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Removal and Recovery of Copper Ions using Chitosan as an Adsorbent

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ABSTRACT

Removal and recovery of copper ions using chitosan as adsorbent was carried out using batch adsorption process. The various parameters viz., pH, contact time, adsorbent dosage, particle size and concentration were optimized to get effective removal of Cu (II) ions. Maximum removal (99.16%) of copper ions (0.01M) was observed at pH5, contact time 90min, adsorbent dosage 0.5g and particle size 600μm.The thermodynamics of adsorption was studied by varying the temperature between30-60℃. From these studies, it was revealed that adsorption of Cu (II) ions on chitosan was spontaneous and endothermic in nature. The adsorption process followed Freundlich, D-R and Temkin isotherms and obeys pseudo first order kinetics. Recovery of Cu (II) ions was found to be 84.87% using 0.1M NaOH as an eluent. The study revealed that chitosan is a potential adsorbent for removal of Cu (II) ions.

Keywords: Chitosan; Adsorption; copper ions; Thermodynamics; Adsorption isotherm; Kinetics; Desorption.

INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substance in aquatic environment. Heavy metals are one of the most toxic types of water pollutants. At least 20 metals are considered to be toxic and approximately half of these metals are emitted to the environment in quantities that are risky to the surrounding, and to the human health [1]. Industrial wastewater contains higher amount of heavy metals that can pollute the water when it is discharged to the nature. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Hence, treatment of industrial wastewater containing soluble heavy metals has become essential. Copper is one of the most widely used heavy metal. It is mainly employed in electrical and electroplating industries in large amount which is toxic to living organisms [2]. Water polluted with Cu (II) ions affect the human health and leads to anaemia, it also affect liver, kidney pancreas, and stomach, and causes intestinal irritation and Wilson's disease [3]. Many treatment processes that have been used to remove heavy metals from wastewater include precipitation, coagulation, ion exchange, electro dialysis, membrane filtration, flotation, reverse osmosis and adsorption [4]. Among this adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness. Different type of adsorbents have been used by many workers such as kaolinite and montmorillonite [5], natural jordian zeolite [6], granular activated carbon and activated clay [7], activated alumina [8], titanates nanoflowers [9], activated sludge [10], calcium alginate beads [11], fly ash [12], coconut husk [13], *couroupita guianensis* leaves [14]. In the present study, we have used chitosan for the removal of heavy metal ions from its aqueous solution. Chitosan is low cost adsorbent which is biodegradable, biocompatible polymer and it is produced by deacetylation of chitin [15-17].

MATERIALS AND METHODS

Materials: Chitosan was purchased from Otto Company with degree of deacetylation of 80%. All other chemicals like copper sulphate, sulphuric acid and sodium hydroxide were of analytical grade. The aqueous solutions were prepared in distilled water.

Characterization of the adsorbent: Chitosan was characterised before and after adsorption using different techniques. The IR spectrum of Chitosan sorbent before and after adsorption was recorded using FTIR spectrophotometer (Shimadzu 8400) in the range of 4000-400 cm^{-1} using KBr disk for reference. Morphological characteristic of adsorbents was studied by Field Emission Scanning Electron Microscopy (FET Nova nano SEM-450). The energy dispersive spectrum X-ray (Brouker SLASH-6I30)) detector measures the number of emitted X-ray versus their energy. A spectrum of the energy versus relative counts of the detected X-ray is obtained and evaluated for qualitative and quantitative determination of the elements present in sample.

Batch adsorption process: The removal of copper ions was carried out by batch adsorption process. In order to get effective removal of Cu (II) ions, various parameters viz; pH, contact time, adsorbent dosage, particle size and concentration were determined. Each time one of the parameters is varied and others are kept constant. To begin with experiment was carried out using 25 mL of 0.01M Cu(II) solution at 27°C adsorbent dose- 0.5 g and contact time-30 min. Solution was continuously stirred on magnetic stirrer, and the equilibrium solution was centrifuged and supernatant solution was analysed for concentration of Cu(II) ions using UV- Visible spectrophotometer. The percentage adsorption was determined using the equation:

$$\%\,Adsorption = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

Where C_o is the initial copper ions concentration (g L^{-1}); C_e is the copper ions concentration in aqueous solution (g L^{-1}) after adsorption.

Desorption of Cu(II) ions: Chitosan loaded with copper ions at optimized conditions was treated with various volumes of (4- 20 ml) 0.1M NaOH with contact time 90 min. Concentration of desorbed copper ions was measured by using UV- Visible spectrophotometer. % Recovery of Cu(II) ions calculated using the following equation:

$$\%\,Desorption = \left(\frac{C_d}{C_a}\right) \times 100 \qquad (2)$$

Where, C_d is amount of metal desorbed and C_a is amount of metal adsorbed.

RESULTS AND DISCUSSION

Optimization of various parameters

Effect of pH: pH of the solution was varied between3-7 and the results are shown in fig.1

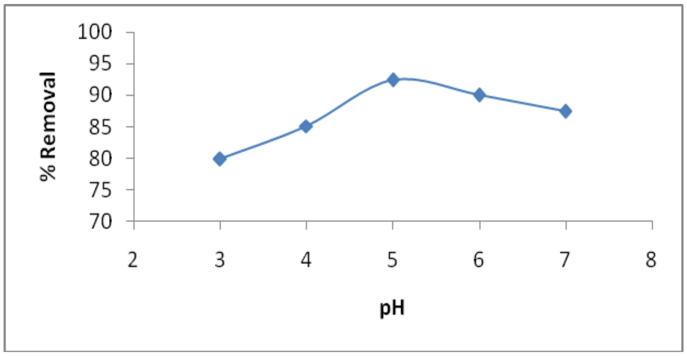

Fig 1: Effect of pH on % removal of Cu(II) ions (0.01M) at contact time 30 min, adsorbent dosage 0.5 g and particle size 420µm.

It can be seen from fig.1 that % removal increases with pH and then decreases. This is attributed to the competition of hydrogen ions with Cu (II) ions for active sites on the adsorbent surface. Increase in deprotonation results in the increase of negatively charged sites which enhanced attractive forces between surface of adsorbent and copper ions resulting into higher adsorption capacity. Further decrease in adsorption capacity was due to the formation of precipitate of copper ions at higher pH.

Effect of Contact time: The effect of contact time on adsorption of copper ions was studied by varying the time between 10 to 100 min. (Fig. 2)

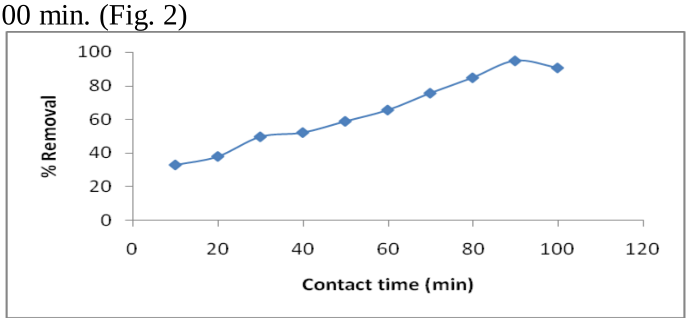

Fig 2: Effect of contact time on % percent removal with Cu (II) ions (0.01M) at pH 5 adsorbent dosage 0.5 g and particle size 420µm.

As can be seen from fig. 2, the removal of copper ions increased with increase in contact time. This means that a large amount of vacant adsorption sites were available in this stage. Further increase in contact time dose not increase the uptake due to unavailability of adsorption sites of the adsorbent material. Initially adsorption was a slow process and then increased rapidly and attains the results of % removal of Cu(II) ions are shown in fig.3

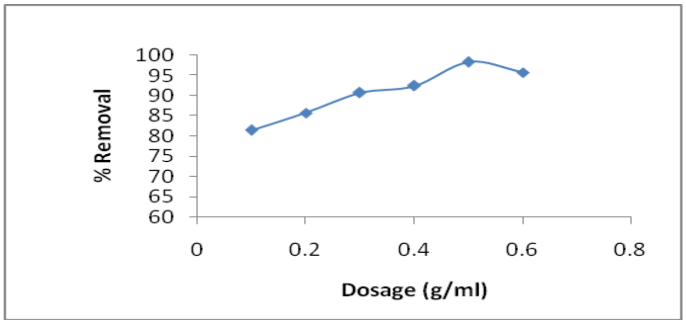

Fig.3: Effect of adsorbent dosage on % removal of Cu(II) ions(0.01M) at pH 5, contact time 90 min and particle size 420µm

As can be seen from this figure, the adsorption efficiency increased with an increasing adsorbent dosage. This is due to an increase in the surface area of the adsorbent which in turn increases the number of binding sites.

Effect of particle size: The percent removal of Cu (II) ions was studied at different Chitosan particle size [125, 250, 420, 610 and 700µm] and is shown in fig. 4

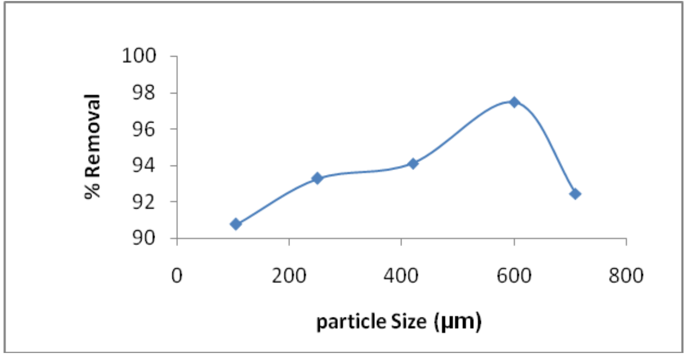

Fig 4: Effect of particle size on % removal of Cu(II) ions(0.01M) at pH 5, contact time 90 min and adsorbent dosage0.5g.

As can be seen from this figure, % removal initially increases and then decreases.

Effect of Concentration: The effect of initial copper concentration on its removal was studied in the range 0.002-0.01 M and is shown in fig. 5.

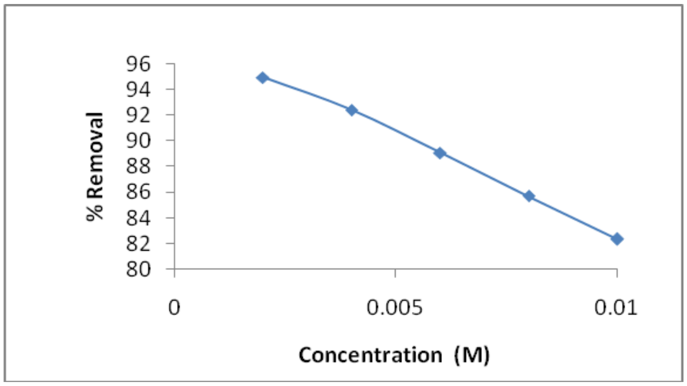

Fig. 5: Effect of concentration on % removal of Cu(II) ions at pH 5, contact time 90 min, adsorbent dosage0.5 g and particle size 610µm.

It can be seen from fig.5 that the percentage removal of Cu (II) decreases with increase in initial copper concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which results in decrease in the removal of adsorbate, consequent to an increase in initial copper concentration. Therefore it was evident from the results that copper adsorption was dependent on the initial metal concentration

Adsorption Characteristics

FTIR studies: The spectra of the virgin chitosan and Cu (II) ion loaded chitosan are shown in Fig. 6. FTIR spectrum of pure chitosan shows a strong broad peak at 3553.00cm^{-1} which indicates the presence of –OH group and –NH stretching vibration. Band at 2900 cm^{-1} is due to –CH stretching vibration of =CH-O-

CH_2-(C-O-C). Two sharp peaks at 1600 cm^{-1} and 1500 cm^{-1} are due to amide I and II groups. Peak 1000 cm^{-1} indicates C-O stretching and 1400-1490 cm^{-1} due to C-N stretching. In the case of loaded chitosan with Cu (II) ion**,** a broad peak occurs at 3500 cm^{-1} due to –OH stretching and amide group of chitosan and the additional intense bands in the ranges 1600–1300, 1200–1000, and 800–600cm^{-1}. It can be seen from Fig. 6 that the intensities of the peaks in case of adsorbed Cu (II) were changed considerably. These changes in intensities indicate binding of the metal ions to the adsorbent by adsorption process.

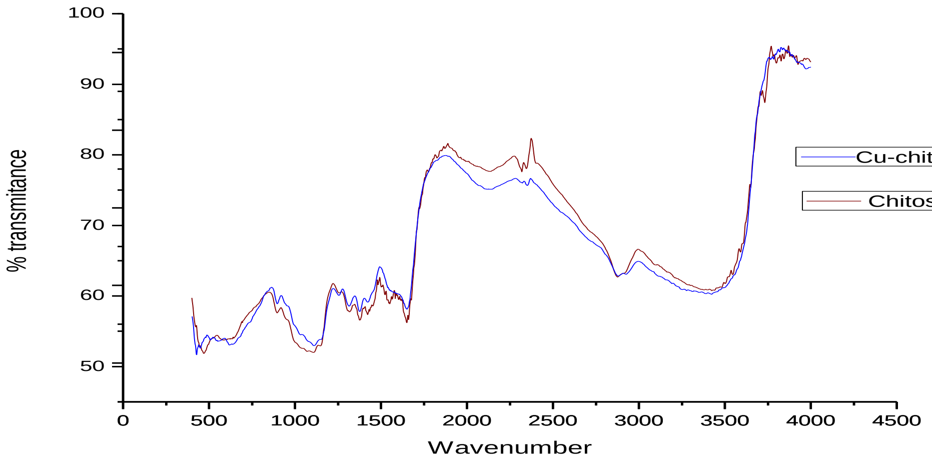

Fig. 6 FTIR Spectrum of virgin chitosan and chitosan loaded with Cu (II) ions

FESEM studies: The morphological characteristics of chitosan were studied using field emission scanning electron microscope. The FESEM micrographs of virgin chitosan and Cu (II) ion loaded chitosan are presented in Fig. 7(a) and 7(b) respectively.

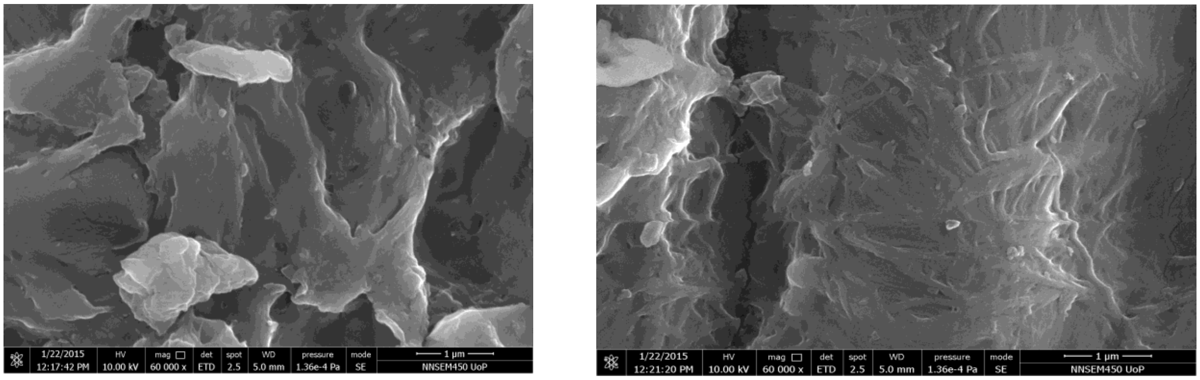

Fig.7 SEM micrograph of (a) Virgin Chitosan, (b) chitosan loaded with Cu (II) ions

The morphology of the virgin chitosan shows that there are number of active sites on adsorbent surface available for adsorption (Fig. 7a) and clearly indicates adsorption of Cu(II) ions on chitosan showing less number of active sites(Fig.7b).

EDX studies: The EDX spectrum of virgin and Cu(II) ions loaded with chitosan is shown in fig. 8a and 8b respectively.

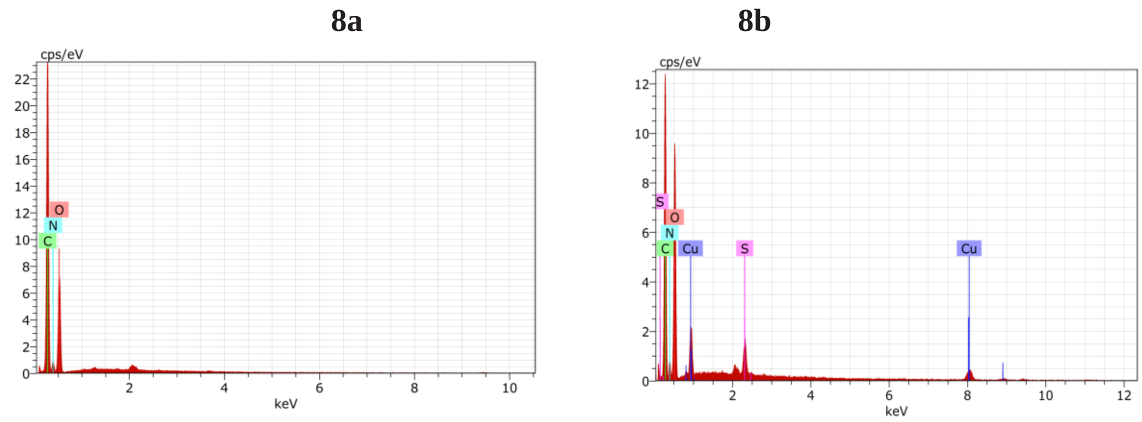

Fig.8.Energy dispersive spectrum (EDS) of **(a)** Virgin chitosan , **(b)** chitosan loaded with Cu (II) ions

The EDX spectrum of chitosan clearly shows presence of Cu(II) ions after adsorption.

Thermodynamic Parameters

Effect of temperature on adsorption process: The effect of temperature on adsorption of copper ions on chitosan was investigated by varying the temperature from 30 to 90°C (Fig 9). For this purpose experiments were carried out at the optimized parameters (initial metal ion concentration 0.01M, pH 5, contact time 90 min, particle size 420μm and adsorbent dose 0.5 g). It was observed that the percentage removal increases with increase in temperature. This may be due to the generation of new active sites on the surface of the adsorbent and also increased rate of pore diffusion of the adsorbent which leads to the endothermic adsorption.

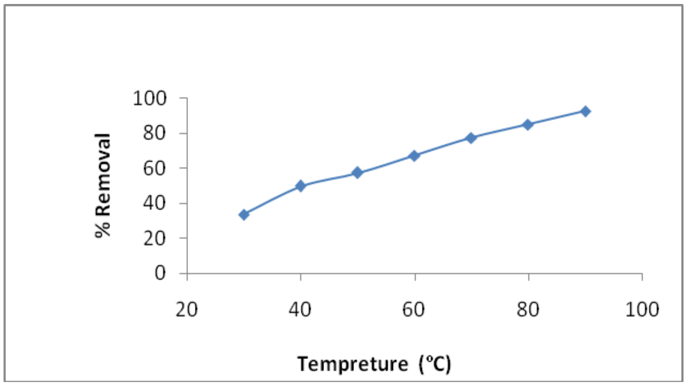

Fig.9: Effect of temperature on the removal of Cu (II) **ions**

The thermodynamic parameters for the adsorption of copper ions were calculated using the following equations.

$$\Delta G^\circ = -RT ln\, K \qquad (3)$$

Where,

$$K = \frac{qe}{Ce} \qquad (4)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (6)$$

Where K is the distribution coefficient for the adsorption in g/l, $\Delta G°$ is the Gibbs free energy in J mol^{-1}, R is the gas constant in J mol^{-1}K, T is the absolute temperature in K, $\Delta S°$ is the entropy change in kJ mol^{-1}K^{-1}and $\Delta H°$ is the enthalpy change in kJ mol^{-1}.

The Van't Hoff plot is presented in fig.10 which is found to be linear

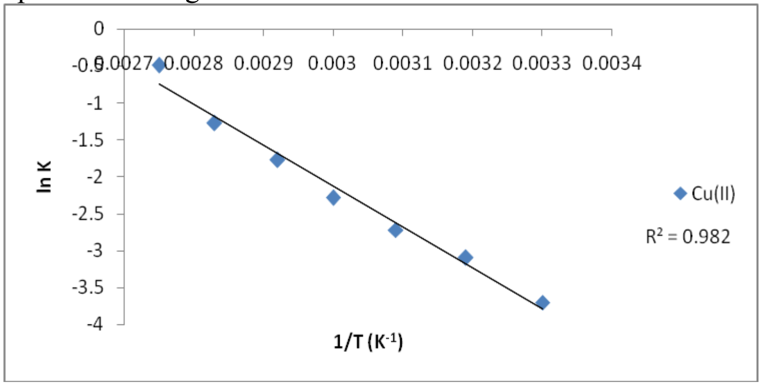

Fig.10: Thermodynamic parameters for adsorption of Cu (II) ions using chitosan

The thermodynamic constants calculated from above data are listed in table 1. The negative values of Gibbs free energy ($\Delta G°$) change indicate the feasibility and spontaneous nature and thermodynamically favourable adsorption. The positive values of $\Delta S°$ indicate the structural change occurs on the surface of the adsorbent and increased randomness during the adsorption process; while the positive values of $\Delta H°$ imply that the interaction between the metal ions and adsorbent is endothermic in nature.

Table1. Thermodynamic parameters for adsorption of Cu(II) ions on chitosan

Element	-$\Delta G°$(kJ/mol K)							$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJmol^{-1}K^{-1})
	303K	313K	323K	333K	343K	353K	363K		
Cu(II)	8.069	9.859	11.65	13.44	15.23	17.02	18.81	46.168	0.179

Adsorption isotherms: Three models of adsorption isotherms viz., namely, Freundlich isotherm, Tempkin isotherm and D-R isotherm were studied.

Freundlich isotherm model: The Freundlich isotherm equation is used for the description of multilayer with the interaction between adsorbed molecules. The linear form of Freundlich isotherm model is given by the equation,

$$\log qe = log\ K_f + \frac{1}{n} \log \mathrm{Ce} \qquad (7)$$

Where, qe= amount of metal ions adsorbed at equilibrium (g/g); Ce= concentration of the metal ions at equilibrium (g/L); K_F =adsorption capacity (L/g); n= intensity of adsorption. Linear plots of log q_e versus log C_e show that the adsorption of metal ions obeys the Freundlich adsorption isotherm (Fig.11).

The values of K_F and n given in table-2 shows that the increase in negative charges on the adsorbent surface that makes electrostatic force like van der Waal's between the adsorbent surface and metal ion. The value clearly shows the dominance of adsorption capacity. The intensity of adsorption is an indication for the bond energies between metal ions and adsorbent. The value of n is greater than one indicating that the adsorption is much more favourable.

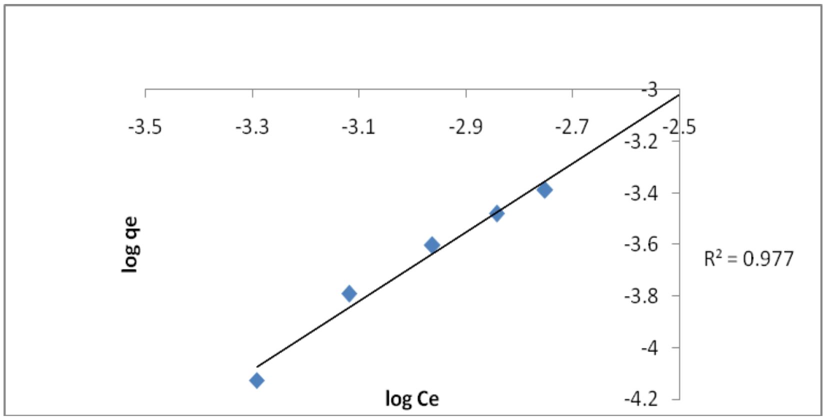

Fig.11: Freundlich isotherm for the adsorption of Cu(II) ions on chitosan

Temkin Isotherm: Temkin isotherm suggests the distribution of uniform binding energy. Temkin isotherm is expressed by the following equation,

$Q_e = B \ln A + B \ln C_e$ (8)

Where, B= RT/b.

A and B are the Temkin isotherm constants, b is the constant related to heat of adsorption, R is the gas constant (8.314 J/mol/k), T the absolute temperature (K), qe the amount of metal ions adsorbed at equilibrium (g/g); Ce the concentration of the metal ions at equilibrium (g L^{-1}).

The isotherm constant A and B are obtained from the plot of qe verses lnCe (Fig.12). The linearity of plot indicates that system obeys Temkin isotherm.

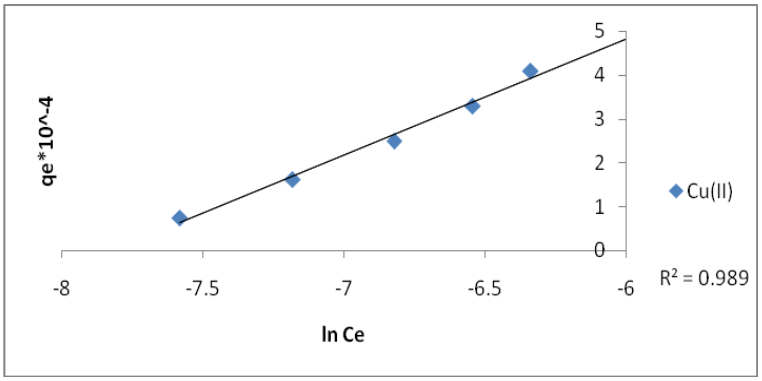

Fig.12:Temkin isotherm for the adsorption of Cu(II) ions on chitosan

Dubinin- Radushkevich (D-R) isotherm: The D-R isotherm equation, distinguishes between physical and chemical adsorption. The linearized form of D-R isotherm model can be stated by the following equation,

$\ln q_e = \ln Q_{DR} + K\varepsilon^2$ (9)

Where q_e **is** the amount of metal ions adsorbed (g g^{-1}), Q_{DR} is the maximum adsorption capacity of metal ions (g g^{-1}), K is the Dubinin- Radushkevich constant (kJ^2 mol^{-1}) and ε is polanyi potential given by the equation

$\varepsilon = RT\ln(1 + \frac{1}{Ce})$ (10)

Where R is the gas constant in J mol^{-1} K. T is the temperature in kelvin and C_e is equilibrium concentration of metal ions (g L^{-1}).

A linearized plot of ln qe Vs ε^2 (Fig.13) gives a straight line with a slope of K and an intercept of Q_{DR} . From the value of Dubinin- Radushkevich constant K, bisorption mean free energy E (kJ mol^{-1}) is determined as follows

$$E= 1/\sqrt{2K} \qquad (11)$$

Where E is the biosorption mean free energy (kJ mol^{-1}), and K is the Dubinin- Radushkevich constant.

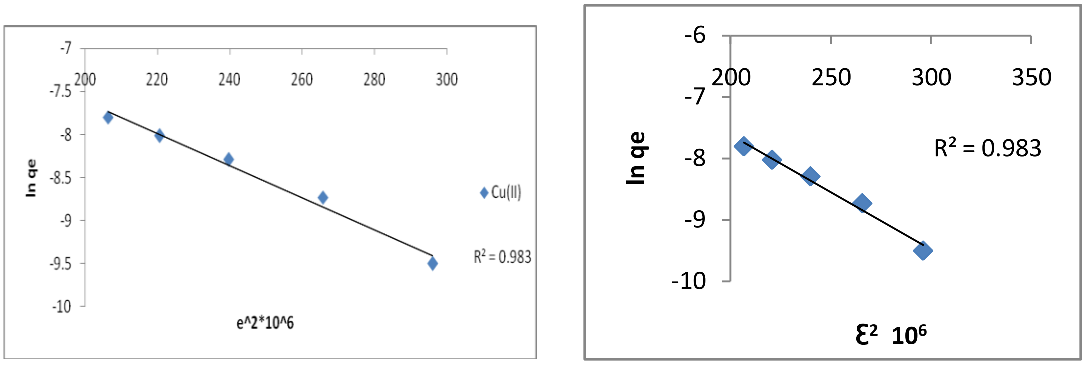

Fig.13: D-R isotherm for adsorption of Cu (II) ions on chitosan

The biosorption mean free energy (E) is involved the transfer of free energy of one mole of solute from infinity (in solution) to the surface of the adsorbent. The adsorption behaviour can be predicted on the basis of mean free energy. If its value is < 8 it indicates physical adsorption and > 8 indicates chemical adsorption [18]. The value (table 2) of the mean free energy of adsorption for Cu (II) ions is 5.271 kJ mol^{-1} reveals that adsorption is predominated by the physical adsorption process.

Table 2 Isotherm constants for Cu (II) ions adsorption onto chitosan

Adsoption Isotherm	Constants.	value
Freundlich isotherm	k_f	2.098
	n	1.060
	R^2	0.977
Temkin isothern	A	2.492×10^3
	B	2.643
	R^2	0.989
D-R isotherm	Q_{DR} (g/g)	0.0207
	K(kJ^2/mol)	0.018
	E (kJ/mol)	5.271
	R^2	0.984

An examination of table 2 reveals that adsorption of Cu (II) ions on chitosan follows freundlich and Dubinin- Radushkevich (D-R) isotherm.

Adsorption Kinetics: The linearized forms of pseudo first order equation is given by equation (12).

$$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303}) \times t \qquad (12)$$

Where q_e is amount of metal ion adsorbed at equilibrium (g g^{-1}); q_t is adsorbed quantity at time t (g g^{-1}); k_1 is pseudo first order rate constant in min^{-1}.

The linear plot of log (q_e-q_t) versus t (Fig.14). It indicates that adsorption process follows pseudo first order kinetics. The rate constant k_1 is found to be 0.02303 min^{-1}.

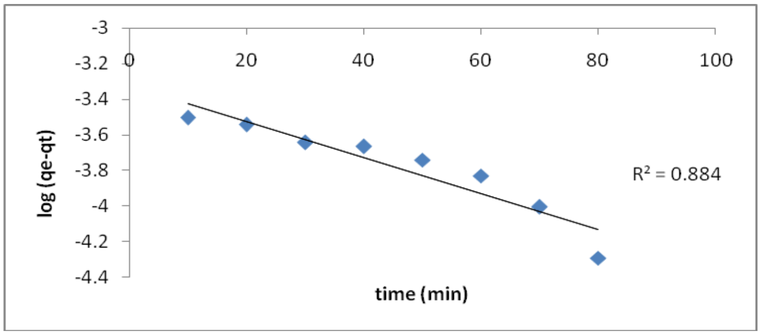

Fig.14: Pseudo first order kinetics of adsorption of Cu (II) ions using chitosan

Intraparticle diffusion model: This model describes about the diffusion of the adsorbate from the outer surface into the pores of the chitosan. The intraparticle diffusion equation is given by

$qt= k_d t^{0.5}+c$ (13)

Where k_d is the particle diffusion rate constant in $mg/g/min^{1/2}$; and c is intercept. A plot of qt versus $t^{0.5}$ (Fig.15) gives the values of k_d and c.

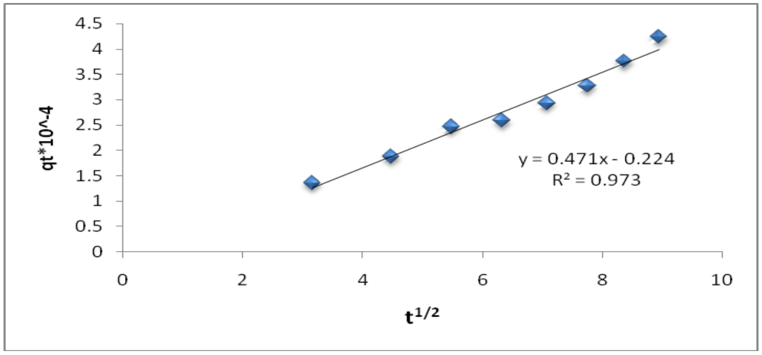

Fig.15: Intraparticle diffusion for adsorption of Cu (II) ions using chitosan

These are found to be 0.471 mg $g^{-1}min^{-1}$ and 0.224 respectively from figure.

Desorption of Cu (II): Desorption of Cu (II) ions (0.01M) loaded on chitosan under optimized conditions was carried out with 0.1M NaOH as an eluent (Fig. 16). Maximum desorption (84.87%) was observed by using 20mL of NaOH. The result shows that the spent copper metal ions can be effectively recovered.

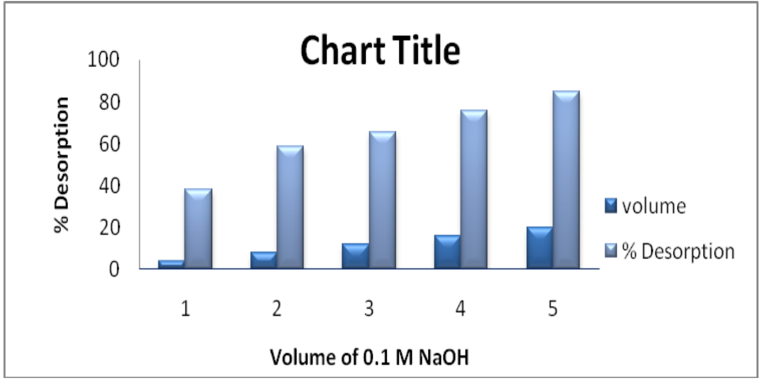

Figure13. Desorption of Cu (II) ions loaded on chitosan using 0.1 NaOH

APPLICATIONS

Chitosan can be used effectively for the removal and recovery of copper ions from aqueous solution. The developed technique is cost effective and efficient and can be applied to other metals also.

CONCLUSIONS

- Maximum removal (99.16%) of copper ions (0.01M) was observed at pH 5, contact time 90min, adsorbent dosage 0.5g and particle size 600µm.
- Thermodynamics study revealed that adsorption of Cu (II) ions is a spontaneous and thermo dynamically favourable adsorption process.
- Isotherm study revealed that adsorption of Cu (II) ions on chitosan follows Freundlich and Dubinin- Radushkevich isotherm.
- Adsorption of Cu(II) ions follow pseudo first order kinetics and intraparticle diffusion model.
- Adsorbed copper ions can be effectively recovered using 0.1M NaOH as an eluent.
- Chitosan acts as an effective adsorbent for removal of Cu(II) ions

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