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Adsorption Studies of Fly Ash for Removing Cu(II) from Aqueous Solution

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In the present study, removal characteristics of Cu (II) ion from waste water using fly ash – a low cost adsorbent has been studied. Experiments were carried out by batch mode. The effect of contact time, initial metal ion concentration, pH, temperature and particle size of the adsorbent on adsorption have been investigated. The adsorption data have been analyzed and discussed by using Lagergren-pseudo-first-order and pseudo-second-order kinetic model. It was observed that the kinetic data follows pseudo-second-order kinetic model. Langmuir adsorption isotherm and Freundlich adsorption isotherm were applied to the equilibrium data and it was found that both models are applicable. Using modified Arrhenius equation, activation energy was calculated and found to be positive which indicates the endothermic nature of adsorption. Sticking probability of the process have been calculated and it has been observed that its value is $\ll 1$, indicating the high probability of adsorption. Thermodynamic parameters such as change in enthalpy, change in entropy and change in free energy have been calculated and it has been observed that the process is feasible, spontaneous and endothermic in nature.

Keyword: Fly ash, adsorption, Copper(II) ion, Langmuir isotherm, Freundlich isotherm, Lagergren first-order equation, pseudo-second-order equation.

1. Introduction

Copper and its compounds are used in many industries. Effluents from these industries are discharged in the nearby river which pollute the water and soil which ultimately cause problem to human health as well as environment. Various methods such as precipitation, ion-exchange, solvent extraction, membrane filtration etc. have been employed to remove heavy metals from aqueous system. Adsorption method is one of them. This method is effective, economical, easy to handle and sludge free. A large number of substances ^[1-3] have been used as adsorbent to remove heavy metals from aqueous system.

Fly ash is a waste by-product produced from a thermal power plant by burning of coal. Many studies [4-6] have shown that it may be used as an adsorbent to remove heavy metal ions from aqueous system. Different parameters such as temperature, pH, particle

size of adsorbent, contact time and initial metal ion concentration have been investigated to characterize fly ash as an adsorbent. Langmuir adsorption isotherm, Freundlich adsorption isotherm, Lagergren-pseudo-first-order kinetic model, pseudo-second-order kinetic model, modified Arrhenius equation, sticking probability and different thermodynamic parameters have been calculated and discussed.

2. Experimental Methods

2.1 Adsorbent

The fly ash used for the present study was of JSPL, a coal burning power plant of Raigarh(C.G.). After washing and drying at 105 °C it was sieved for 45 μ , 75 μ and 150 μ size. To characterize it SEM, FTIR and XRF analysis were obtained from SAIF-IIT Bombay (India).

2.2 Preparation of waste water solution: A.R. grade of CuSO_4 was used to prepare a stock solution of concentration of 500 mgL^{-1} . From this stock solution different working solutions were prepared by dilution method. For a particular solution, the pH was kept at 6.5, particle size was 45μ and temperature was 303 K.

2.3 Different parameters for investigation

For rate study, concentration of solution containing metal ion was: 100, 150, 200 and 250 mgL^{-1} . For equilibrium study it was: 25, 50, 75, 100, 125, 150, 175, 200, 225 and 250 mgL^{-1} . Different temperatures were: 303 K, 313 K and 323 K. Various pH values were: 2.0, 4.0, 6.5 and 8.0 and different particle size of fly ash were: 45μ , 75μ and 150μ .

2.4 Batch mode adsorption experiment:

In 25 mL of aqueous solution of desired concentration of Cu(II) taken in different glass bottles, 1.0 g of fly ash of desired particle size was added. The pH of the solution was adjusted using 0.1M HCl or 0.1 M NaOH as required. It was then agitated by keeping it in a shaking machine at desired temperature. After pre-determined time interval, the solution was centrifuged, filtered and the filtrate was analysed for concentration of remaining metal ion by Systronic Spectrophotometer 118 model.

To determine the amount of Cu(II) ions adsorbed (q_e) in mgg^{-1} and for percentage removal following mass balance equations^[7] were used:

$$q_e = V (C_i - C_e) / m$$

$$\text{Removal \%} = 100 (C_i - C_e) / C_i$$

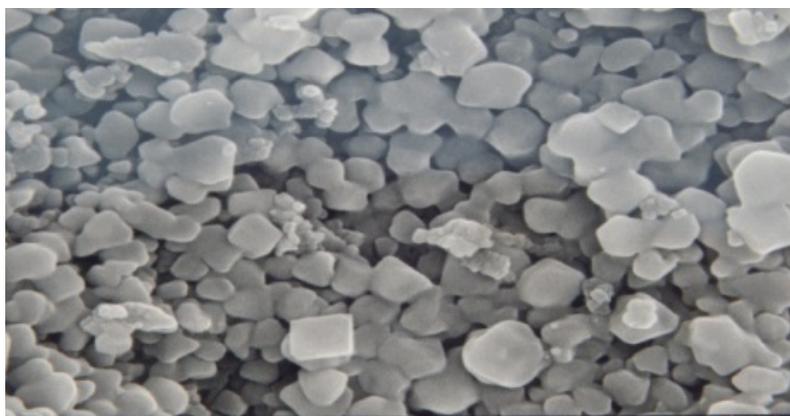


Fig 1(a): Before adsorption (45μ)

Where C_i and C_e are Cu(II) ion concentration in mgL^{-1} before and after adsorption respectively, V is the volume of adsorbate solution in litre, and m is the weight of the adsorbent in grams.

3. Result and Discussion

3.1 Characterisation of fly ash

Different fly ash contain the same basic chemical elements but in different proportions. The chemical composition (wt %) of the present fly ash sample obtained from XRF studies are given in Table 1:

Table 1: Chemical composition of the fly ash

| Constituent | wt (%) |
|-------------------------|--------|
| SiO_2 | 43.170 |
| Al_2O_3 | 13.248 |
| Fe_2O_3 | 41.198 |
| CaO | 1.090 |
| MgO | 0.727 |
| TiO_2 | 1.262 |

It is evident from the above table that SiO_2 and Al_2O_3 make up about 56.42 % of fly ash. Fe_2O_3 and CaO contents compose about 42.29%. This fly ash can be classified as class F^[8] as SiO_2 , Al_2O_3 and Fe_2O_3 content is greater than 70% and CaO content is less than 10%.

Figure-1 shows the SEM image of fly ash. It is evident that finer fly ash particles (45μ) are primarily spherical whereas the coarser particles (150μ) are mainly composed of irregular shape. Figure- 1(c) is the SEM image of fly ash (45μ) after adsorption.

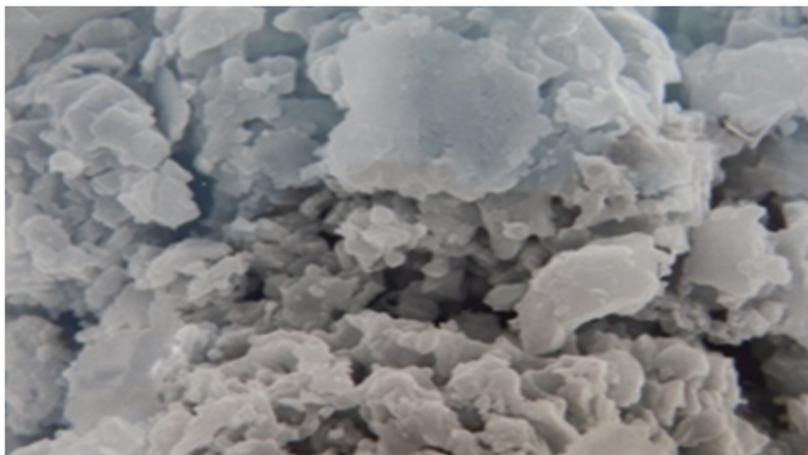


Fig 1(b): Before adsorption (150 μ)

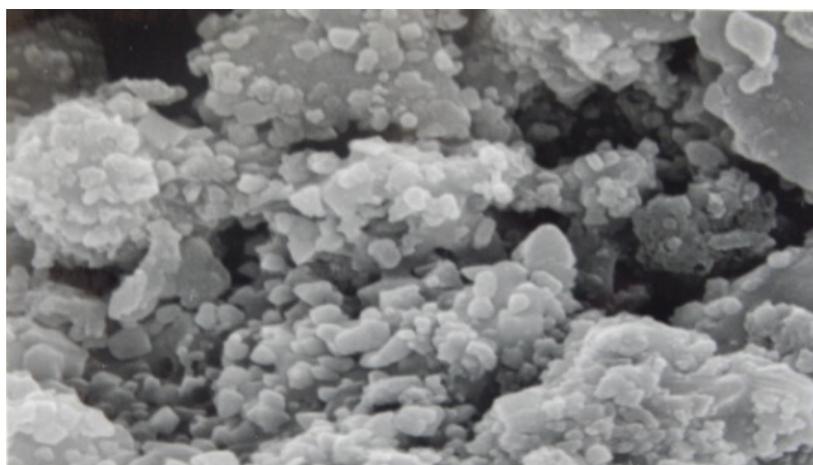


Fig 1(c): After adsorption

The FTIR spectra of fly ash before and after adsorption is shown in Figure 2. A peak around 1622.19 cm^{-1} is attributed to bending mode (δ O-H) of water molecule [8].

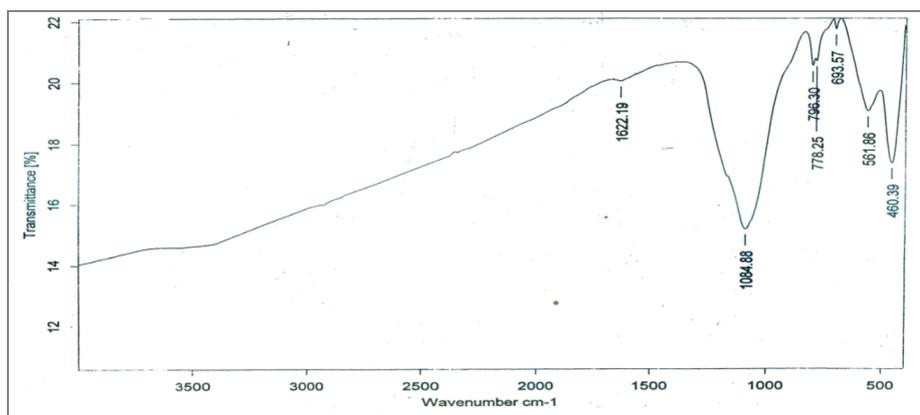


Fig 2(a): FTIR Before adsorption.

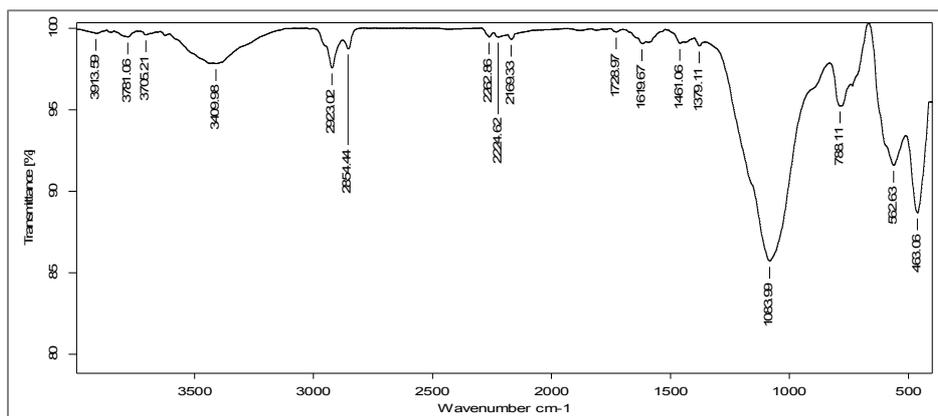


Fig 2(b): FTIR after adsorption

The main broad band at 1084.88 cm^{-1} in the fly ash before adsorption, corresponding to asymmetric stretching vibrations of Si-O-Si and Al-O-Si becomes sharper and shifts toward lower frequency 1083.99 cm^{-1} as a result of the formation of new reaction products. The bands located at 796.30 cm^{-1} and 460.39 cm^{-1} are ascribed to bending vibrations of Si-O-Si and O-Si-O bonds, implying the presence of quartz. The bands located at 693.57 cm^{-1} and 561.86 cm^{-1} indicate the presence of mullite [9]. After adsorption appearing of new bands and shifting of old bands indicate that adsorption has taken place.

3.2 Effect of initial Cu(II) ion concentration

The rate of adsorption depends on the initial concentration of the adsorbate. The effect of different initial concentration of Cu(II) ion has been shown in Figure 3 and 4. Figure 3 represents the percentage removal of Cu(II) ion vs C_i (initial metal ion concentration). The percentage removal of Cu(II) ion decreases from 74.8% at 100 mgL^{-1} to 63.04% at 250 mgL^{-1} . Figure 4 represents relationship between q_e (amount adsorbed at equilibrium) vs C_i . It can be observed that q_e increases from 1.87 mgg^{-1} at 100 mgL^{-1} to 3.94 mgg^{-1} at 250 mgL^{-1} . The reason that percentage removal decreases with increase in metal ion concentration might be due to the fact that adsorbents possess a limited number of active sites which becomes saturated at certain concentration. However, actual amount adsorbed (q_e) increases with initial metal ion concentration. The reason might be that higher concentration provides necessary driving force to overcome the mass transfer resistance of

Cu(II) ion between the aqueous phase and solid phase [10].

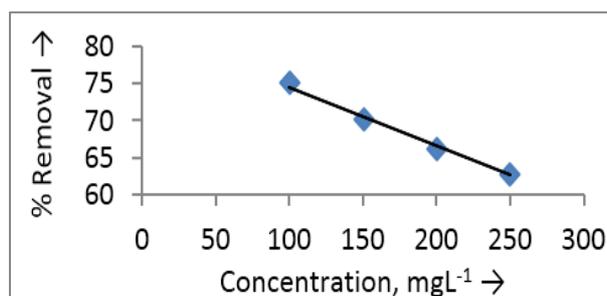


Fig 3: Initial Cu(II) conc. vs % removal

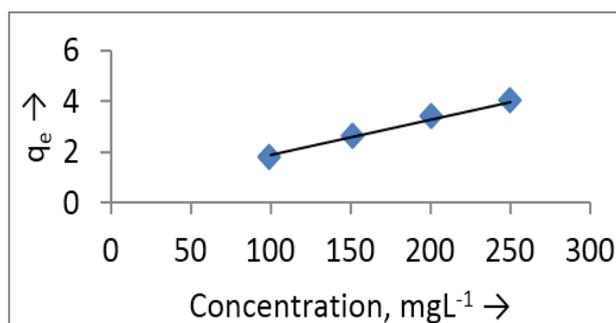


Fig 4: Initial Cu(II) conc. vs q_e

3.3 Effect of contact time

Figure-5 represents the relationship between amount adsorbed and contact time at different initial metal ion concentration. It is evident that the adsorbed amount of metal ion increases as time increases. The adsorption rate is high initially and it decreases till equilibrium is attained. The reason might be that

before adsorption the number of active sites present in the adsorbent is maximum. As adsorption progresses, the number of these active sites decreases, thereby decreasing the rate of adsorption [11-12].

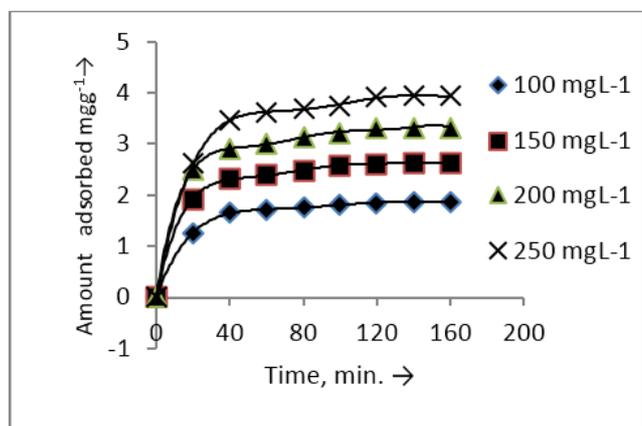


Fig 5: Effect of contact time on adsorption

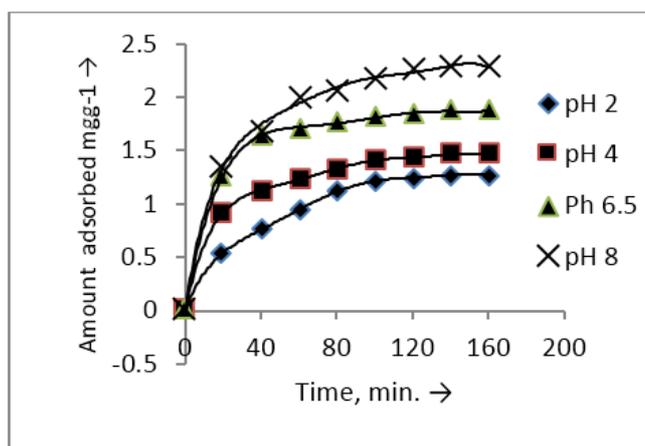


Fig 6: Effect of pH on adsorption

3.4 Effect of pH

The relationship between amount adsorbed at various pH has been shown in Figure 6. It is evident that as pH increases, the amount adsorbed increases. At pH 2.0 the amount adsorbed is 1.27 mg g^{-1} (50.8%) which increases upto 2.28 mg g^{-1} (91.2%) at pH 8.0. Studies have shown [13] that fly ash particles are positively charged at low pH and are negatively charged at high pH. As Cu(II) ions are positively charged so it is less attracted towards fly ash surface at low pH and is more attracted at higher pH due to electrostatic force of attraction.

3.5 Effect of temperature

As temperature increases the amount adsorbed also increases. Figure 7 shows this relationship. It is

evident that at 303K the amount of Cu(II) ion adsorbed is 1.87 mg g^{-1} (74.8%) which increases upto 2.21 mg g^{-1} (88.4%) at 323K. As adsorption increases with rise in temperature so it is evident that the process is endothermic. The rate constant of adsorption are 4.8×10^{-2} and 5.7×10^{-2} at 303K, and 323K respectively further supporting the endothermic nature of adsorption. The reason of more adsorption at higher temperature might be due to increase in mobility of ions and increase of pore size of the adsorbent.

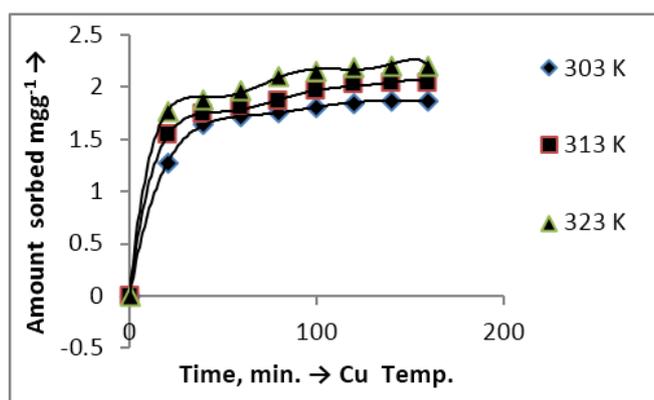


Fig 7: Effect of temperature on adsorption

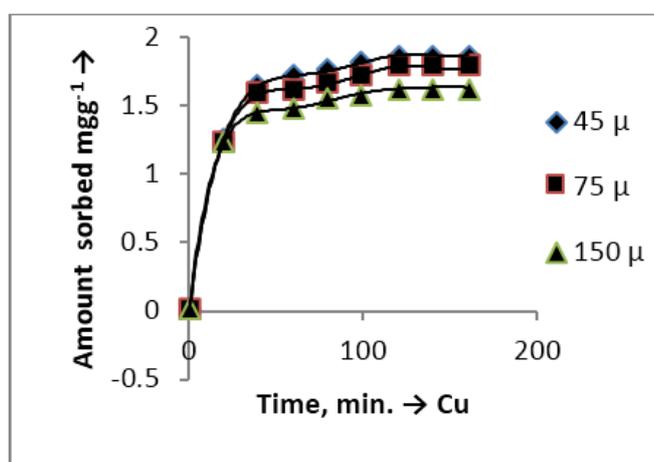


Fig 8: Effect of particle size on adsorption

3.6 Effect of particle size

The relationship between amount adsorbed vs particle size has been shown in Figure 8. It is evident that as particle size of the adsorbent decreases, the amount adsorbed increases. At 150μ , the amount adsorbed was 1.63 mg g^{-1} (65.2%) which increased upto 1.87 mg g^{-1} (74.8%) at particle size 45μ . The reason of this observation is that as particle size decreases, the surface area increases. As a result the number of

active sites increases thereby increasing the adsorption.

3.7 Adsorption Isotherm

The relationship between adsorbate concentration in liquid phase and on solid adsorbent phase at equilibrium is represented by different isotherms. The Langmuir adsorption is applicable for homogeneous surface by monolayer adsorption and its linear form is given by the following equation ^[14]:

$$C_e/q_e = 1/\phi \cdot b + C_e/\phi$$

Where C_e (mgL^{-1}) is equilibrium concentration of Cu(II) and ϕ and b are Langmuir constants. ϕ is related to adsorption capacity and b is related to adsorption energy. Relationship between C_e/q_e versus C_e have been shown in Figure 9. The graph is linear which suggests that Langmuir isotherm is applicable. ϕ and b have been calculated from slope and intercept of the straight line respectively and are given in Table- 2. It is evident from the result that the values of ϕ and b increases on increasing the temperature.

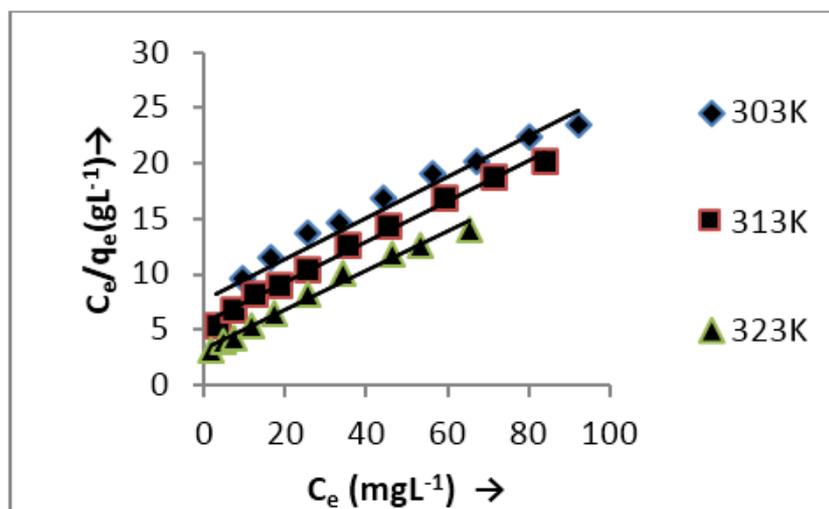


Fig 9: Langmuir isotherm for the adsorption

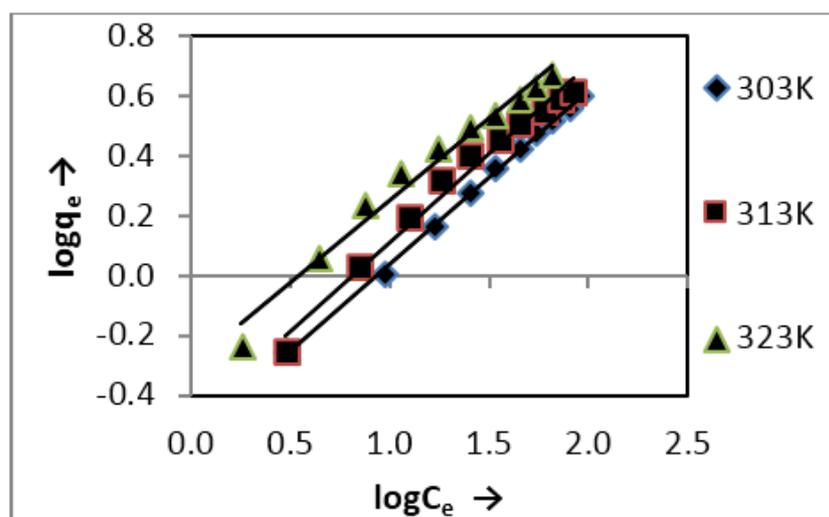


Fig 10: Freundlich isotherm for adsorption

The Freundlich equation ^[14] has also been employed which is represented as:

$$\log q_e = \log K_f + 1/n \log C_e$$

Where q_e is the amount of copper ion adsorbed (mgg^{-1}), C_e is the equilibrium concentration of copper ion in solution (mgL^{-1}) and K_f and n are constants for the

adsorption capacity and intensity of adsorption respectively. Figure 10 represents the plot of $\log q_e$ vs $\log C_e$ and values of K_f , n and R^2 (correlation coefficient) values have been obtained and given in Table-2. It is evident from comparing R^2 values obtained from Langmuir plots and Freundlich plots that both isotherms are applicable. However, the experimental data fits better in Freundlich equation.

Table 2: Adsorption isotherm constants for adsorption of Cu(II) on fly ash

| Langmuir Isotherm Results | | | | Freundlich Isotherm Results | | |
|---------------------------|-------|--------|-------|-----------------------------|-------|------|
| Temp.(K) | R^2 | ϕ | b | R^2 | K_f | n |
| 303 | 0.953 | 5.41 | 0.024 | 0.998 | 0.285 | 1.72 |
| 313 | 0.994 | 5.46 | 0.033 | 0.983 | 0.328 | 1.69 |
| 323 | 0.988 | 5.65 | 0.055 | 0.976 | 0.500 | 1.81 |

A dimensionless separation factor (R_L) is defined as ^[15]

$$R_L = 1/1+b.C_i$$

Where C_i is the initial concentration in mgL^{-1} and b is Langmuir constant (L/mg) related to adsorption energy. This factor R_L gives important information

regarding the nature of adsorption. The adsorption process is favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$. Besides $b > 0$ indicates the favourable adsorption process ^[16]. The calculated values of b and R_L have been given in Table-2 and 3 respectively. As $b > 0$ and $0 < R_L < 1$, it suggests that the process is favourable.

Table 3: Dimensionless separation factor (R_L)

| ----- C_i (mgL^{-1}) | R_L | | |
|--------------------------------------|-------|-------|-------|
| | 303 K | 313 K | 323 K |
| 25 | 0.625 | 0.548 | 0.422 |
| 50 | 0.455 | 0.377 | 0.268 |
| 75 | 0.357 | 0.288 | 0.196 |
| 100 | 0.294 | 0.233 | 0.155 |
| 125 | 0.250 | 0.195 | 0.128 |
| 150 | 0.217 | 0.168 | 0.109 |
| 175 | 0.192 | 0.148 | 0.095 |
| 200 | 0.172 | 0.132 | 0.084 |
| 225 | 0.156 | 0.119 | 0.075 |
| 250 | 0.143 | 0.108 | 0.068 |

3.8 The Lagergren first order kinetic model

Adsorption data were applied to Lagergren pseudo-first-order equation and pseudo-second-order equation to analyze rate of adsorption and possible adsorption mechanism.

The Lagergren pseudo-first-order rate equation ^[17] is represented as:

$$\log(q_e - q_t) = \log q_e - K_1.t/2.303$$

Where q_e and q_t are the amounts of Cu(II) adsorbed (mgg^{-1}) at equilibrium and at time t , respectively. K_1 is the Lagergren rate constant (min^{-1}). Plot of $\log(q_e - q_t)$ versus t has been shown in Figure 11. Slope and intercept of the straight lines obtained give the values

of q_e and k_1 respectively. These values have been given in Table- 4.

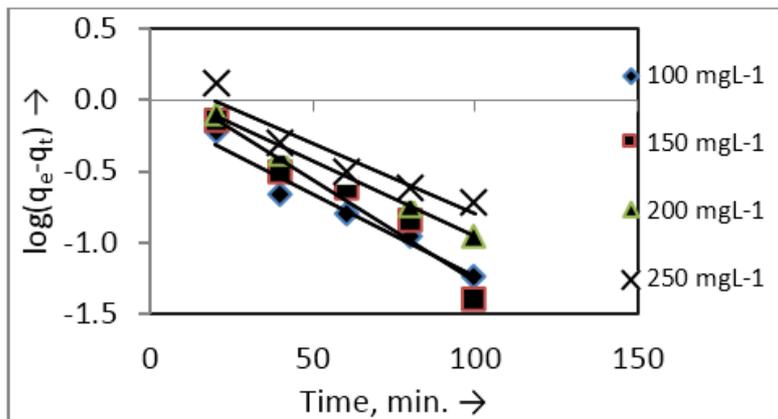


Fig 11: Lagergren first-order kinetic plot

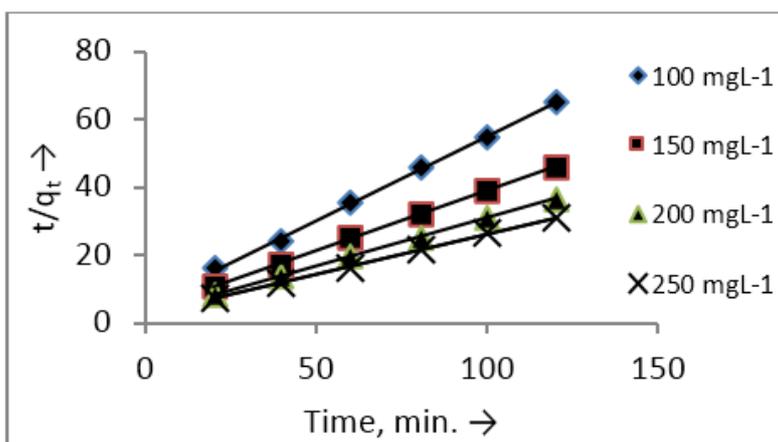


Fig 12: Pseudo-second-order kinetic plot

3.9 The pseudo-second-order kinetic model

The linear form of pseudo-second-order kinetic model [18] is represented as:

$$t/q_t = 1/K_2 \cdot q_e^2 + t/q_t$$

Where K_2 is the rate constant of second order adsorption (g/mg/min.). Plot of t/q_t versus t has been shown in Figure 12. The value of K_2 and q_e have been calculated from the slope of the graph and have been given in Table- 4.

Table 4: Kinetic parameters for adsorption of Cu(II) ion on Fly ash

| Conc mgL ⁻¹ | Lagergren first order | | | | Pseudo- second- order | | |
|------------------------|----------------------------------|------------------------------------|------------------------------------|----------------|-------------------------|------------------------------------|----------------|
| | K ₁ min ⁻¹ | q _{exp} mgg ⁻¹ | q _{cal} mgg ⁻¹ | R ² | K ₂ g/mg/min | q _{cal} mgg ⁻¹ | R ² |
| 100 | 2.53x10 ⁻² | 1.87 | 1.19 | 0.954 | 4.64x10 ⁻² | 2.01 | 0.999 |
| 150 | 3.22x10 ⁻² | 2.63 | 1.42 | 0.941 | 3.75x10 ⁻² | 2.82 | 0.999 |
| 200 | 2.30x10 ⁻² | 3.32 | 1.26 | 0.993 | 3.11x10 ⁻² | 3.53 | 0.999 |
| 250 | 2.07x10 ⁻² | 3.94 | 1.54 | 0.897 | 2.10x10 ⁻² | 4.26 | 0.998 |

It is evident from Table-4 that kinetic data fit better in pseudo-second-order kinetic model than Lagergren pseudo-first-order kinetic model as R^2 values are higher in the case of pseudo-second-order kinetic model. Moreover, $q_e(\text{cal})$ values agree better with the experimental data in the case of pseudo-second-order kinetic model.

3.10 Thermodynamic treatment of the adsorption process

Thermodynamic parameters such as free energy, enthalpy and entropy changes indicate the spontaneity and feasibility of the process and can be calculated using the equations^[19]:

$$K_c = C_s/C_e$$

$$\Delta G = -RT \ln K_c$$

$$\log K_c = \Delta S/2.303 R - \Delta H/2.303 RT$$

Where C_e is the equilibrium concentration in solution in mgL^{-1} , C_s is the equilibrium concentration on adsorbent in mgL^{-1} and K_c is the equilibrium constant. The Gibbs free energy change (ΔG) was calculated from the above equation. Slope and intercept of the plot between $\log K_c$ versus $1/T$ (not shown) gives the values of ΔH and ΔS respectively. All these calculated values have been presented in Table- 5.

Table 5: Thermodynamic parameters for adsorption of Cu(II) ion on fly ash

| Temp. K | ΔG , kJ/mol | ΔH , kJ/mol | ΔS , J/mol | E_a , kJ/mol | S^* , J K mol ⁻¹ |
|---------|---------------------|---------------------|--------------------|----------------|----------------------------------|
| 303 | -2.741 | 38.29 | 135.198 | 31.48 | 9.66×10^{-07} |
| 313 | -3.876 | | | | |
| 323 | -5.454 | | | | |

It is evident from Table 5 that ΔG values are negative which indicate the spontaneous nature of the process. As temperature increases, negative value of ΔG increases. This indicates the endothermic nature of the process which is further supported by positive value of ΔH . The positive value of ΔS indicate the affinity of the adsorbent for the Cu(II) ions.

Following modified Arrhenius type equation^[20] has been used to calculate the activation energy and sticking probability(S^*) from the experimental data.

$$\theta = (1 - C_e/C_i),$$

Where θ is surface coverage.

$$S^* = (1 - \theta)e^{-E_a/RT}$$

The sticking probability S^* is a function of the adsorbate/adsorbent system under consideration and depends on the temperature of the system. It must satisfy the condition $0 < S^* < 1$. The plot of $\ln(1-\theta)$ versus $1/T$ give straight line (not shown). The values of E_a and S^* has been calculated from slope and

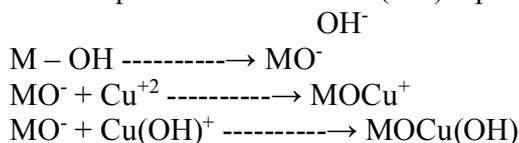
intercept of the straight line obtained and have been shown in Table-5.

The value of E_a has been found to be $31.48 \text{ kJ mol}^{-1}$ for the adsorption. Positive value of E_a also support the endothermic nature of the adsorption process. Since $S^* \ll 1$, it indicates that the probability to stick on surface of fly ash is very high^[21].

3.11 Mechanism:

Speciation^[22] of Cu(II) with varying pH has been shown in Figure 13.

It is evident that at lower pH, copper is in the form of Cu^{+2} and at higher pH it is in the form of $\text{Cu}(\text{OH})^+$. It is probable that in acidic medium positively charged surface of adsorbent does not favour the association of cationic adsorbate species. In alkaline medium negatively charged surface offers the suitable sites for the adsorption of Cu^{+2} and $\text{Cu}(\text{OH})^+$ species [23-24].



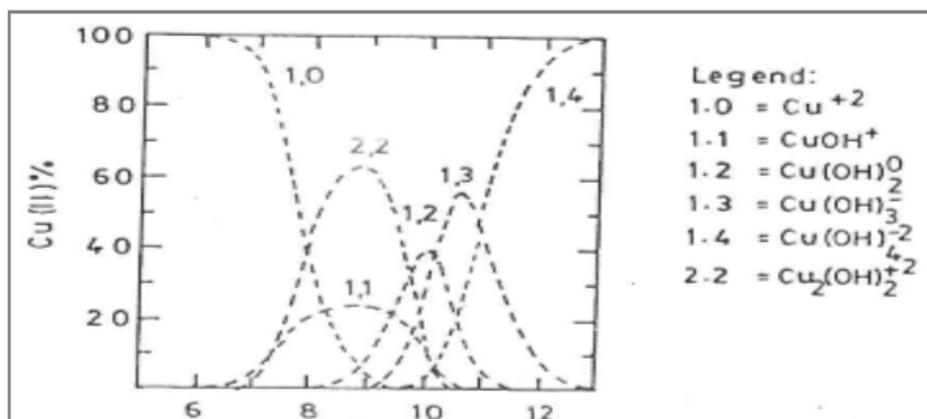


Fig 13: Speciation of Cu(II) with varying pH

4. Conclusion

It is evident that initial Cu(II) ion concentration, contact time, pH, temperature and particle size have marked effect on adsorption. The equilibrium data fits better in Freundlich adsorption isotherm. Kinetic data for adsorption follows second order rate equation. Thermodynamic parameters also favour the adsorption. It is expected that due to chemical composition, structure, more adsorption sites, cheap, availability in plenty etc. fly ash may prove to be an efficient adsorbent.

5. Acknowledgement

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