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Adsorption of Copper by Ethylenediamine-modified cross-linked magnetic chitosan resin (EMCMCR)

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Abstract: The adsorption of Copper (II) ions from aqueous solution by ethylenediamine modified cross linked magnetic chitosan resin (EMCMCR) was studied in a batch adsorption system. For 100 ppm, maximum removal of copper (II) was observed at a contact time of 4hours. Copper (II) removal is pH dependant and the maximum removal was observed at pH 6.0 and temperature of 25^{0}C for 200 ppm. The adsorption could be well interpreted by Langmuir adsorption model.

Keywords: *Adsorption of Copper, Ethylene diamine, Effect of parameters*

I. INTRODUCTION

Chitosan (Fig.1) is a modified carbohydrate polymer derived industrially by hydrolyzing the amino acetyl groups of chitin. It is a natural, biodegradable, biocompatible, non-toxic, and anti-bacterial poly-saccharide available in different forms such as solution, powder, flake, fibre and film. Due to its wide range of physical forms, chitosan has broad applications in different fields. Chitosan, a naturally occurring polysaccharide, is a cationic polysaccharide composed of [a2-amino-2-deoxy-â-D-glucan] (Figure 1) obtained by the alkaline deacetylation of chitin. This chitin is present in shells of insects and marine crustacean such as shrimps and crabs. The unique properties of chitosan including availability, biodegradability, biocompatibility, bioactivity, non-toxicity as well as good adhesion and sorption are the major reasons for its multiple applications. Another main reason for this increasing interest of chitosan is its wide range of physical forms which can be obtained by using an appropriate technological process. Chitosan has already been used in a variety of fields such as wastewater treatment, medicine, agriculture, food, paper industry and cosmetics.

Due to the importance of the physical forms of chitosan in various fields of science and technology, this short review attempts to present the recent studies involved with chitosan as well as its blends in different physical forms. Finally the most important applications of the physical forms of chitosan and its blends in different fields are also depicted.

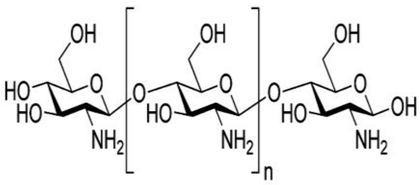

Fig.1.Chitosan-Structure

In the present work, we prepared ethylenediamine-modified glutaraldehyde-crosslinked magnetic chitosan resin (EMCMCR) and used it to adsorb Cu (1I) ions in a batch system. The effects of the process parameters such as pH, temperature, dosage of EMCMCR, initial Cu (II) concentration on Cu (II) removal were investigated. In order to better understand the adsorption characteristic, some isotherm models were investigated.

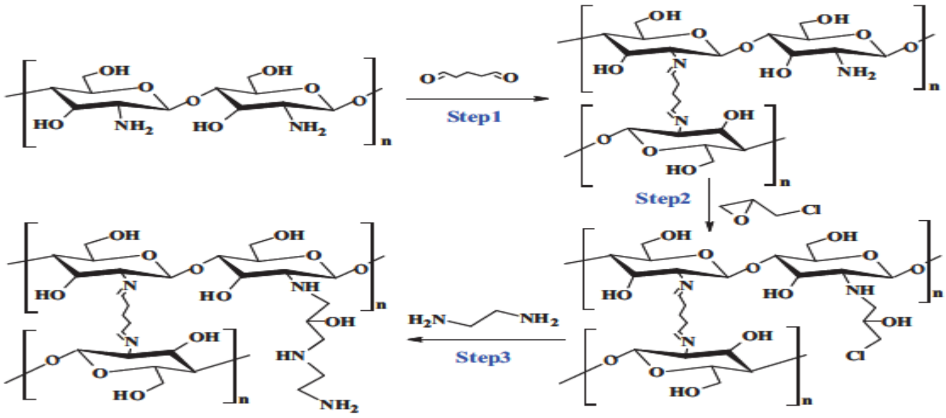

Fig. 2.1 Scheme for the synthesis of EMCMCR: (step1) expected cross-linking mechanism for chitosan using glutaraldehyde; (step2) expected mechanism of action for cross-linked chitosan using Epichlorohydrin; (step3) expected mechanism for aminated chitosan beads.

II. MATERIALS AND METHODS

2.1 Materials

Chitosan, Glutaraldehyde, Epichlorohydrin, Ethylenediamine. All reagents above were of chemical grade. Stock solutions (1000 mg L^{-1}) of Cu(II) was prepared by dissolving 392.682 g in 1000 ml distilled water. Acetic acid, Glutaraldehyde, Epichlorohydrin, Tween 80, Ethylenediamine, Aloe-vera extract powder, Hydrochloric acid, Sodium hydroxide pellets.

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2.2. Preparation of EMCMCR

2.2.1 Preparation of Magnetic fluid

Magnetic fluid was prepared at a temperature of 45^0 C, a mixture of $FeCl_3$ (15 ml, 0.6 mol.L^{-1}) and $FeSO_4$ (15 ml, 0.4 mol.L^{-1}) was stirred in a beaker. Sodium hydroxide was added into the mixture quickly to keep the pH value 10.0.After stirring for 10 minutes the temperature rises to 55^0 C by setting the mixture in a water bath ,thereafter surfactant (Tween 80) is added to modify the surface of $Fe_3\,O_4$ and kept for 30 minutes and then the pH was adjusted to 7.0 .

EMCMCR was prepared by dissolving chitosan in acetic acid solution with stirring until completely dissolved at 50 ° C and then the magnetic fluid was added to the solution slowly. Glutaraldehyde and ethylenediamine were used to form the gel. Meanwhile, ethylenediamine was introduced into the mixture to modify the resin of EMCMCR. Fig. 3 shows the photos of the chitosan and EMCMCR.

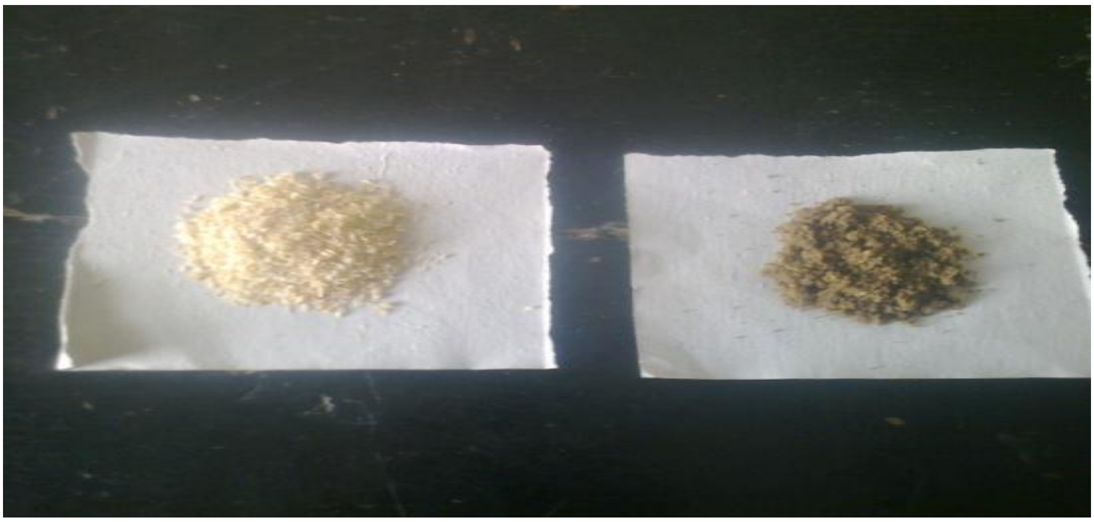

Fig.2.2. Photos of Chitosan and EMCMCR

2.3. Batch adsorption experiments

All batch experiments were carried out with adsorbent samples in a 250 mL beaker with 100 ppm Cu (II) aqueous solutions on a mechanical stirrer at slow speed. The 100 ppm solution was contacted i.e; stirred for various hours (1 hr,2 hr,3 hr,4 hr,5 hr,6 hr etc.) The concentration of Cu (II) ions was determined spectrophotometrically at 820 nm .At the end of 4 hrs there was maximum adsorption (i,e: 100%) .

The study of the pH (1.0–8.0) dependency of Cu (II) adsorp-tion onto EMCMCR was carried out in Cu (II) solutions with different initial concentration of 100, 200 and 300 mg L^{-1} at a temperature (25^0 C).Since at 100ppm we got 100% for 4 hrs of stirring, we use 200 ppm Cu(II) solution with varying pH(1.0-10.0) The pH value was adjusted by 1 M NaOH or 1 M HCl.

Isotherm studies were conducted by contacting 1 g EMCMCR with 100 mL of Cu (II) solution at different initial concentration (100, 200, and 300 mg L^{-1}) stirring for 240 min. The experiments were performed at different temperature (25, 35 and 45 and 55 ° C). Adsorption isotherms are plots of the equilibrium adsorption capacity (**q_e**) (according to Eq. (1)) versus the equilibrium concentration of the residual Cu (II) in the solution (**C_e**).

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where **q_e** is the equilibrium adsorption capacity (mg g^{-1}), **C_0** and **C_e** are the initial and equilibrium liquid phase solute concentration (mg L^{-1}), respectively. **V** is the liquid phase volume (L) and **W (or m)** is the amount of adsorbent (g).

Table 1

Sl.No	Isotherm	Nonlinear form	Linear form	Plot	Reference
1	Langmuir	$q_e = Q_0bC_e/1+bC_e$	$C_e/q_e = 1/bQ_0 + C_e/Q_0$ $1/q_e = 1/Q_0 + 1/bQ_0C_e$ $q_e = Q_0 - q_e/bC_e$ $q_e/C_e = bQ_0 - bq_e$	C_e/q_e vs C_e $1/q_e$ vs $1/C_e$ q_e vs q_e/bC_e q_e/C_e vs q_e	[11]
2	Freundlich	$q_e = K_FC_e^{1/n}$	$\log q_e = \log K_F + 1/n \log C_e$	$\log q_e$ vs $\log C_e$	[12]
3	Tempkin	$q_e = RT/b_T \ln A_T C_e$	$q_e = RT/b_T \ln A_T + (RT/b_T) \ln C_e$	q_e vs $\ln C_e$	[13]

Lists of adsorption isotherms models

III. RESULTS AND DISCUSSION

3.1.1 Effect of Contact time on Cu (II) adsorption by EMCMCR (for 100 ppm)

Initial Concentration: 100 ppm (39.268 mg/l), Dosage m : 1 gm,Temperature:25 ^{0}C
pH: 4.85

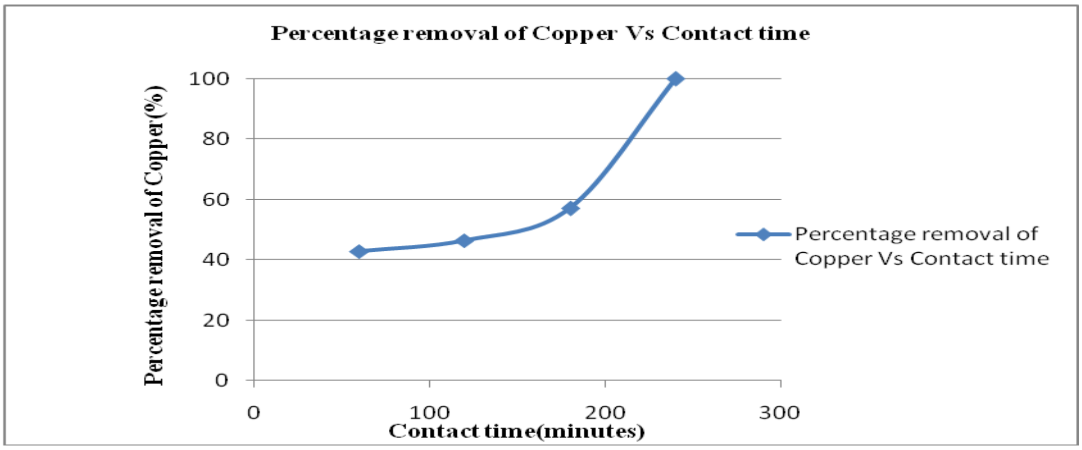

Fig 3.1 Graph of Percentage of removal of Copper vs Contact Time(For 100 ppm)

Percentage removal of copper increases with increase in contact time .The maximum removal resulted in 100% for 100 ppm for stirring it for 4 hours at temperature 25^{0}C. The pH was 4.85

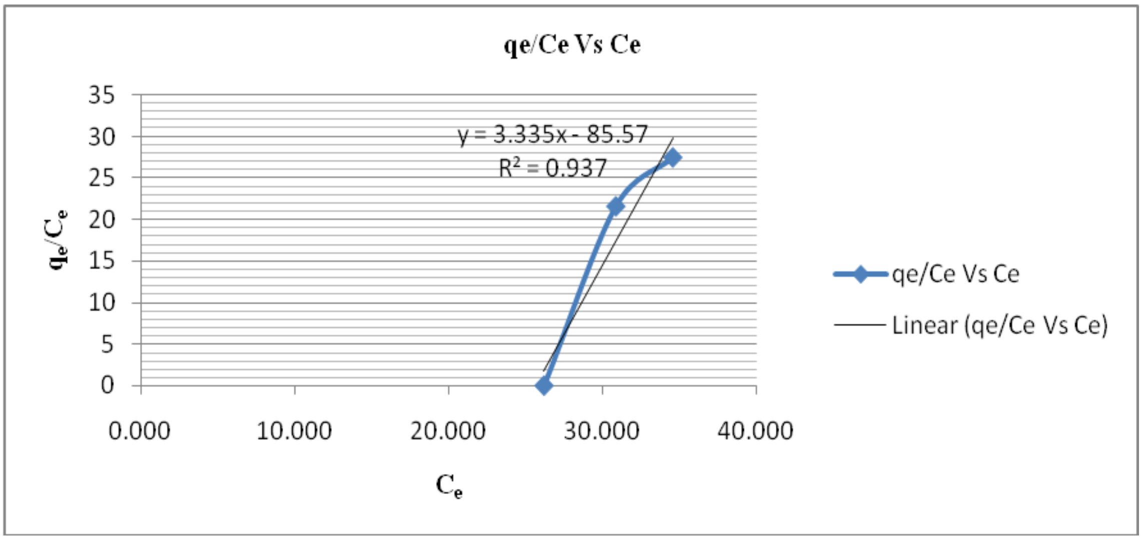

Fig 3.2 Graph of q_e/C_e vs C_e (For 100 ppm)

From the above graph with R-square(R^2).Langmuir adsorption isotherm have R^2 =0.937.Since Langmuir adsorption is having highest R^2 value and close to 1.This parameter follows Langmuir adsorption isotherm .The R-square values of the linear regression performed were used to determine whether the isotherm was a good fit for the given experimental adsorption data. The R-square value close to 1 indicates a good fit by the model for the given experimental data whereas R-square value near 0 indicates that the model is not a good fit for the given experimental data.

3.1.2 For 200 ppm

Initial Concentration: 200 ppm (78.536 mg/l),Dosage m : 1 gm,Temperature:25 ^{0}C
pH :4.85

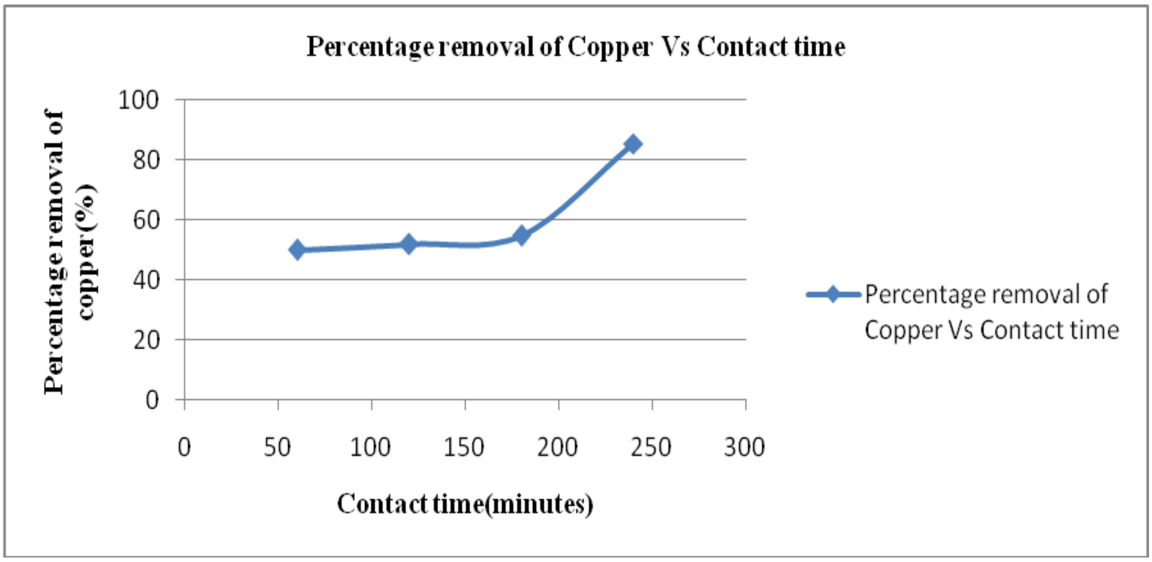

Fig 3.3 Graph of Percentage of removal of Copper vs Contact Time(For 200 ppm)

Percentage removal of copper increases with increase in contact time .The maximum removal resulted in 85.29% for 200 ppm by keeping 4hours as constant temperature 25^{0}C .The pH was 4.85

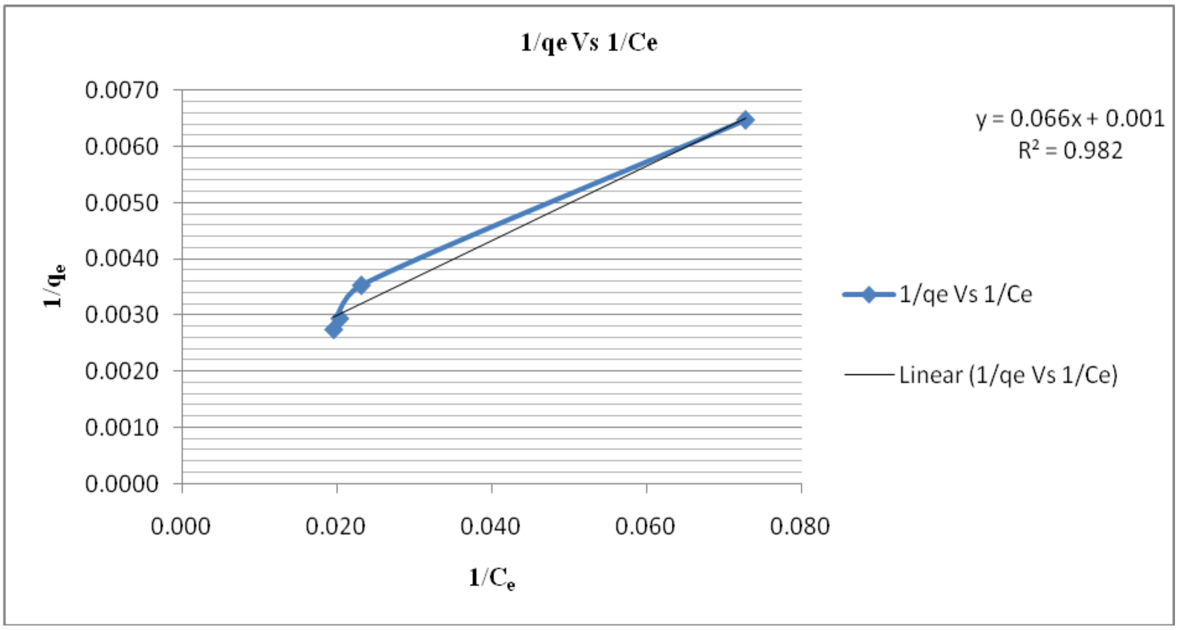

Fig 3.4 Graph of $1/q_e$ vs $1/C_e$(For 200ppm)

For 200 ppm it follows Langmuir Adsorption model since it has highest R^2 value and is equal to 0.982

3.1.3 For 300 ppm

Initial Concentration: 300 ppm(117.8 mg/l),Dosage m : 1 gm, Temperature:25 ^{0}C,pH : 4.85

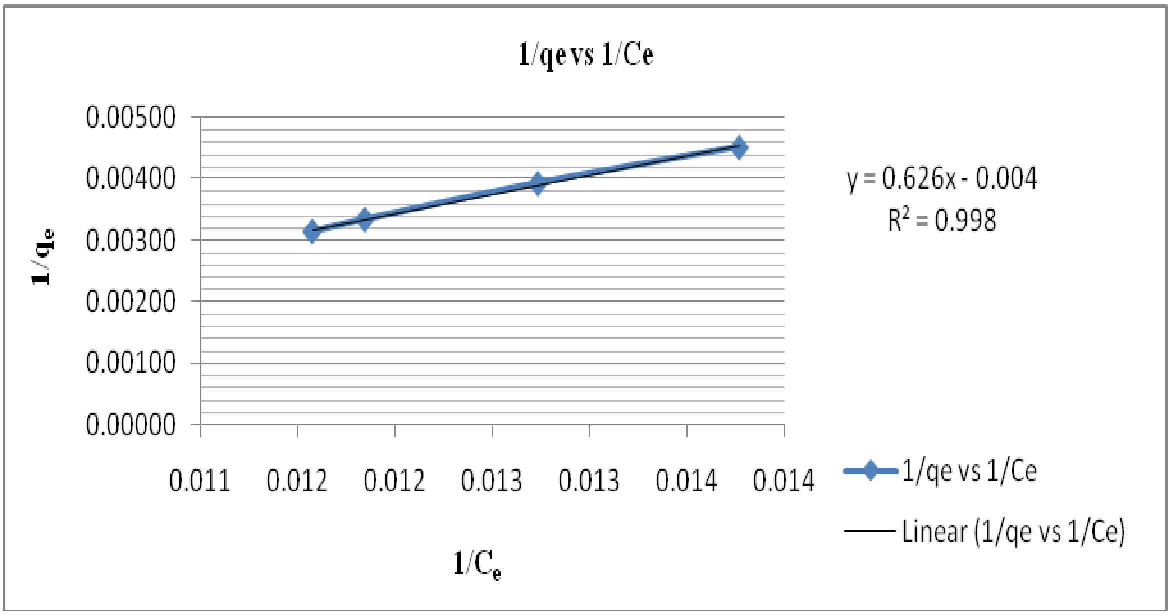

Fig 3.5 Graph of $1/q_e$ vs $1/C_e$ (For 300ppm)

Percentage removal of copper increases with increase in contact time .The maximum removal of copper resulted in 36.29% for 300 ppm by keeping 4hours as constant at temperature 25^{0}C.For 300ppm too it follows Langmuir adsorption Isotherm with R^2 =0.998

3.2 For 200ppm

pH Variation

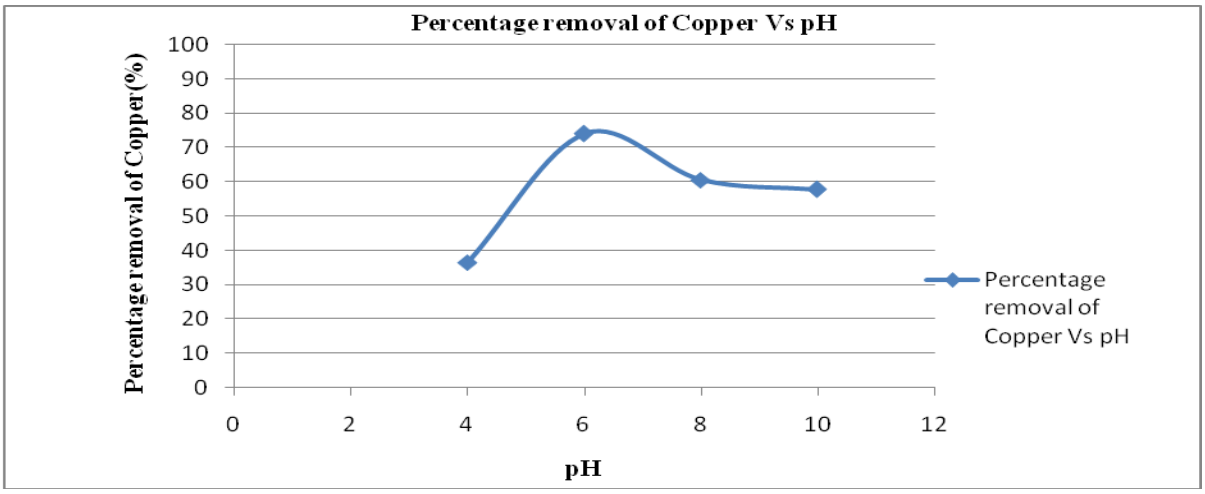

Fig 3.7 Graph of Percentage of removal of Copper vs pH (For 200 ppm)

Maximum percentage of copper removal is attained at pH 6 at concentration 200 ppm and temperature 25^0C The percentage removal resulted in 74.038 %

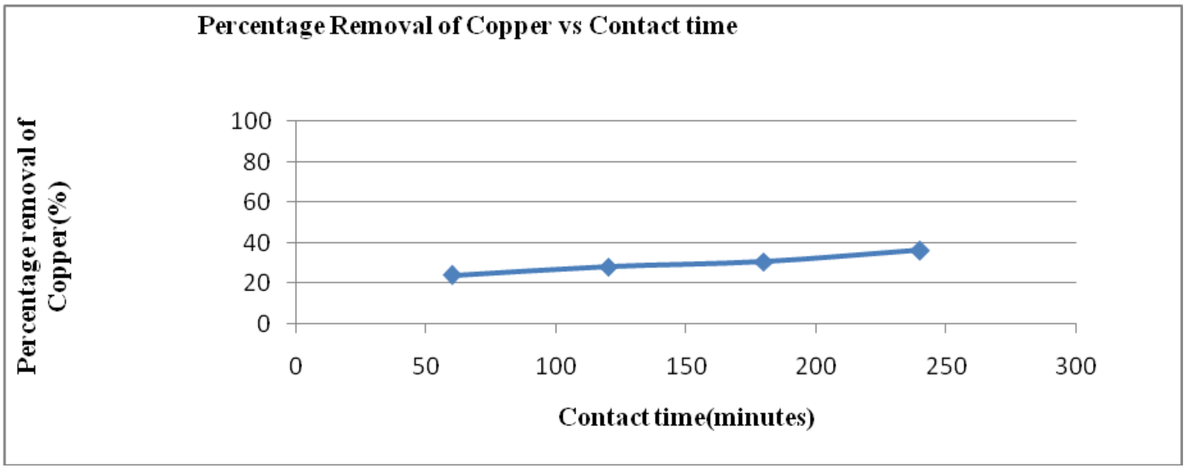

Fig 3.6 Graph of Percentage of removal of Copper vs Contact Time(For 300 ppm)

3.3 Temperature Variation

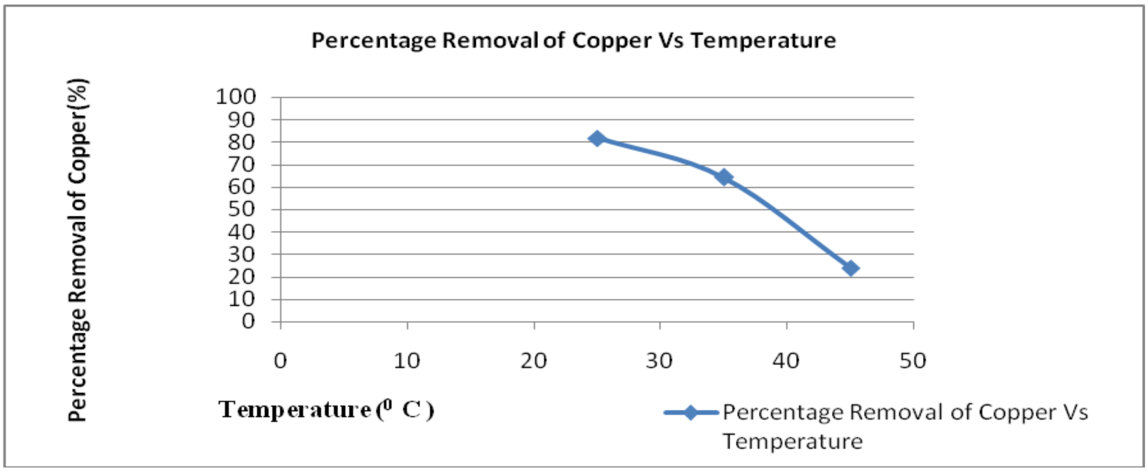

Fig 3.8 Graph of Percentage of removal of Copper vs Temperature (For 200 ppm)

As the temperature increases percentage removal of copper reduces. Maximum percentage removal is attained at 25^0C and pH 4.85.The percentage removal of copper resulted in 81.73% at an initial concentration 200 ppm.

3.4 Concentration variation

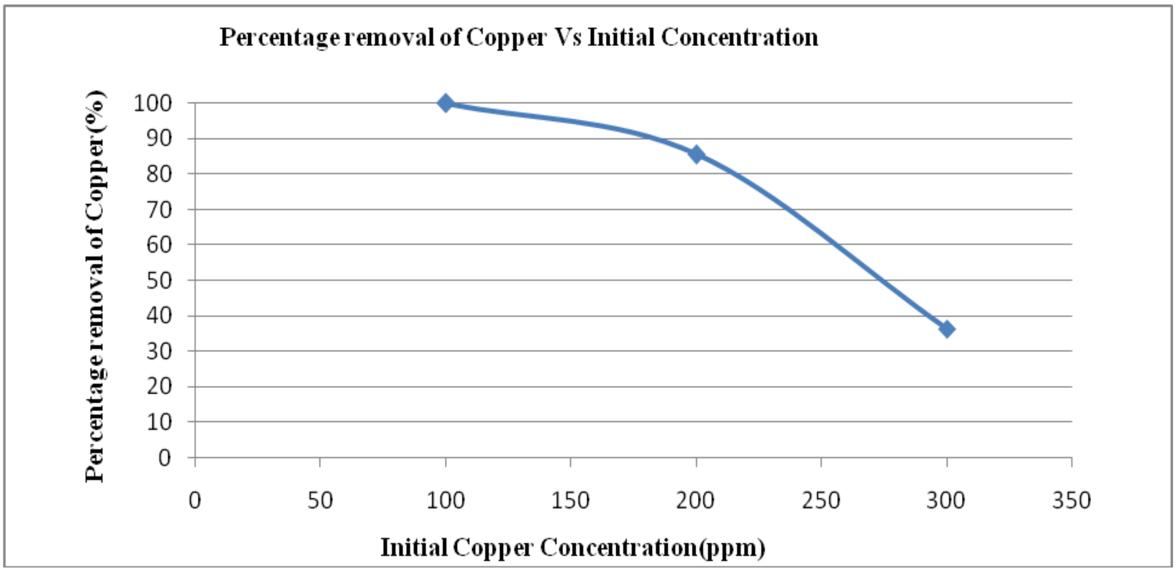

Fig 3.9 Graph of Percentage of removal of Copper vs Initial Concentration

Percentage removal of copper is maximum for 100ppm for four hours of stirring time(contact time).It resulted in 100% removal of copper. Now keeping 4 hours of contact time as constant, percentage removal of copper reduces to 85.29% for 200 ppm .For 300ppm it reduced to 36.29 % for 4 hours of contact time

3.5 Maximum Equilibrium Isotherm

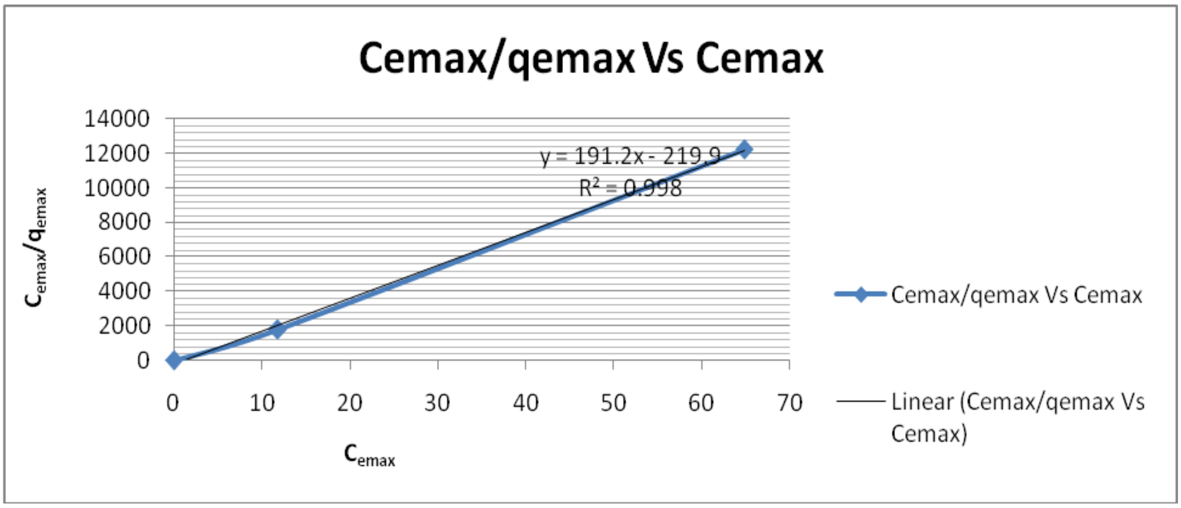

Fig 3.10 Graph of C_{emax}/q_{emax} vs C_{emax}

Since the mean square value R^2 has value and is equal to 0.998 and is very close to 1 it best fits Langmuir adsorption isotherm .Hence the plot C_{emax}/q_{emax} Vs C_{emax} follows a linear curve and have maximum mean square value equal to 1.Hence our study of batch adsorption of copper by ethylene-di-amine modified cross-linked chitosan resin is best described by Langmuir Adsorption Isotherm.

The below given graph shows decrease in percentage of copper removal with respect to increase in concentration (ppm)

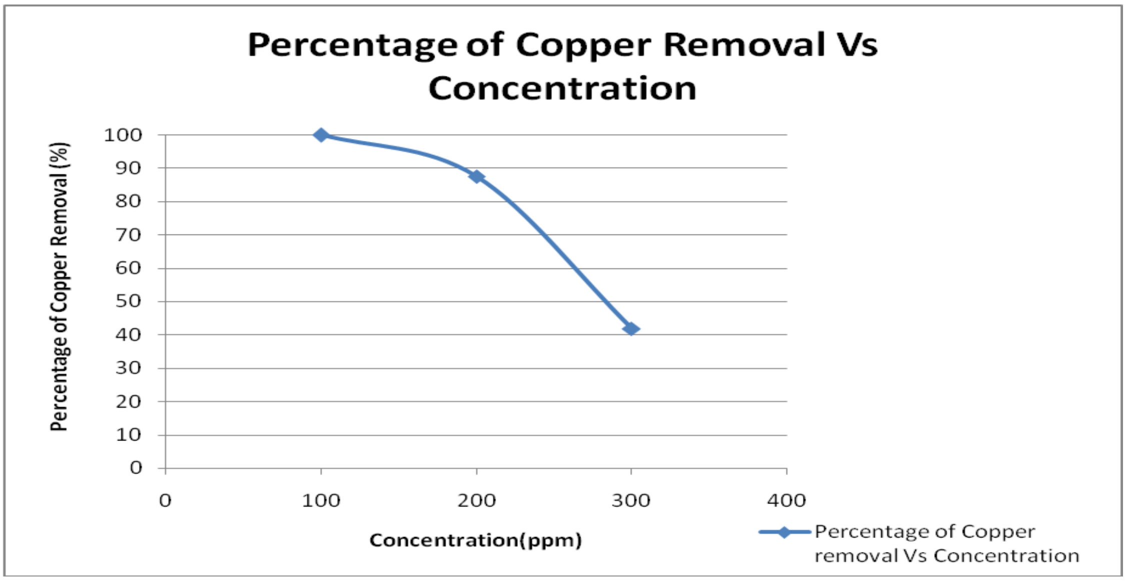

Fig 3.11 Graph of Percentage of removal of Copper vs Initial Concentration for maximum equilibrium adsorption

IV. CONCLUSION

Ethylenediamine modified crosslinked magnetic (EMCMCR) chitosan resins were prepared. From the above results it is obvious that adsorption efficiency was dependent on various factors or operating conditions such as pH, contact time, initial concentration, temperature and dosage of the adsorbent.

The optimum concentration and pH for maximum removal of Cu (II) ions was found to 100ppm and pH 6 for EMCMCR. Increase of adsorbent dose prominently increased the adsorption due to an increase in the surface area. With the increase in temperature adsorption efficiency gradually decreased and was found to have maximum percentage of removal of Cu (II) at 25^0C.

The equilibrium data were analyzed by Langmuir, Freundlich and Tempkin isotherm models. The Langmuir adsorption isotherm provided the best fit by giving maximum R^2 value i.e; 0.998 suggesting a monolayer adsorption on a homogenous surface.

The obtained results showed the prepared EMCMCR proves its high efficiency in removing the copper (II) ions from aqueous solution. On the economical front application of EMCMCR for heavy metal removal could be tested in industrial environments.

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