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REMOVAL OF Zn(II) AND Cu(II) HEAVY METAL IONS FROM WATER AND WASTEWATERS USING INDUSTRIAL WASTE LIKE FLY ASH AS LOW COST POTENTIAL ADSORBENT

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ABSTRACT
This study evaluated the effectiveness of fly ash collected from industry in removing Cu^{2+}. and Zn^{2+} from aqueous solutions. Batch adsorption studies were performed on the effects of temperature, adsorbent dosage, contact time, and initial metal ion concentration. The optimum contact time, adsorbent dosage and pH value of fly ash were 65 min, 1.2 g and 6.0, respectively. The adsorption of metal ions by the adsorbent conformed to the Langmuir isotherm. Kinetic studies show that the adsorption process follows a pseudo-second-order model. The calculated thermodynamic parameters indicate that the adsorption process is feasible and exothermic. These results suggest that the use of adsorbents in the removal of metal ions could provide an alternative approach to treating and exploiting these highly problematic invasive species.

KEYWORDS: Fly ash, Adsorption, Cu^{2+}, Cd^{2+}, Adsorption isotherm, pH.

INTRODUCTION
The rapid increase in human industrial activities such as agriculture, mining, and manufacturing has resulted in the discharge of heavy metal- contaminated sewage[1,2] into major water bodies. The non- biodegradability of toxic heavy metals leads to their bioaccumulation in aquatic plants and animals.[3,4] Among the toxic heavy metal pollutants, zinc and copper are commonly found in industrial wastewater. These heavy metals come from various industrial processes such as electroplating, textiles, photographic materials, paints, electroplating, batteries, paper and explosives production.[5] According to USEPA and Indian Standard the permissible limit of Cadmium was 0.005 mg/L and 0.01 mg/L respectively. Similarly, The permissible limit of Copper were 1.3 mg/L (USEPA) and 1.0 mg/L (WHO) respectively. There is a need to develop efficient and cost- effective methods for removing heavy metal contaminants from industrial wastewater. Several industrial wastewater techniques such as ion exchange, solvent extraction, chemical precipitation, and activated carbon adsorption are commonly used to remove heavy metal pollutants.[6-8] However, these techniques suffer from incomplete removal of pollutants, high reagent or energy requirements, and formation of toxic sludge.[9] Adsorption has been described as an emerging, efficient, competitive and low-cost technology due to its high efficiency and easy removal of heavy metal ions.[10] Due to the existence of various functional groups, heavy metal adsorption occurs on the surface of the adsorption material. This study evaluated the effectiveness of industrially sourced fly ash in removing Cu^{2+} and Zn^{2+} from aqueous solutions. Kinetics and isotherm studies of the adsorption of these metal ions to fly ash were investigated.

Preparation and Characterization of the Adsorbent
The physico-chemical nature of the adsorbates significantly affects the rate and extent of adsorption of pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents is quite essential in order to have a better insight into the mechanism of the adsorption process. Fly ash was obtained from Obera Thermal Power Plant, Mirzapur, UP (INDIA). They were used as such without any pretreatment just after sieving through 53µm pore size sieve (Table: 1).

Table1: Chemical analysis of Fly ash as Adsorbent.

Constituents	Percentage by weight
SiO_2	56.04
Al_2O_3	25.90
CaO	2.22
Fe_2O_3	1.26
MgO	0.94
Loss of ignition	13.64
Particle size	53µm
Mean Particle size diameter	$48x10^{-4}$ cm
Surface Area	5.77 m^2g^{-1}
Porosity	0.360
Density	3.420 gcm^{-3}

Batch Adsorption Experiments

Stock solutions (1000 mg L^{-1}) of Cu^{2+} and Zn^{2+} were prepared by dissolving appropriate amounts of nitrate precursor salts in deionized water and acidified with concentrated HNO_3 (5 mL). Batch adsorption experiments were carried out in tightly closed 250 mL Erlenmeyer flasks containing 100 mL of separate metal ion solutions. The flasks containing 1.0 g adsorbent was continuously agitated (150 rpm) at room temperature on a shaker for 120 min. The resultant solutions were filtered on What man 42 filter paper, and the supernatant liquid was analyzed on a flame atomic absorption spectrometer. The percentage of metal ion removal was calculated using equation,

$R = (Co - Ce)\,100/Co$ (1)

The adsorption efficiency was calculated according to the following equation:

$qe = (Co - Ce)\,V/M$ (2)

Where, qe is the amount (mg g^{-1}) of metal ion adsorbed by adsorbent, Co and Ce are the metal ion concentrations (mg L^{-1}) in the solution initially and after adsorption, respectively, V is the volume (L) of the solution, and m is the mass (g) of adsorbent. The influence of pH on the removal of metal ions was monitored in the pH range 2-10.pH adjustments were done using aqueous NaOH or HCl. The effects of other parameters on metal ion adsorption were monitored at different parameter ranges: temperature (25- 50)^{0}C, adsorbent dosage (0.2-2.0 g), contact time (30 -120 min), and initial metal ion concentration (20-100 mg L^{-1}).

RESULT AND DISCUSSION OF BATCH ADSORPTION STUDIES

1- Effect of pH

The pH of the solution is a key parameter affecting the surface ionization of the functional groups of the adsorbent and the speciation of metal ions.[11-12] The effect of pH on Zn^{2+} and Cu^{2+} removal is shown in Figure 1. Maximum metal ion adsorption was observed at pH 6. The addition of iron oxide particles to fly ash creates more adsorption sites through electrostatic interactions.[13] The maximum adsorption efficiencies for fly ash were 92% and 79% for Cu^{2+} and Zn^{2+}, respectively. At low pH, hydroxide ions and metal ions compete for adsorption sites.[14] As pH increases, the adsorbent surface becomes more negative, making it more accessible for metal ion adsorption. Beyond the optimum pH, a reduction in metal ion adsorption due to the formation of soluble metal ion complexes was observed.

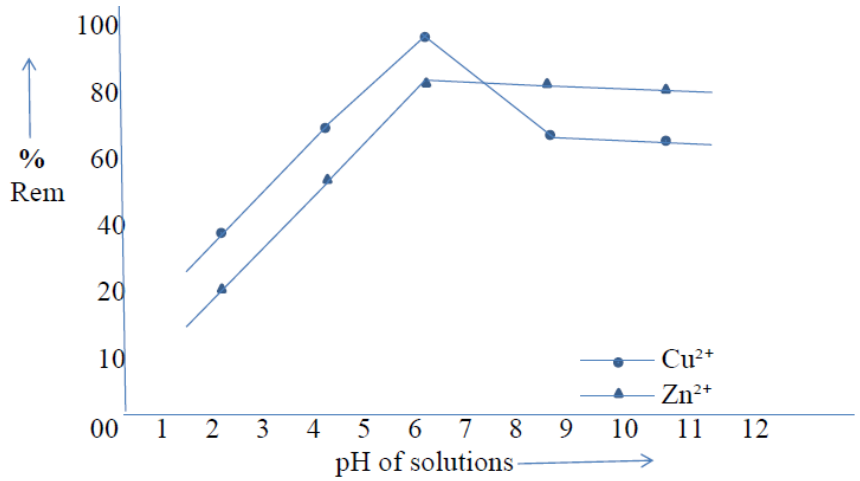

Figure 1: Effect of pH on metal ions removal using Fly ash.

2- Effect of Contact Time

The effect of contact time on metal ion adsorption is shown in Figure 2. The metal ion removal efficiency is high in the initial stage. This can be attributed to the adsorption of metal ions on the outer surface of the adsorbent and the availability of more free surface binding sites.[15] The subsequent gradual uptake of metal ions due to ion diffusion to the inner surface then plateaus within 65 min due to saturation and repulsion between the adsorbed species and the main phase.[16-17] The maximum adsorption efficiencies of fly ash for Zn^2 were 79.5% and 91.8%; and Cu^{2+}.

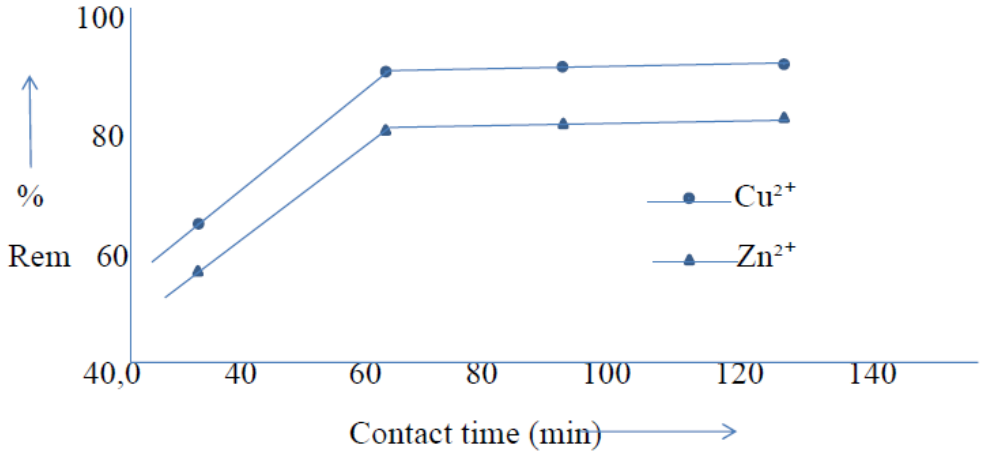

Figure 2: Effect of contact time on metal ions removal using Fly ash.

3- Effect of Initial Metal Ion Concentration

Figure: 3shows, the effect of initial metal ion concentration on adsorption. A decrease in adsorption efficiency was observed with increasing initial metal ion concentration. At low metal ion concentration most of the metal ions in solution are adsorbed onto vacant active sites of the adsorbent resulting in significantly high metal ion adsorption efficiency.[9] As the initial metal ion concentration increases active sites become saturated leaving most metal ions in solution. Similar trends were previously reported using other adsorbents.[18]

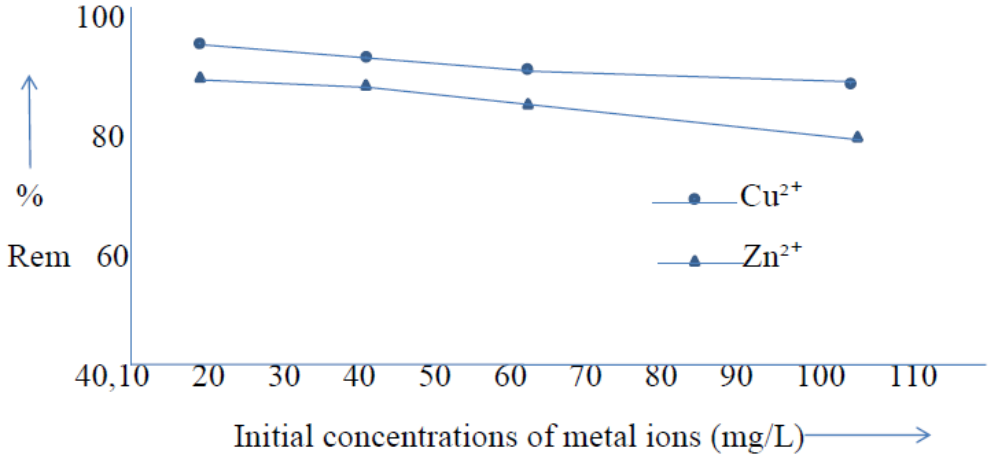

Figure 3: Effect of Initial concentrations of metal ions removal using Fly ash.

4-Effect of Adsorbent Dosage

According to Sari and Tuzen[19], adsorbent dosage determines the pollutant removal capacity for a given initial concentration. The effect of adsorbent dosage on metal ion removal is shown in Figure 4. The metal ion removal efficient increased with increasing adsorbent dosage until it leveled off at 1.2 g. Maximum metal ion removal of 79.9% and 86.0% for Zn^{2+} and Cu^{2+}, respectively, was attained using Fly ash. An increase in metal adsorption with increasing adsorbent is attributed to enhanced adsorption sites. A constant percentage for metal ion removal beyond 1.2 g was due to overcrowding of adsorbent particles as a result of excessive adsorbent dosage leading to overlapping of adsorption sites.

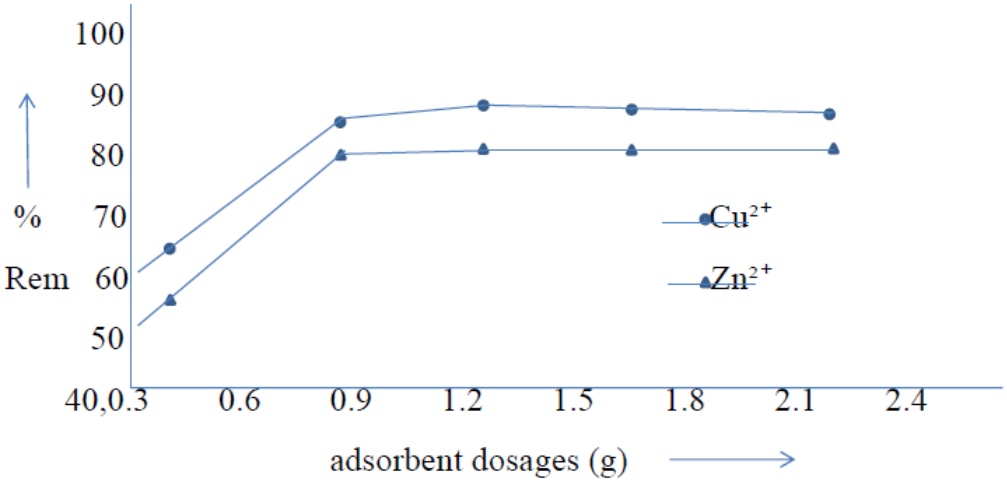

Figure 4: Effect of adsorbent dosages on metal ions removal using Fly ash.

5-Effect of Temperature

The effect of solution temperature on metal ion adsorption on the adsorbents is shown in Figure:5. The optimum temperature for metal ion adsorption was in the 25-30^{0}C range. As the temperature was raised beyond 30^{0}C metal ion adsorption decreased. This could be attributed to degrading stability of adsorption sites with increasing temperature.

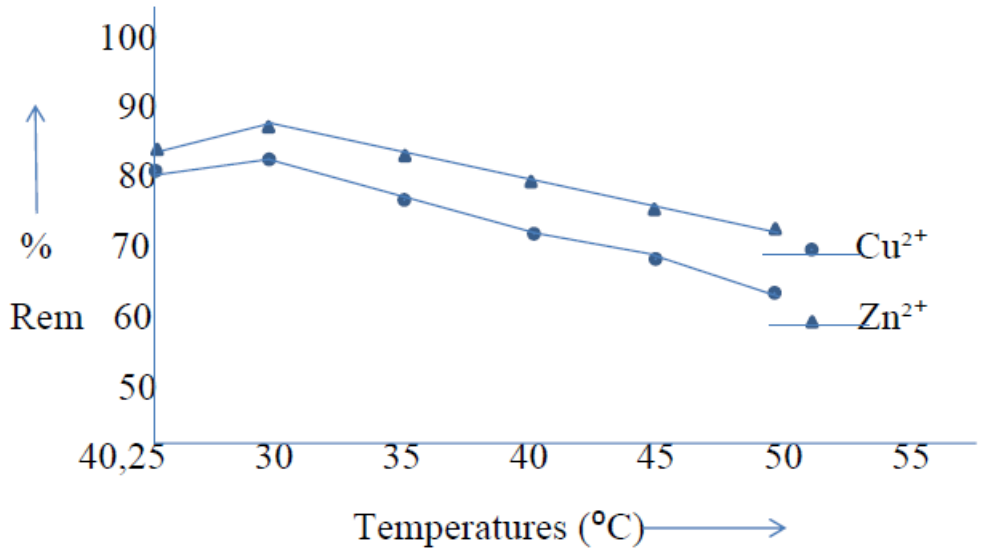

Figure 5: Effect of temperatures on metal ions removal using Fly ash.

Adsorption Isotherms

Adsorption isotherms play a fundamental role in predicting the nature of adsorbate-adsorbent interactions. Such studies help in designing adsorption systems for industrial applications since they provide data for maximum adsorption capacities of adsorbents.[20] Freundlich[21] and Langmuir[22] isotherms were applied in this study to interpret experimental data. The linearized form of the Langmuir isotherm (Figure: 6) is represented by the following equation:

$$\frac{1}{qe} = \frac{1}{K_1.qmax.Ce} + \frac{1}{qmax} \quad (3)$$

Table 2: Langmuir and Freundlich constants for the metal ions adsorption on Fly ash.

Adsorbates	Langmuir			Freundlich		
	qmax (mgg^{-1})	KL (Lmg^{-1})	R^2	KF (Lmg^{-1})	n	R^2
Cu^{2+}	3.53	5.92	0.998	3.31	1.70	0.987
Zn^{2+}	9.42	0.32	0.995	3.85	1.12	0.910

Table 3: Thermodynamic parameters derived from Vant Hoff's plots.

Temp	ΔG^0 (kJ/mol)						ΔS^0 (kJ/mol/K)	ΔH^0 (kJ/mol)
	25°C	30°C	35°C	40°C	45°C	50°C		
Adsorbates								
Cu^{2+}	-9.57	-8.04	-6.52	-4.99	-3.46	-1.94	-0.31	-100.61
Zn^{2+}	-9.32	-7.60	-5.90	-4.18	-2.46	-0.75	-0.34	-111.47

Where, qmax is the maximum adsorption capacity (mg g^{-1}), Ce (mg L^{-1}) is the equilibrium concentration, and KL is the Langmuir adsorption constant (L mg^{-1}) related to the free energy of adsorption. A plot of $1/qe$ versus $1/Ce$ produces a straight line with intercept $1/q$max and gradient 1/KL.$q$max can be used to calculate $q$max. Linearized form for Freundlich isotherm is represented as,

$$\ln qe = \ln K_F + \frac{1}{n} \ln Ce \quad (4)$$

A plot of ln qe versus ln Ce produces a straight line which is used to calculate Freundlich constants KF and n from the intercept and slope, respectively. Calculated values of Langmuir and Freundlich parameters for metal ion adsorption on Fly ash are shown in Table 2. Based on R^2 values presented, metal ion adsorption conformed more to the Langmuir isotherm.

Maximum adsorption capacities for Zn^{2+} were higher than that of Cu^{2+} due to lower ionic radius of Zn^{2+} (0.71 A^0) than Cu^{2+} (0.73 A^0). The higher charge density of Zn^{2+} enhances the attraction for the adsorbent. The constant n measures the deviation of adsorption from linearity (intensity of adsorption).The values of n greater than 1 for Zn^{2+} and Cu^{2+} ions indicate the favorable nature of adsorption.[23]

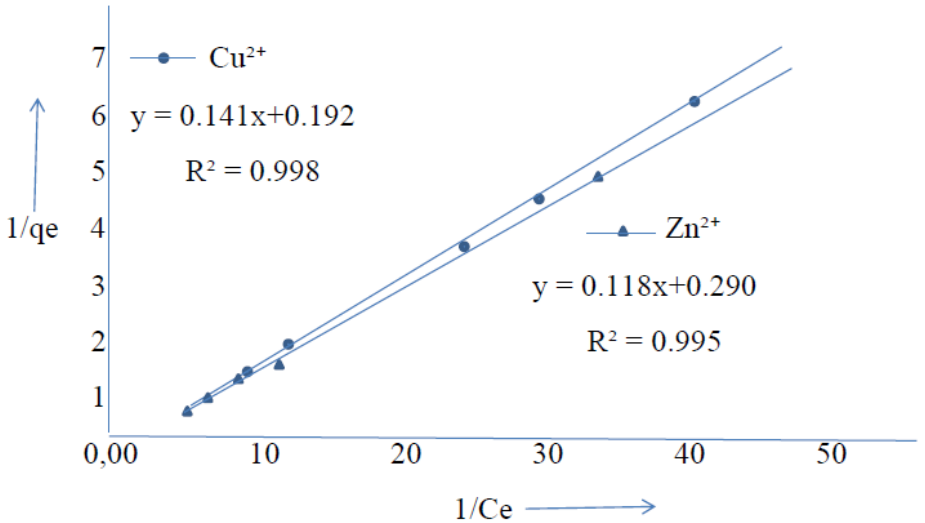

Figure 6: Langmuir isotherm for Cu^{2+} and Zn^{2+} adsorption on Fly ash. Adsorption Thermodynamics.

Thermodynamic parameters such as entropy change (ΔS), enthalpy change (ΔH) and the Gibbs free energy change (ΔG) are essential in the determination of industrial applications of adsorbents. ΔG^0 is a critical thermodynamic parameter that provides adsorbent characteristics on the adsorption process.[24] These thermodynamic parameters were calculated using the following equations:

$$K_T = \frac{qe}{Ce} \quad (5)$$

$$\ln K_T = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T.\Delta S^0 \quad (7)$$

where R is the ideal gas constant, T is temperature in Kelvins, and KT is the thermodynamic equilibrium constant. The intercept and gradient derived from the Vant Hoff's (equation 6) plot of ln KT as an inverse function of temperature were used to calculate ΔH^0 and ΔS^0 shown in Table 3. The calculated Gibbs free energy change values for the adsorption of Cu^{2+} and Zn^{2+} were all negative confirming the feasibility and spontaneity nature of the adsorption process. The negative ΔH^0 values indicate the exothermic nature of the adsorption processes. The entropy change values for metal ions adsorption were negative indicating that the adsorption process involves an associative mechanism.[25] Metal ion adsorption leads to order through the formation of an activated complex between the adsorbate and adsorbent. The negative values of ΔS^0 reflected that no significant change occurs in the internal structures of the adsorbent during adsorption.

Adsorption Kinetics

Adsorption kinetics provide essential information for determining the adsorption rate controlling mechanisms. Two frequently used integrated linearized kinetic models: Lagergren and Ho-McKay (equation 8 and 9)[26-27] were used to analyses the experimental data. The parameters qt and qe (mg g^{-1}) are the respective adsorption capacities at time, t, and equilibrium, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the Lagergren's pseudo first and Ho- McKay's second-order constants, respectively.

$$\ln (qe - qt) = \ln qe - k_1.t \quad (8)$$

$$\frac{t}{qt} = \frac{1}{k_2.q^2e} + \frac{t}{qe} \quad (9)$$

Equation (8) hypothesize an adsorption rate that is proportional to the population of vacant sites whilst (equation 9) is based on the hypothesis that the adsorption rate is closely related to the square of the population of vacant sites. The adsorption kinetic parameters are shown in Table: 4 The correlation coefficient values of the pseudo-second- order kinetic model were 0.993 and 0.998 for Zn^{2+} and Cu^{2+}, respectively. Higher and good agreement between calculated and experimental values and high correlation coefficient values show that the pseudo-second-order kinetic model conforms to the Fly ash systems. Such kinetic data show that chemisorption was the rate limiting step in the uptake of the metal ions by the adsorbents.

Table 4: First and second-order kinetic parameters for metal ions adsorption on Fly ash.

Ions	qexp (mg/g)	Pseudo first Order Kinetics Parameters			Pseudo Second Order Kinetics Parameters		
		qe (mg/g)	k_1 (min^{-1})	R^2	qe (mg/g)	k_2 (g/mgmin^{-1})	R^2
Cu^{2+}	3.25	1.41	0.09	0.598	3.24	0.05	0.998
Zn^{2+}	7.91	7.43	0.35	0.971	8.09	0.02	0.993

CONCLUSION

In this study, fly ash showed great potential in removing aqueous metal ion contaminants. This approach provides a useful way to deal with this highly problematic invasive species. The metal ion adsorption on the adsorbent corresponds to the Langmuir isotherm. The adsorption of metal ions by the adsorbent is most consistent with the second-order pseudo kinetics. Thermodynamic parameters indicate that the adsorption process is feasible, spontaneous, and exothermic. The metal ion adsorption efficiency of fly ash exceeded 80% in all studies, indicating its high reusability. This study focuses on adsorption of single metal ions from spiked solutions. The wastewater is more complex than the simulated water used in this study.

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