Est. 1984

Removal of Copper (II) from Aqueous Solutions using Chalk Powder

S. MUMTAZUDDIN[1]*, A. K. AZAD[1] and RAHILA FIRDAUS[1]

Department of Chemistry, B. R. A. Bihar University, Muzaffarpur - 842 001, India.
*Corresponding author E-mail: s_mumtazuddin@rediffmail.com

ABSTRACT

Adsorption of copper (II) from aqueous solutions on powdered chalk has been studied as a function of different parameters : contact time (t), mass of the adsorbent (w) and initial concentration (C_i) of the adsorbate. The amount of Cu (II) adsorbed increased with increased contact time and equilibrium reached at 60 minutes for powdered chalk. The minimum adsorbent dose for an optimal removal within the concentration range considered (7-30 ppm) was 1g. Maximum removal percentage was found to be 98.2. Adsorption isotherms observed were in agreement with the Langmuir adsorption isotherm. The adsorption kinetics data obtained fitted the pseudo-first order kinetics. These results showed that the powdered chalk can efficiently be used to remediate copper (II) from waste water.

Key words: Copper (II), Adsorption, Chalk powder.

INTRODUCTION

Copper is a toxic heavy metal discharged into the environment due to various industrial operations[1] and agricultural activities[2]. Anthropogenic sources of copper contamination include smelters, iron foundries, power plant stations and incinerators[3]. Copper has been found to cause stomach and intestinal distress, kidney damage and anaemia[4] and prolonged inhalation of copper containing fumes has been linked to increase in lung cancer[5]. US EPA has regulated drinking water concentration not to exceed 1.3 ppm for copper[6].

The coventional physico-chemical methods for the removal of toxic heavy metals from industrial waste water such as chemical precipitation, electroplating, membrane separation, evaporation or resin ion exchange are usually expensive and sometimes not effective. Therefore, there is a need for some alternative technique which is efficient and cost effective. The search for new technologies involving the removal of toxic metals from waste water has directed attention to biosorption and chemisorption.

In pursuit of low cost adsorbents for the removal of metal ions from aqueous solutions, our attention was drawn towards a readily available and commonly used amorphous solid material - class room chalk. We tried powdered chalk for the removal of arsenic, iron and copper from aqueous solutions for the reason that it has large surface

area and microporous character. But we got encouraging results only for copper ions.

In the present work, adsorption of copper (II) from aqueous solutions on powdered chalk was studied as a function of different parameters : contact time (t), mass of the adsorbent (w) and initial concentration (C_i) of the adsorbate. Sorption isotherms were tested for Langmuir and Fruendlich as well as for first and second order kinetic equations.

MATERIAL AND METHODS

The adsorbent, powdered chalk, was primarily heated in an oven at 105^0 C for 24 hours and cooled in a desiccator before use in the adsorption process.

Kinetics Batch Adsorption Experiments

Batch adsorption experiments were carried out at ambient temperature. The effects of contact time and mass of the adsorbents were studied by using some common kinetics and equilibrium models. The estimation of Cu (II) ion was carried out spectrophotometrically[7].

Effect of agitation time

For the determination of the effect of the agitation time, 1 g of the adsorbent was stirred with a 25 mL solution of copper (II) ions of initial concentration 15 mg/L at specific time intervals. At the end of each time, the solution was filtered rapidly and the copper (II) ion content of the filtrate determined. The difference between the initial (Ci) and the final (equilibrium) (Ce) concentrations was used to calculate the percent removal (% R) of cupric ions using equation (1):

$$\% \, R = \frac{C_i - C_e}{C_i} \times 100 \qquad ...(1)$$

Effect of the amount of adsorbent

In order to determine the effect of the amount of adsorbent, different masses of the adsorbents (0.5-3g) were treated with 25 ml solution of the copper (II) ion of initial concentration 15 mg/L.

Batch equilibrium experiments

For each run the adsorbent was mixed with 25 ml solution of cupric ion at different initial concentrations (7-30 mg/L). The suspensions were stirred for 60 minutes by using a magnetic stirrer. The amount of copper ions adsorbed per unit mass of the adsorbent at aquilibrium, q_e (mg/g) was calculated using equation (2):

$$q_e \; = \; \frac{V \times (\, C_i - C_e)}{W \times 1000} \qquad ...(2)$$

where, Ci and Ce are copper ion concentrations initially and at equilibrium respectively, V the volume of the solution (mL) and w (gm) the adsorbent mass. The equilibrium data were then fitted by using the Langmuir and the Freundlich adsorption isotherm models.

Langmuir adsorption isotherm:

One of the most common isotherm equations for modelling equilibrium data in solid-liquid systems, the Langmuir adsorption equation, is valid for monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface[8]. The general form of the Langmuir equation is :

$$q_e \; = \; \frac{q_m b C_e}{1 + b C_e} \qquad ...(3)$$

where, C_e is the equilibrium concentration of Cu^{2+} ion (g/L), q_e is the amount of Cu^{2+} ion adsorbed per unit mass of the adsorbent , b is the Langmuir adsorption constant (L/mg) and q_m is the maximum amount of adsorbate per unit mass of adsorbent to form a complete monolayer on the surface (mg/g). The linear form of this equation is as follows :

$$\frac{C_e}{q_e} \; = \; \frac{1}{b q_m} + \frac{C_e}{q_m} \qquad ...(4)$$

where,
k_a = adsorption rate constant.
k_b = desorption rate constant.

Freundlich Adsorption Isotherm

Freundlich equation is an empirical equation based on the adsorption on a heterogeneous surface.

$$q_e = k_f C_e^{1/n} \qquad ...(5)$$

where, C_e is the equilibrium concentration of copper ions (g/L) , qe is the amount of copper ions bound per gram of the adsorbent at equilibrium (mg/g) , k_f and n are the Freundlich constants related to sorption capacity and sorption intensity of the sorbent, respectively. The linear form of the Freundlich isotherm equation is:

$$\log q_e = \log k_f + \log C_e \qquad ...(6)$$

[$n = 1/n_f$: where , n_f =Adsorption affinity (dimentionless)]

Kinetic adsorption experiments

Kinetic adsorption experiments were conducted using a series of 25 mL solutions containing fixed amounts of adsorbent and cupric ions. The solutions were vigorously agitated with a magnetic stirrer for increasing time intervals. At the end of each run, the solution was filtered and the Cu^{2+} ion concentration in the filtrate was determined. This study has been carried out for two different Cu^{2+} concentration. Following kinetics models have been used to fit experimental data.

The pseudo-first order model:

The pseudo-first order equation of Lagergran is generally expressed as follows[9]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad ...(7)$$

where, q_e and q_t are the sorption capacities at equilibrium and at time, t respectively (mg.g⁻¹) and k_1 is the rate constant of pseudo-first order sorption (L.min⁻¹). Equation (7), after integration and

applying boundary conditions, t = 0 to t = t and q_t = 0 to qt = qt, becomes :

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad ...(8)$$

The pseudo-second order model:

The pseudo-second order chemisorption kinetic rate equation is expressed as [10] :

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad ...(9)$$

where, k_2 is the rate constant of pseudo-second order sorption (g.mg⁻¹.min⁻¹).
The integrated and rearranged form of equation (9) is :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad ...(10)$$

RESULTS AND DISCUSSION

Effect of agitation time

The plot of % removal of cupric ions against varying contact times are shown in figure 1. Cu^{2+} ion uptake increases with increasing agitation time within 60 minutes and then it becomes nearly constant.

Effect of the amount of adsorbent

For this experiment, different masses of adsorbents were stirred with cupric ion solution for 60 minutes. The results are depicted in figure 2. Copper (II) ion adsorption percentage increases with adsorbent mass (m) significantly upto 1 g and then becomes constant. Increase in adsorption percentage is due to the increase in available number of binding sites when the amount of adsorbent mass increases[11]. Maximum adsorption percentage is 98.2% using powdered chalk at 1g sample weight.

Table 1: Isotherm parameters for Cu²⁺ uptake from aqueous solutions

Adsorbent	Langmuir Parameters			Freundlich Parameters		
	b	q_m (mg/g)	r^2	k_f	1/n	r^2
Powdered Chalk	0.06	53.2	0.9724	0.33	0.88	0.9663

Adsorption Isotherms

Equilibrium studies were conducted with 1g of powdered chalk. These results are shown in figure 3.

Adsorption isotherm on powdered chalk is type I adsorption isotherm, characteristic of microporous adsorbent, chemical adsorption or physical adsorption limited to monolayer coverage.

Table 2: Kinetic model parameters for Cu^{2+} adsorption on powdered chalk

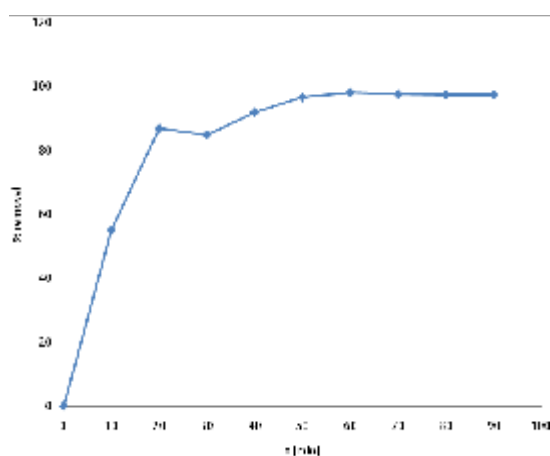| Adsorbent		Powdered Chalk	
C_i (mg.L^{-1})		17	28.5
Pseudo-first order	$k_1/10^{-2}$ min^{-1}	8.978	4.9
	q_e (mg/g)	3.9	6.1
	r^2	0.9949	0.9954
Pseudo-second order	$k_1/g.mg^{-1}.min^{-1}$	7.843 x 10^{-3}	1.083 x 10^{-3}
	q_e(mg/g)	-	-
	r^2	0.9923	0.7614

Data obtained from these studies have been tested with the Langmuir and Freundlich linearized equations. These results are summarized in table 1. As these results show, adsorption isotherm is in agreement with the Langmuir adsorption isotherm. The higher is the b value, the stronger is the adsorbate-adsorbent interaction.

**Kinetic modelling of Cu^{2+} ion adsorption**

The kinetics of the adsorption of cupric ions has been studied using two kinetics models. In order to obtain parameters related to each kinetic model, experimental data have been tested with linear

forms of these models. The straight-line plots are presented in figures 4 & 5. Parameters are given in table 2.

As evident from above results the adsorption of cupric ion on powdered chalk can be well described by the pseudo-first order kinetic model, with a correlation coefficient greater than 0.9900. The value of the rate constant decreases when initial Cu^{2+} ion concentration increases, suggesting that the adsorption mechanism of cupric ions on powdered chalk is the rate-limiting step[12].
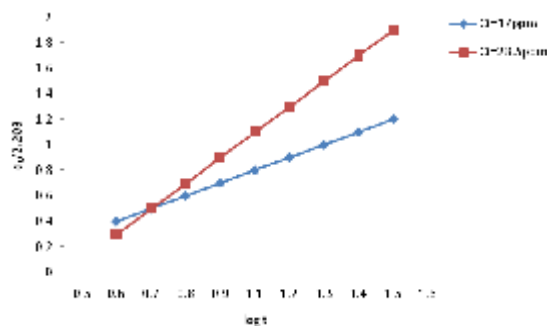

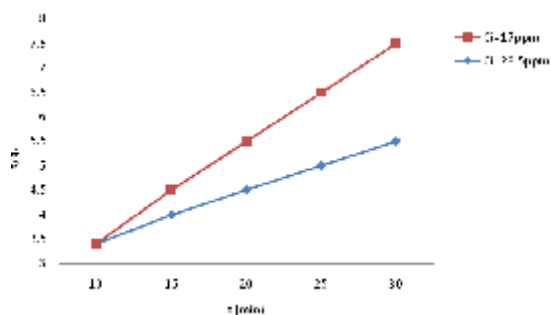**Fig. 1: Effect of agitation time on the adsorption of copper ions on powdered chalk**
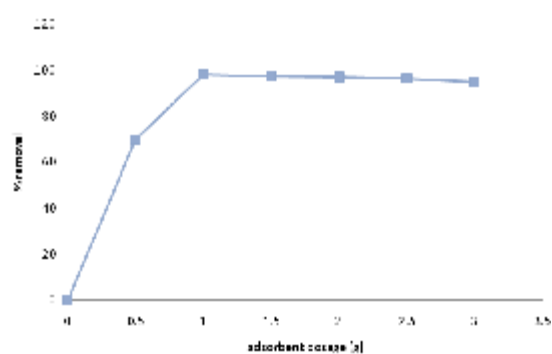
Fig. 2: Effect of adsorbent mass on Cu(II) adsorption on powdered chalk
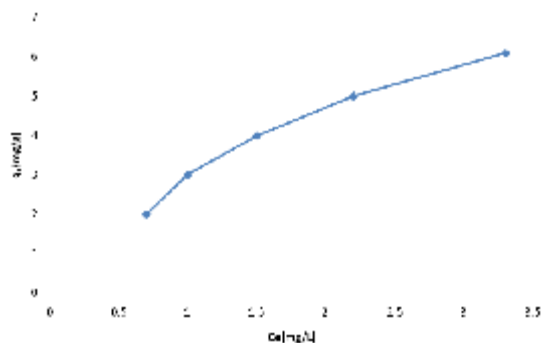
**Fig. 3: Adsorption isotherm
of Cu²⁺ on powdered chalk**

Fig. 4 : Linearized Pseudo-first order plot

Fig. 5: Linearized Pseudo-second order plot

CONCLUSION

The present investigation reveals that powdered chalk is an efficient material for the remediation of copper (II) ion contamination. Maximum removal percentage of 98.2% can be achieved. Adsorption capacity is also quite high (q_m =53.2 mg/g). Adsorbate-adsorbent interactions are also strong. Adsorption kinetics is pseudo- first order.

ACKNOWLEDGEMENTS

REFERENCES

1. Klimmek S., Stan H. J., Wilke A., Bunke G. & Buchholz R., *Environ. Sci. Technol.*, **35**: 4283-4288 (2001)**.**
2. Hawari A. H. & Mulligan C. N., *Bioresour Technol.,* **97**: 692–700 (2006).
3. Vilar V.J.P., Botelho C.M.S. & Boaventura A.A.R., *Bioresour Technol.,* **99**: 750-762 (2008).
4. Yu B., Zhang Y.,Shukla A., Shukla S. S. & Dorris K. L., *J. Hazard Mater.,* B **80**: 33-42 (2000).
5. Carson B. L., Ellis V. & McCann J. L., Toxicology and Biological Monitoring of Metals in Humans, **71,** Lewis Publishers, Chelsa, Michigan, 133 (1986).
6. Wang J., *Process Biochem.*, **37**: 847-850 (2002).
7. APHA, Standard Methods of Examination of Water and Wastewater, 19th edition, American Public Health Association, Washington DC (1996).
8. Ateesa Yazdanipour and Mona Akbari., *Orient J. Chem.*, **28**(3): (2012)
9. Langmuir I., *J. Am. Chem. Soc.*, **40**: 1361-1368 (1916).
10. Lagergran S. & Kungliga S., *Handlingar Band.*, **24(4)**: 1 (1898).
11. Ho Y. S. & Mckay E., *Can J. Chem. Eng.*, **76**: 822-827 (1998).
12. Krishnan K. A. & Anirudhan T.S., *J. Hazard. Mater.*, **92:** 161-183 (2002).
13. Kushwaha Shilpi & Sodaye Srparna P., *PETWAS.*, **33:** 617 – 623 (2008).
14. K.S. Beenakumari, *Orient J. Chem.*, **29**(1): (2013)