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Removal of Copper Ion from Synthetic Wastewater using Aloe Vera as an Adsorbent

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ABSTRACT

Biosorption is a cost-effective technology for the removal of soluble heavy metals from aqueous solution. In the present investigation, Aloe Vera has been used as an adsorbent for removal of heavy metal copper from synthetic aqueous solution of copper sulphate by biosorption using batch process. Aloe Vera for copper ion removal was investigated as a function of pH, dose, initial concentration, contact time and temperature. The kinetics, isotherms and thermodynamics were also studied for this batch study.

Keywords: Heavy metals, copper ion, Adsorption, isotherms, kinetics

INTRODUCTION

The various industrial activities such as metal plating, mining, painting, wire drawing, batteries and printed circuit board manufacturing, as well as agricultural sources where fertilizers and fungicidal sprays discharge different heavy metals into the water bodies which results in polluting the surface and ground water. The heavy metals released in to the water bodies are copper, zinc, lead, chromium, cadmium, etc, considered as toxic pollutants [1-2]. Copper ions (Cu^{2+}) are water-soluble, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, they are poisonous to higher organisms, at lower concentrations it is an essential trace nutrient to all higher plant and animal life. The main areas where copper is found in animals are tissues, liver, muscle and bone. Excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death. A variety of suitable methods can be used for the removal of metal pollutants from such liquid wastes, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption. Ion exchange and adsorption are the most common and effective processes for the removal of heavy metal ions [3-4]. From last few decades, biosorption process has emerged as a cost effective and efficient alternative for water and wastewater treatment utilizing naturally occurring and agricultural waste materials as biosorbents as these are cheaper, renewable and abundantly available [5,6]. Aloe Vera is a cost effective adsorbent for removal of copper (II) ions. [3] studied removal of pb from wastewater by Aloe Vera powder and maximum capacity was observed at pH 4.5. The experimental data gave good fits with both Langmuir and Freundlich isotherms. [4] investigate the chromium adsorption from aqueous solution by Aloe Vera and this study showed that adsorption equilibrium after 180 minute. Higher chromium adsorption was observed at lower pH and maximum chromium removal 60 % obtained at pH of 2. In this work removal of copper (II) ions from wastewater by Aloe Vera has been studied using batch adsorption technique. The adsorption equilibrium was determined as a function of contact time, initial concentration, adsorbent dose, pH and temperature. Adsorption isotherms of copper (II) on adsorbent were determined and correlated with common isotherms equation such as Langmuir, Freundlich and Temkin models. The kinetics and the factors controlling the adsorption process were also studied and thermodynamics parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy change (ΔS°) for the adsorption of copper (II) were computed to predict the nature of adsorption process.

MATERIALS

Adsorbent

The Aloe Vera leaves were collected from nearby area and washed several times with water to remove dust and extra undesired impurities and cut into small pieces followed by gel and colour removal. The leaves were dried and grinded using domestic grinder and sieved using standard sieve to separate powder with 0.2-0.3µm.

Copper Sulphate Stock Solution

Stock solution of 1000 ppm of copper(II) was prepared by dissolving 3.92gm copper sulphate into distilled water. This stock was diluted as per the requirement by distilled water for experiment as well as analysis.

METHODOLOGY

Analysis and Measurement

Copper ion in the solution was analysed as per standard method at wavelength 324.6nm using Atomic Absorption Spectrophotometer model 4141 make EC Electronic Corporation of India Limited. pH of solution was analysed using pH meter model CL 120. The pH of the mixture was adjusted by adding small amount of 0.1M HCl and 0.1M NaOH solution.

Kinetics Study

The batch experiments were carried out in 250ml borosil conical flasks with cap, in which 0.5gm of the Aloe Vera powder and 100ml of copper solution were added. The flasks were then placed in an orbital incubator shaker (Metrex Scientific Instruments private limited) at 150 rpm, at temperature 25˚C and at pH 7 for 30min-180min time period. After agitation solution was filtered with Whatman filter paper and then filtrate was analysed for unabsorbed copper (II) ions.

The amount of copper (II) adsorbed per unit mass of the adsorbent was determined by using the equation (1) -

$$q = \frac{(C0-Ce)}{m}V \qquad (1)$$

Where C_0 and C_e are copper (II) concentration (mg/l) in solution initially and any time (t). V is solution volume taken in the flask and m is the weight of adsorbent used. The percentage removal was calculated using equation (2)

$$\%\ \text{removal} = \frac{(C0-Ce)}{C0} * 100 \qquad (2)$$

Equilibrium Study

The batch experiments were carried out in 250ml borosil conical flasks with cap, in which a determined amount 0.5gm of the Aloe Vera powder and 100ml (20-70ppm) of copper solution were added. The pH inside the flasks was adjusted by adding small amount of 0.1M HCl and 0.1M NaOH solution. The flasks were then placed in an orbital incubator shaker at 150 rpm, at temperature 25˚C and at 7 pH for 120min time period. After agitation the flasks solution was filtered with Whatman filter paper and then filtrate was analysed for unabsorbed copper (II) ions. The amount of copper (II) adsorbed per unit mass of the adsorbent was determined by using equation (1) and the percentage removal was found from the equation (2).

RESULT AND DISCUSSION

Effect of Contact Time

In adsorption contact time is an important parameter and it helps in the designing of adsorption system. Hence in this study effect of contact time on percentage removal of copper ion from the solution was study. This study was done at 298 K and pH 7 is shown in Fig.1. from the results it can be seen that at start percentage copper ion removal increases rapidly and then became constant after 120 min of contact time. Hence in all for further studies the contact time upto 120 min was used. The increase in percent removal efficiency may be due to existence of abundant vacant active adsorption sites within adsorbent. All these adsorbent sites get saturated percent copper ion become constant [5-6].

Effect of Adsorbent Dose

One of the parameters that strongly affect the adsorption process in the aqueous solution is the adsorbent dose. Hence in this study effect of adsorbent dose on percentage copper ion removal from the solution was study. The result of the experiments with varying adsorbent dose 0.5-3.0 gm is presented in Fig.2. Percentage copper ion removal increases rapidly and then became constant as more and more of the Aloe Vera powder added. The adsorption increased from 46%-52% when the adsorbent amount was increased from 0.5-2gm then adsorption decreased from 52%-51% when the adsorbent amount was increased from 2-3gm. Increasing the amount of the Aloe Vera powder makes a large number of site available leading to an increase in adsorption and All these adsorbent sites get saturated percentage copper ion removal become constant [5].

Effect of Initial Concentration

The mechanism of the metal adsorption from an aqueous solution is dependent on the initial concentration in the solution. Effect of initial concentration of copper (II) on percentage removal at 298 K and pH 7 was studied. The results are shown in Fig.3. from the results it can be seen that at start percentage copper ion removal decreases rapidly when copper concentration was added. Fig.3 show that at low concentration of ion absorption is very high as well as concentration increases copper ion percentage removal decreases from 75% -53%. The effect of initial concentration on copper (II) adsorption capacity 0.753mg/g and removal efficiency 75.3% was achieved in 20ppm. The percentage copper ion removal decrease with increasing the copper ion initial concentration 20-70ppm because of all the active sites was filled of Aloe Vera powder [7].

Effect of pH

pH is one of the important parameter because of adsorbent have surface charge density as well as metallic ions also have charge and both charge depends on the pH. The effect of pH on adsorption of copper (II) ion on Aloe Vera powder was studied at 298 K, 20ppm and by varying pH from 4 to 9. Hence in this study effect of pH on percentage copper ion removal from the solution was study. The results are shown in Fig.4. from the results it can be seen that at start percentage copper ion decreases rapidly when pH was added. Fig.4 show as pH increased percentage copper removal slightly increased and then decreased. The effect of pH on copper (II) adsorption capacity and removal efficiency 0.9286mg/g and 92.86% was achieved at pH 5. At lower pH, the solution contains high concentration of H^+ ions which were characterized by high mobility and compete with the metal ions for the active sites on the Aloe Vera powder. With increase pH the concentration of H^+ ions decreased and decreased the % removal [8].

Effect of Temperature

In the present study effect of temperature on percentage copper ion removal from the solution was study. The percentage removal was increases with temperature as shown in Fig 5. This experiment was studied at different temperature 25˚C, 35˚C and 45˚C with varying contact time 30 to 180 minute. The effect of temperature on copper (II) adsorption capacity and removal efficiency 0.9646mg/g and 96.4% was achieved in temperature 45˚C.

Adsorption Isotherms

Adsorption of copper (II) ions was studied for determining the adsorption capacity of Aloe Vera by using taking equilibrium data. For this studied initial concentration was varying in the range of 20ppm to 70ppm. The equilibrium data was analyzed using different adsorption isotherms. In the present work equilibrium data has been analyzed using model isotherms as shown in Table 1 such as Langmuir, Freundlich and Temkin isotherm.

Table -1 Adsorption Isotherms Models

Isotherm	Equations	References	
Langmuir	$\frac{1}{qe} = \frac{1}{kL*qmax*Ce} + \frac{1}{qmax}$	Neto *et al*, 2011	(3)
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	Neto *et al*, 2011	(4)
Temkin	$q_e = \frac{RT}{bT} \ln(K_T) + \frac{RT}{bT} \ln(C_e)$	Neto *et al*, 2011	(5)

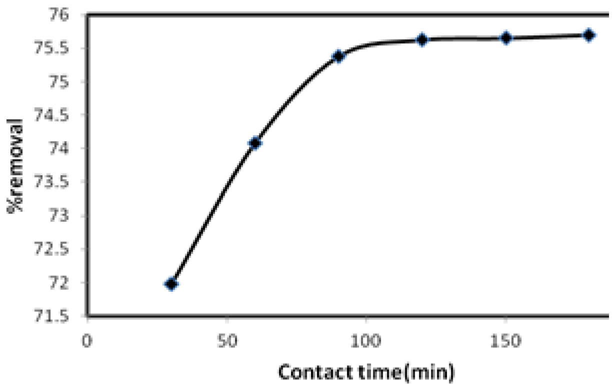

Fig. 1 Effect of contact time on removal of copper(II) by Aloe Vera powder

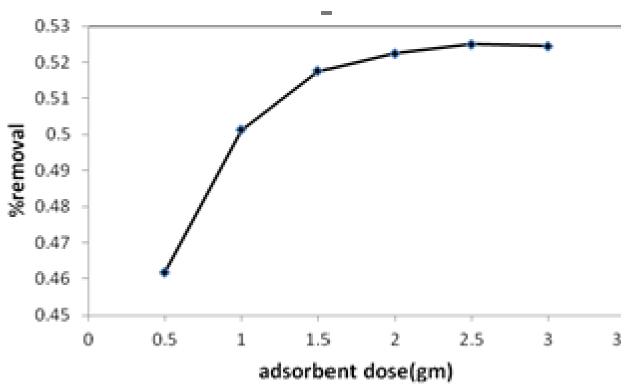

Fig. 2 Effect of adsorbents dose on removal of copper(II) by Aloe Vera powder

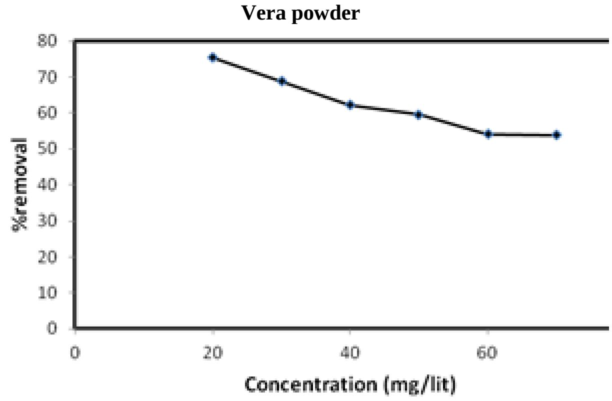

Fig. 3 Effect of initial concentration on removal of copper(II) by Aloe Vera powder

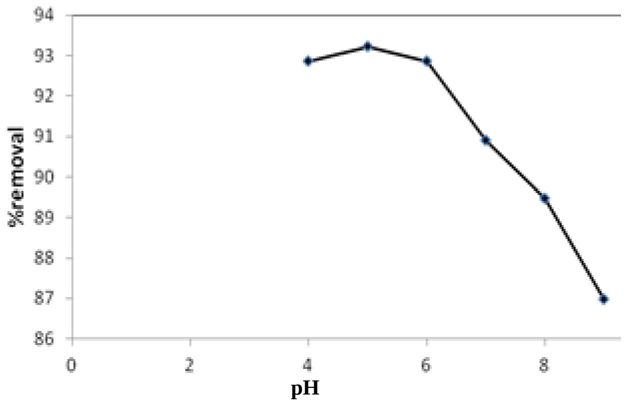

Fig. 4 Effect of pH on removal of copper(II) by Aloe Vera powder

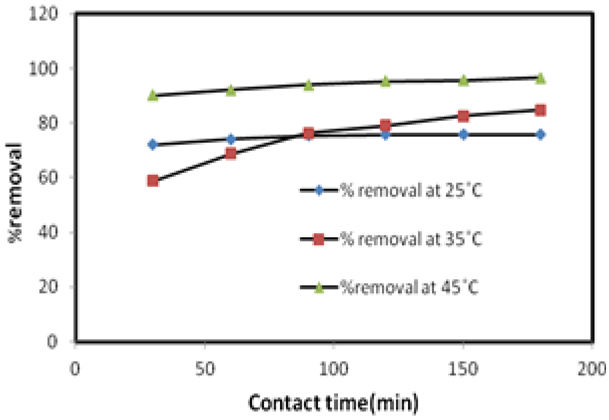

Fig. 5 Effect of pH on removal of copper(II) by Aloe Vera powder

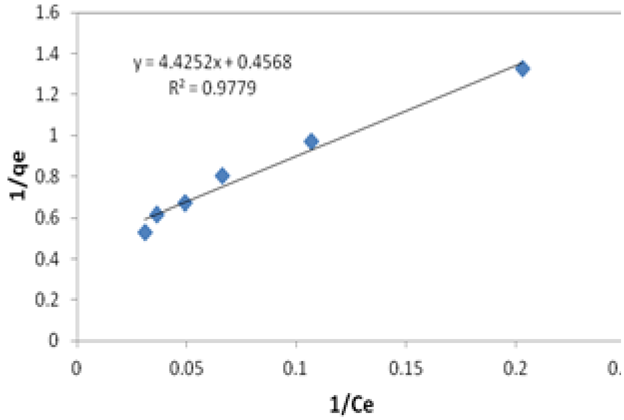

Fig. 6 Linear plot of Langmuir isotherm

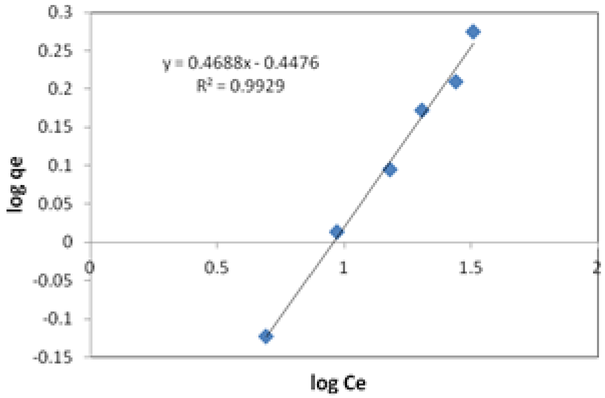

Fig. 7 Linear plot of Freundlich isotherm

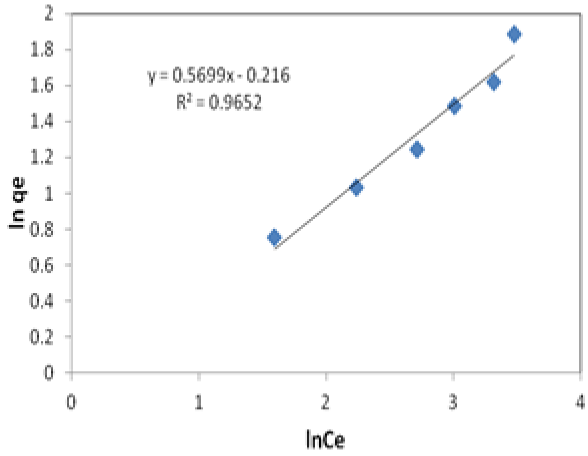

Fig. 8 Linear plot of Temkin isotherm

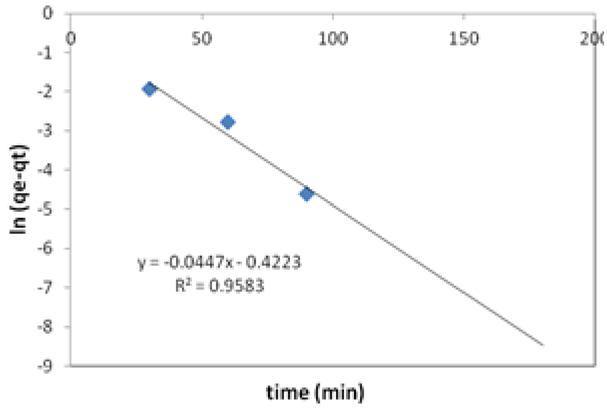

Fig. 9 Linear plot of Pseudo first order

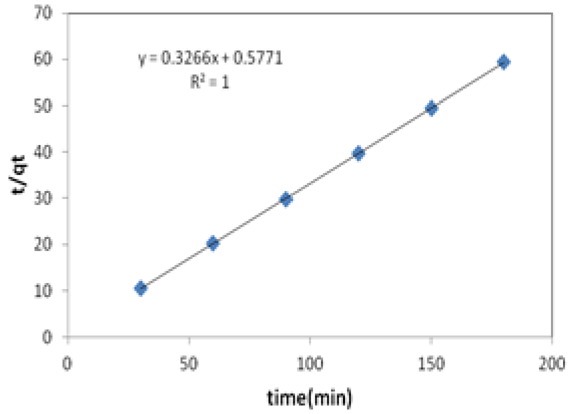

Fig. 10 Linear plot of Pseudo second order

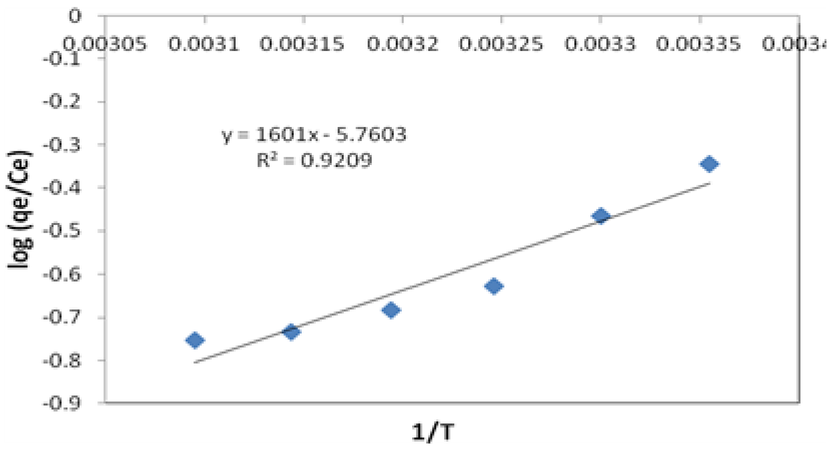

Fig. 11 Linear plot of log(q_e/C_e) VS 1/T

Langmuir Isotherm

This model is based on the assumption that maximum adsorption gives the saturated monolayer of solute on the adsorbent surface [7-8]. This isotherm model plotted between 1/q_e versus 1/C_e using equation 3 and result are shown in Fig.6. For determine the adsorption process is favourable or not so Langmuir isotherm define a term R_L [Pandey *et al*, 2015] [Neto *et al*, 2012] [weber 1974] know as separation factor also known as dimensionless equilibrium parameters. This separation factor defines as –

$$R_L = \frac{1}{1+KLC0} \quad (6)$$

This R_L given the information as absorption process is irreversible (R_L = 0), favourable (0<R_L>1), linear favourable (R_L =1) or unfavourable (R_L>1). The R_L values were found in all the experiment system in the range 0 to 1. This adsorption process is favourable.

Freundlich Isotherm

Freundlich model described heterogeneous system [10]. Fig.7 was plotted between log qe versus log C_e using equation 4.

Temkin Isotherm

Temkin isotherm model plotted between q_e versus ln C_e using equation 5. Fig. 8 shows linear plot between qe VS ln C_e. Correlation coefficient and constants of the isotherm models are given in Table -2. The experimental results fit best with the Langmuir isotherm.

Adsorption Kinetics

Study of adsorption kinetics describe the required time period for equilibrium achieved. Parameters of adsorption kinetics given the information for determine the adsorption rate as well as adsorption mechanism which are used for design the system [11]. Various kinetics models are used for analyzed the adsorption data such as pseudo first order, pseudo second order given below in Table 3.

The rate parameters calculated by plotting above equations 6 and equation 7. Pseudo first order model plotted between log (q_e-q_t) versus time period t with slop k_1 and intercept log (q_e) as shown Fig.9 and Pseudo second order model plotted between t/q_t versus t with slop 1/q_e and intercept $1/k_2q_e^2$ as shown Fig.10. Calculated adsorption kinetics rate parameters are shown in Table 4.

Table -2 Adsorption Isotherm Parameters

Adsorption Isotherms	Parameters		
Langmuir isotherm	q_{max}(mg/g) - 2.27	K_L(L/mg) - 10.31	R^2 - 0.977
Freundlich isotherm	N - 2.1	K_F(mg/g) - 0.635	R^2 - 0.992
Temkin isotherm	b(J/mol) - 4427.3	K_T(L/g) - 2.27	R^2 - 0.993

Table -3 Adsorption Kinetics Models

Adsorption kinetics models	Mathematical Models	References
Pseudo first order model	log (q_e-q_t) = log(q_e) - k_1*t (6)	[7-8]
Pseudo second order model	$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe}$ (7)	[7-8]

Table -4 Adsorption Kinetics Parameters

Adsorption kinetics models	**Parameters**		
First order kinetics model	k_1 (min^{-1}) - 0.044	q_e (mg/g) - 0.655	R^2 - 0.958

Second order kinetics model	k_2 (g/mg.min) - 0.189	q_e(mg/g) - 3.026	R^2 -1

Table 5- Thermodynamics Parameters

Temperatures (K)	ΔGº (kJ/mol)	ΔHº (kJ/mole)	ΔSº (KJ/mol)
298	63.42		
303	63.97		
308	64.52	30.56	-0.11028
313	65.07		
318	65.62		
323	66.18		

Thermodynamics Parameters

Gibbs energy (ΔGº), enthalpy of adsorption (ΔHº) and entropy of adsorption (ΔSº) are thermodynamics parameters for adsorption process. These parameters are determined by adsorption experiment at six different temperatures and using following equations.

$$\log (q_e/C_e) = -\Delta H/2.303RT + \Delta S/2.303R \quad (8)$$

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

The value of ΔHº and ΔSº were determined from the slop and intercept of the linear plot of log (q_e/C_e) versus 1/T as shown in Fig.11. Where q_e/C_e is called adsorption affinity and R 0.008314J/molK. Table 5 described the value of gibbs energy, enthalpy and entropy and these values are calculated by equation 8 and 9.

CONCLUSION

From this study it can be concluded that Aloe Vera is a good adsorbent for the removal of heavy metal copper (II) from the wastewater. For copper (II) ion removal adsorption process is used for easy operation and simplicity in design. Significant data were generated for removal of copper ion and data give best result for remove the copper from waste water. For copper removal the optimum condition comes out contact time 2 hour, initial concentration 20ppm, adsorbent dose 2gm, pH 5 and temperature 45˚C. Langmuir isotherm model is the best fit for the removal of copper ion from the waste water. The adsorption process is endothermic and could be best described by the pseudo second order kinetics models.

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