56.16 % for FA-HCl after desorption at pH 6 given in fig 4.

3.3. Effect of contact time

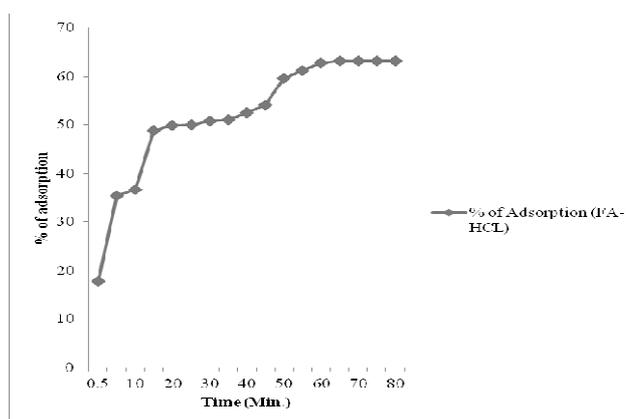


Fig. 5. Effect of Time on adsorption of Zn(II) ions onto FA-HCl. optimum conditions: pH 6, Dose 0.2g/50 mL, Concentration: 0.1g/L

Aqueous Zn(II) ion solutions with initial ion concentration of 100 mg/L were kept in contact with FA-HCl from 5 minutes to 60 minutes. The rate of removal was rapid for first 20 minutes and thereafter the rate of metal removal attains equilibrium. No significant change in metal ion removal after 50 minutes for FA-HCl. During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface. The maximum uptake of

Zn(II) ions at pH 6 for FA-HCl was found to be 63.2% and it was clearly given in the fig. 5.

3.4. Adsorption Kinetics

The adsorption process of Zn(II) ions can be well fitted using the pseudo second order rate for FA-HCl. The kinetic parameters were given in the Table 1. The q_e value (18.15) obtained from second order kinetic equation for FA-HCl was close to the experimental q_e value (11.84) and the linear regression coefficient value R^2 value (0.9326) obtained for pseudo second order kinetics was close to unity compared to the R^2 value (0.6399) obtained from first order kinetics. The values on initial sorption (h) that represents the rate of initial adsorption, is $19.56 \text{ mg(gmin)}^{-1}$ for FA-HCl. This indicates the adsorption of Zn(II) ions onto FA-HCl follows pseudo second order kinetics.

The Elovich equation, the linear coefficient value (R^2) for FA-HCl was found to be 0.9547. Elovich constants A_E (desorption constant, g mg^{-1}) and B_E (Initial adsorption rate, for FA-HCl were 0.3737 mg/g min and 43.94 g/min respectively.

In intraparticle diffusion model, 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. $K_d = 1.2 \text{ mg g}^{-1} \text{ min}^{-1/2}$, $R^2 = 0.9046$, $C = 5.4972$ for FA-HCl were obtained using intraparticle diffusion model. The R^2 values were found to be close to unity indicating the application of this model is fitted to FA-HCl. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step. The values of intercept C (Table 1) provide information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase.

3.5. Effect of adsorbent dose.

The fig. 6 the maximum adsorption capacities of FA-HCl at pH 6 recorded as 63.38 % for the

dosage of $0.2 \text{ g}/50 \text{ mL}$. This was increased to 75.18% for FA-HCl. This was due to the increase in the adsorption sites as increase the dose from 0.2 g to 1 g in 50 mL .

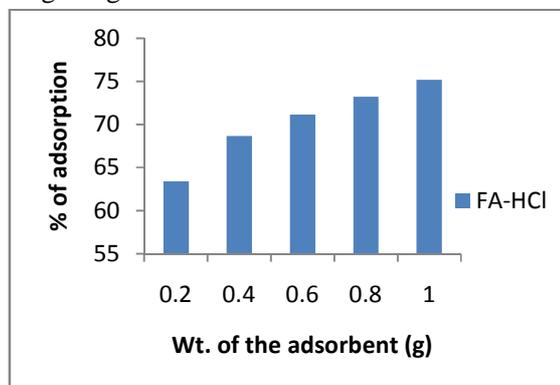


Fig. 6. Effect of adsorbent dose on adsorption of Zn(II) ions optimum conditions: pH 6, Concentration: 0.1 g/L

3.6. Effect of Zn(II) ion concentration on adsorption

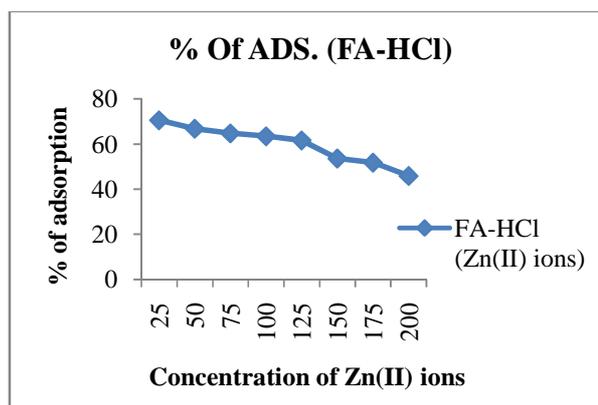


Fig. 7. Effect of Zn(II) ions concentration onto FA-HCl. optimum conditions: pH 6, Dose $0.2 \text{ g}/50 \text{ mL}$.

The initial metal concentration provides an important driving force; hence, a higher initial concentration of metal ions will increase the sorption rate. The fig. 7. provides the effect of changing the initial concentration of Zn(II) ions on adsorption, while keeping the dosage of FA-HCl constant at room temperature and equilibrium pH values. As the concentration of Zn(II) ions increased from 25 mg/L to 200 mg/L , the percentage of adsorption decreased. The percentage of adsorption of Zn(II) ions onto FA-HCl was found be decreased to 45.81%. This was

due to the increase in concentration of Zn(II) ions for lesser number of adsorption sites.

3.7. Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of Adsorbate, it is important to establish the most appropriate isotherm model. Various isotherm equations like those of Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Harkin Jura and Frenkel Halsey isotherm have been used to describe the mono-component equilibrium characteristics of adsorption of Zn(II) ions onto FA-HCl. The experimental equilibrium adsorption data were obtained by varying the concentration of Zn(II) ions with fixed dosage of FA-HCl.

The adsorption parameters for each metal ion obtained from the fitting of different isotherm models with the experimental data are listed in Table 2 along with the linear regression coefficients, R^2 . FA-HCl has a homogeneous surface for the adsorption of metal ions.

Therefore, it is expected that the Langmuir isotherm equation can be had better represent the equilibrium adsorption data. The R^2 value is closer to unity for Langmuir model than that for the other isotherm models for FA ($R^2 = 0.9862$). As seen in Table 2, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient $R^2 > 0.99$), whereas, the low correlation coefficients ($R^2 < 0.96$) show poor agreement of Freundlich and Temkin isotherms with the experimental data. The monolayer adsorption capacity according to this model was 11.04mg/g at 30 °C. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto FA-HCl surface, since the Langmuir equation assumes that the surface is homogenous. Therefore, the equilibrium adsorption data of Zn(II) ion adsorption on FA-HCl can be represented appropriately by the Langmuir model in the studied concentration range.

The calculated value of D-R parameters is given in Table 2. The saturation adsorption capacity Q_m

obtained using D-R isotherm model for adsorption of Zn(II) ions onto FA-HCl and 13.82mg/g. The values of E calculated using Eq. 8 is 0.408KJ mole⁻¹ for FA-HCl, which indicating that there was no ion exchange mechanism taking place in the adsorption of Zn(II) ions adsorption onto FA-HCl (for Ion exchange mechanism the value of E was found to be within 1.3 to 9.6 KJ mole⁻¹)[48].

3.8. Influence of other metals on adsorption of Zn(II) ions

3.8.1. Influence of Ni(II) ions and Cu (II) ions on adsorption of Zn(II) ions.

The concentration of Zn(II) ion solution was kept as 100 mg/L. The concentration of Cu(II) ion was varied as 10, 20, 30 and 40 mg/L. Each solution was taken in the bottles and the pH was adjusted to 6 for FA-HCl and after shaking 1.15h, the percentage of adsorption was calculated. The percentage of adsorption decreased from 63.14% to 42.95 % as the concentration of Cu(II) solution increased. This showed that there was a competitive adsorption taking place to certain extends between the Zn(II) ions and the Cu(II) ions. The same procedure was repeated for Zn(II) ions in presence of Ni(II) ions. The adsorption percentage of Zn(II) ions was decreased to 63.14% to 41.8% in presence of Ni(II) ions and clearly shown in fig. 8.

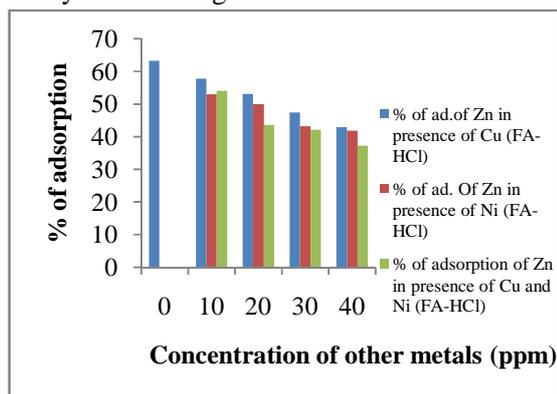


Fig. 8. Effect of Cu(II) ions and Ni(II) ions concentration onto FA-HCl. optimum conditions: pH 6, Dose 0.2g/50 mL.

The concentration of Zn(II) ion solution was kept as 100 mg/L. The concentration of Ni(II) ion solutions and Cu(II) ion solutions were varied as 10, 20, 30 and 40 mg/L. Each solution was taken

in the bottles which were added to Zn(II) solution and the pH was adjusted to 6 for FA-HCl and after shaking 1.15h, the percentage of adsorption was calculated. The percentage of adsorption decreased from 63.2% to 37.26% as the concentration of both Ni(II) ions and Cu (II) ions increased. This showed that there was a competitive adsorption taking place to certain extends between the Zn(II) ions, the Ni(II) ions and Cu(II) ions and this was shown in fig.8. The percentage of adsorption of Zn(II) in presence of other metals was decreased.

3.9. Column studies

Breakthrough capacity curves are important in process design because they are directly related to the feasibility and economics of a given process[49]. The time taken for elution is very less compared to batch mode studies where it took 50 minutes to attain equilibrium. Fig. 9 was the breakthrough curve obtained for FA-HCl, when 50 mL of Zn(II) ion solution(100 mg/L) of pH 6 for FA-HCl could be passed through a column without any Zn(II) ions being detected in the effluent when 0.2 g adsorbent used. The results obtained at 5 mL/min were calculated from the breakthrough curve. The retention time of the analyte (V_R) determined as 24.92 ml for FA-HCl corresponding to the volume respect to the half the initial concentration[50].

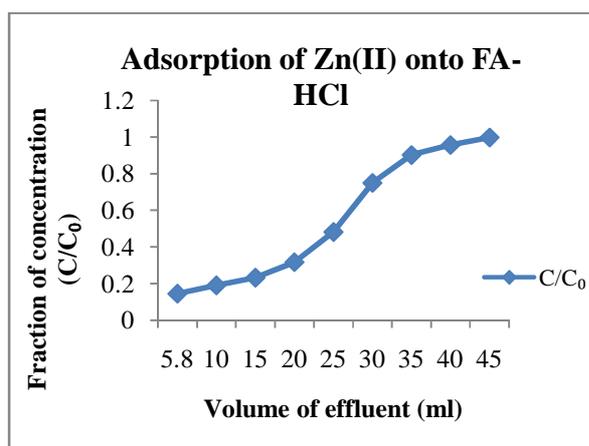


Fig. 9. Breakthrough curve for the adsorption of Zn(II) ions onto FA-HCl

$$V_R = 0.5(V_0) \quad (12)$$

The breakthrough volume (V_B) is usually defined

$$V_B = V_R - 2\sigma_v \quad (13)$$

where σ_v is the standard deviation which can be determined graphically from the breakthrough curve. σ_v is in direct relation to the efficiency of the solid phase extraction column, the number of theoretical plates (N) which can be calculated from the breakthrough curve shown in Fig. 9 using the equation:

$$N = V_R (V_R - \sigma_v) / \sigma_v^2 \quad (14)$$

The capacity factor of the solute (k), can be calculated from the fundamental equation of chromatography:

$$k = \frac{V_R}{V_B} - 1 \quad (15)$$

The recovery factor 'r' can also directly related to the breakthrough curve. The recovery factor can be calculated by using the equation:

$$r = \frac{V_M k}{V_0} \times 100 \% \quad (16)$$

where V_M represents the hold up volume of the solid phase extraction cartridge. The parameters calculated by using the above relationships for both FA-HCl were given in the Table. 3.

For the desorption experiments, several solvents [acid (0.1M HCl), base (0.1MNaOH) and water] have been used. Desorption with HCl was 30.2% which was higher than for other desorbing agents used for FA-HCl.

4. CONCLUSION

Treating the fly ash with HCl (4M) solutions, the surface was modified by dissolution and reprecipitation reactions. By dissolution of acid oxides, the specific surface area was enhanced and activated and the efficiency of heavy metal removal increases. The adsorption of Zn(II) ions was pH-dependent with maximum adsorption of 63.14% occurring at pH 6 for FA-HCl. The

adsorption data was well fitted by the Langmuir isotherm model which shows monolayer adsorption capacity of FA-HCl. Adsorption of Zn(II) ions onto FA-HCl obeyed pseudo second order kinetics. The adsorbed Zn(II) ions can be desorbed from the adsorbent using water and was found to be 23.7%. The percentage of adsorption of Zn(II) ions on FA-HCl was slightly higher in single system than binary and tertiary system which shows the competitive adsorption between the metal ions. In column studies, the removal efficiency of Zn(II) ions were 51.86% which is less compared to batch mode studies, but the time taken for adsorption was only 10 minutes. The desorption of Zn(II) ions from FA-HCl were 30.2% for the desorbing agent 0.1M HCl. For other desorbing agents (0.1M NaOH and water), the desorption of Zn(II) ions from FA-HCl were less compared to 0.1M HCl. With these conditions, we found the column study was much suitable compared to batch mode studies for removal of Zn(II) ions onto FA-HCl. The experimental results shows that this can be an up-scalable solution and represent a step in investigating the process of complex treatment of wastewater containing heavy metals.

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Tables:

diffusion	Pseudo-first-order equation		Pseudo-second-order equation			Elovich equation		Intraparticle				
	Adsorbent	$q_{e, cal}(mg/g)$	$k_{1sec}^{-1} q_{e, exp}(mg/g)$	R^2	$k_2(Lmole^{-1}sec^{-1})$	h	$q_{e, cal}(mg/g)$	R^2	$A_E (mg/g min)$	$B_E (g/min)$	R^2	$k_d (mg/g min^{1/2})$
FA-HCl	22.15	0.074	11.84	0.6399	0.059	19.56	18.15	0.9326	0.3737	43.94	0.9547	1.2
	0.9046	5.4972										

Table 1. Comparison of kinetic parameters of Zn(II) ions adsorption on FA-HCl

Isotherm model	FA-HCl	Isotherm model	FA-HCl
Langmuir		Dubinir-Radushkevich	
$Q_m (mg/g)$	11.04	$Q_m (mg/g)$	13.817
$K_a (l/mg)$	0.5877	$K (x10^{-6} mol^2/KJ^2)$	3
R^2	0.9862	$E (kJ mol^{-1})$	0.408
Freundlich		R^2	0.3451
$1/n$	0.1535	Harkin-Jura	
$K_F (mg/g)$	25.194	R^2	0.7492
R^2	0.8261	A	277.76
Tempkin		B	0.1667
$\alpha (l/g)$	2.744	q_e	13.47
$\beta (mg/l)$	2.1955	Frenkel-Halsey-Hill	
b	$1.147x10^3$	R^2	0.8261
R^2	0.861	$1/n$	0.1535
		K	$1.047x10^{21}$

Table 2: Isotherm constants and coefficients of determinations for FA-HCl.

Parameters	% of adsorption						% of desorption			
		VB (ml)	VR (ml)	VM (ml)	N	r%	HCl	Water	NaOH	K
FA-HCl	51.86	12.46	24.92	4.2	12	41.41	30.2	22.8	8.5	4.93

Table 3: The parameters calculated for FAN and FA-HCl for adsorption of Zn(II) ions