

Scientific paper

# Removal of Cu(II) from Aqueous Solutions Using Magnetite Exchanger Resin

Sunil Kumar Bajpai,<sup>1,\*</sup> Mukesh Kumar Armo<sup>2</sup> and Mini Namdeo<sup>1</sup><sup>1</sup> Department of Chemistry, Polymer Research Laboratory, Govt. Model Science College, Jabalpur (M.P.) – 482001, INDIA<sup>2</sup> Department of Chemistry, Govt. Chandravijay College, Dindori (M.P.), INDIA\* Corresponding author: E-mail: mnlbpi@rediffmail.com; sunil.mnlbpi@gmail.com  
Phone: +917612410541; mobile: +91-9993220651

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## Abstract

This research focuses on removal of Cu(II) from aqueous solution using magnetite loaded cationic resin (MLCR) at three different temperatures 15, 30 and 40 °C. The uptake of Cu(II) follows Freundlich sorption isotherm and is endothermic in nature. Out of various kinetic models proposed, the 'second order' seems to fit in the experimental data in the best way. The sorption appears to be governed by chemical forces rather than physical electrostatic interactions. The Dubinin-Radushkevich isotherm with mean sorption energy value of 9.45 kJ mol<sup>-1</sup> also supports chemical nature of sorption process. The sorption capacity of MLCR particles for Cu(II) was found to increase with pH of the sorbate solution, thus reaching maximum at pH 6.0. The positive value of  $\Delta H^\circ$  indicates endothermic nature of uptake process and positive  $\Delta S^\circ$  indicates increased randomness due to sorption.

**Keywords:** Magnetite, adsorption, Freundlich sorption isotherm, cationic resin, copper (II)

## 1. Introduction

Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing, metal processing etc.<sup>1</sup> The presence of these metals in the environment has become a serious threat for the human life as they enter into domestic water sources like rivers, lakes, ponds etc. These heavy metals are not biodegradable and their presence in water leads to bioaccumulation in living organism, causing health problems in animals, plants and human beings.<sup>2</sup>

Copper is a potential microelement which serves as a co-factor for some oxidases, oxygenases and some other enzymes. However, if it is present in excess concentrations, it catalyzes formation of highly reactive oxygen species leading to lipid peroxidation, the lack of the reduced form of glutathione, and enhancement of methemoglobin content.<sup>3</sup> The free or incorrectly bound Cu<sup>2+</sup> can also catalyze generation of the most damaging radicals, such as hydroxyl radicals, which cause chemical modification of the protein thus altering the protein

structure and finally resulting in oxidative damage of surrounding tissues<sup>4</sup>. Moreover, in Wilson disease and Indian Childhood Cirrhosis (ICC), copper accumulates in the liver, resulting in poor hepatocyte regeneration and fibrosis.<sup>5</sup>

Recent past has witnessed tremendous research work on sorption studies for removal of Cu(II) from aqueous solution using a wide range of different types of sorbents such as inorganic clay materials,<sup>6,7</sup> natural polymers,<sup>8</sup> synthetic polymers,<sup>9-12</sup> lignocellulosic materials,<sup>13-15</sup> etc. In addition, ion-exchange resins have also been exploited for the removal of toxic metal ions.<sup>16-17</sup> However, these sorbents have only been confined to laboratory experiments due to classical problems related to plugging and fouling of packed column and membranes etc. Moreover, the soft nature and the tendency to agglomerate are also major drawbacks associated with these sorbents. Recently, High Gradient Magnetic Separation (HGMS) technology has been successfully exploited for the separation of metal ions.<sup>18-19</sup> The major advantage of using magnetic particles as sorbent is that the sorbent particles can easily be removed from the adsorption system

by applying moderate magnetic field, and the overall separation process is cost-effective.

In the present study, we have reported a novel strategy to load magnetite nanoparticles in a commercially available strong cationic resin Seralite SRC-120 to use it as a potential sorbent for the magnetic removal of Cu(II). The significance of the study lies in the fact that the magnetite-loaded cationic resin (MLCR) particles exhibit magnetic field responsiveness while maintaining their ion-exchange capacity. To the best of our knowledge, such a sorbent material has probably been reported for the first time.

## 2. Experimental

### 2. 1. Materials

Chemicals Fe(II) chloride, Fe(III) chloride, sodium hydroxide and copper chloride were obtained from Hi-Media laboratories, Mumbai India. Strong cationic resin Seralite SRC-120 was a gift from Sisco Research laboratories Mumbai, India. Double distilled water was used throughout the experiments.

### 2. 2. Preparation of Magnetite-Loaded Cationic Resin (MLCR)

We developed a new method to prepare magnetite-loaded cationic resin (MLCR) particles. The resin-particles were immersed in aqueous solutions of FeCl<sub>2</sub> and FeCl<sub>3</sub>, taken in 1:2 molar ratio, for 24 h and then put in 5% NaOH solution at 70 °C for a period of 2 h. The formation of magnetite took place within the resin particles. The magnetite-loaded resin particles were washed with distilled water and then finally dried in a dust-free chamber at 40 °C. Fig. 1 (A) and (B) depict physical appearance of the plain and the magnetite-loaded ion-exchange resin particles. The dark-brown colour and their retention by bar-magnet (Fig. 1(C)) indicate the presence of magnetite within the resin particles.

### 2. 3. FTIR Spectral Analysis

The FTIR spectrum of MLCR particles was recorded by FTIR spectrophotometer (Shimadzu, 8201) using KBr.

### 2. 4. Thermogravimetric Analysis (TGA)

TGA was performed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851<sup>®</sup>) controlled by STAR<sup>®</sup> software (Mettler Toledo GmbH, Switzerland). About 10mg of powder sample was placed in ceramic crucible and analyzed over the temperature range of 20 to 600 °C at the heating rate of 10 °C min<sup>-1</sup> under dry flow of N<sub>2</sub> at the rate of 30 ml min<sup>-1</sup>.

### 2. 5. Cu (II) Uptake Studies

The stock solution of Cu(II) was prepared by dissolving a pre-calculated quantity of CuCl<sub>2</sub> in double distilled water to give final concentration of 100 (mg l<sup>-1</sup>). The stock solution was diluted to obtain standard solutions with concentrations in the range of 20 to 100 (mg l<sup>-1</sup>). 50 ml of Cu(II) solution of desired concentration was placed in a 125-ml Erlenmeyer flask, containing 0.02g of MLCR sorbent and was agitated in a thermostatic water bath at a constant speed of 50 rpm for 2 hour. At the end of the experiment the magnetic sorbent particles were separated by introducing magnet in the solution and supernatant was analyzed spectrophotometrically<sup>20</sup> to determine concentration of Cu(II).

## 3. Results and Discussion

### 3. 1. Formation of MLCR Particles

When cation exchanger resin particles are put in the aqueous solution of Fe(II)/Fe(III) ions, there operates an 'ion exchange process' between exchangeable Na<sup>+</sup> cations of resin and Fe<sup>2+</sup>/Fe<sup>3+</sup> ions present in the outer solution. Later on, when these Fe (II)/Fe (III) ions loaded resin particles are placed in NaOH solution, these ferrous/ferric ions undergo co-precipitation within the resin matrix thus resulting in formation of magnetite inside the resin particles. In addition, Na<sup>+</sup> ions (from NaOH solution) also bind to the negatively charged sulfonate groups along the macromolecular chains within the resin matrix. In this way magnetite-loaded cation exchanger resin particles are prepared.



Figure 1: Photographs of (A) magnetite loaded cationic resin (MLCR), (B) plain resin and (C) their retention on the magnet surface.

### 3. 2. FTIR Spectral Analysis

The simultaneous presence of band in the regions 3616–3300 (cm<sup>-1</sup>) is due to OH<sup>-</sup> stretching of hydroxyl groups of resin (see Fig. 2). CH<sub>2</sub> stretching is obtained at 2914 (cm<sup>-1</sup>) and C=O (carbonyl groups) stretching of resin is obtained at 1761 (cm<sup>-1</sup>). Likewise, band observed at 650 (cm<sup>-1</sup>) is due to metal oxygen stretching. These bands were sharp and of strong intensity thus indicating the high degree of crystallinity of the samples.

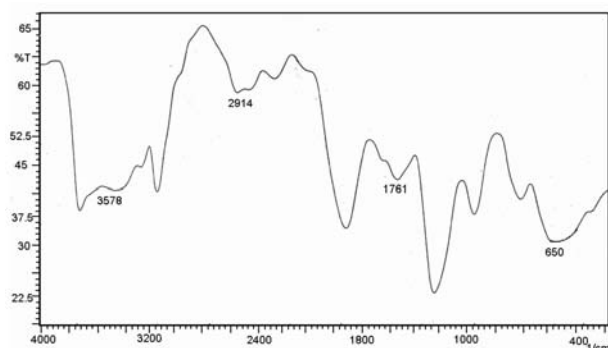


Figure 2: FTIR spectrum of (MLCR) particles.

### 3. 3. TGA Analysis

The thermal stabilities of resin and magnetite-loaded resin particles were investigated by recording their thermograms, as depicted in Fig. 3. The comparative depiction of the two profiles clearly reveals that resin particles suffer a major weight loss at 297 °C whereas the magnetite-loaded resin particles begin to lose their weight at 455 °C. The observed enhancement in decomposition

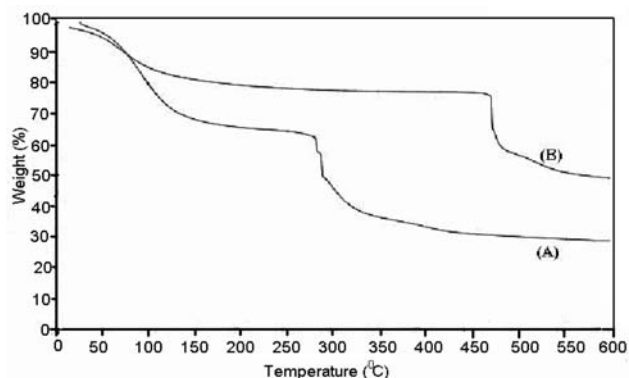


Figure 3: Thermograms of (A) plain resin and (B) MLCR particles.

temperature of magnetite-loaded resin particles may simply be attributed to the presence of magnetite nanoparticles which have fair thermal stability. Moreover, the total weight loss, suffered by the resin and the magnetite-loaded resin particles are 72 and 47 percent respectively. In this way, it may be concluded that magnetite-loaded resin particles show higher thermal stability as compared to the plain resin particles.

### 3. 4. Dynamic Uptake of Cu(II) at Different Temperatures

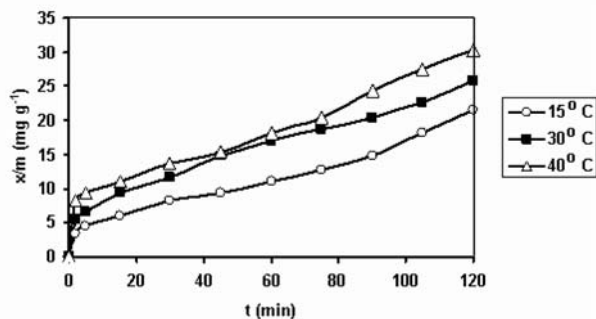
The kinetic of sorption process describes the solute uptake which, in turn, governs the residence time of the adsorption reaction. In order to understand the kinetic aspects of Cu(II) uptake by MLCR particles, the adsorption kinetic experiments were carried out at three temperatures, namely 15, 30, 40 °C for the initial Cu(II) concentration of 20 (mg l<sup>-1</sup>) (see Fig. 4). It is clear that amount of Cu(II) sorbed in mg per g of sorbent (i.e. x/m) increases with temperature, thus indicating that adsorption is favou-

Table 1: Parameters of various kinetic models fitted to experimental data obtained for Cu(II) uptake by MLCR sorbent particles at different temperatures.

S. No.	Kinetic Model	Equation	Parameters obtained at different temperatures		
			15 °C	30 °C	40 °C
1.	Pseudo 1 <sup>st</sup> order	$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t$	R <sup>2</sup> = 0.8946 k <sub>1</sub> = 0.0135	R <sup>2</sup> = 0.9776 k <sub>1</sub> = 0.0015	R <sup>2</sup> = 0.8761 k <sub>1</sub> = 0.0017
2.	Pseudo 2 <sup>nd</sup> order	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$	R <sup>2</sup> = 0.787 k <sub>2</sub> = 0.043	R <sup>2</sup> = 0.918 k <sub>2</sub> = 0.0361	R <sup>2</sup> = 0.8679 k <sub>2</sub> = 0.0311
3.	1 <sup>st</sup> order	$-\ln\left(\frac{C}{C_0}\right) = kt$	R <sup>2</sup> = 0.9835 k <sub>1</sub> = 0.0011	R <sup>2</sup> = 0.9863 k <sub>1</sub> = 0.0015	R <sup>2</sup> = 0.9881 k <sub>1</sub> = 0.0017
4.	2 <sup>nd</sup> order	$\frac{1}{C} - \frac{1}{C_0} = kt$	R <sup>2</sup> = 0.9745 k <sub>2</sub> = 3E-05	R <sup>2</sup> = 0.9911 k <sub>2</sub> = 4E-05	R <sup>2</sup> = 0.9842 k <sub>2</sub> = 5E-05
5.	Simple Elovich	$q = a + 2.303 b \log t$	R <sup>2</sup> = 0.7705 a = -2.0774 b = 3.7675	R <sup>2</sup> = 0.8684 a = -0.8259 b = 4.6492	R <sup>2</sup> = 0.7732 a = 0.9518 b = 4.8849
6.	Power Function	$\log q = \log a + b \log t$	R <sup>2</sup> = 0.9472 a = 2.1434 b = 0.428	R <sup>2</sup> = 0.705 a = 3.711 b = 0.3763	R <sup>2</sup> = 0.8965 a = 5.6027 b = 0.3095

\* All notations carry their usual meaning

red at higher temperatures. The kinetic uptake data was fitted on some kinetic models<sup>21</sup> such as Lagergren equation,<sup>22</sup> Pseudo second order equation,<sup>23</sup> First order equation,<sup>24</sup> Power function model and Simple Elovich equation.<sup>25</sup> The estimated models and their related kinetic parameters are listed in Table 1. Based on linear regression values it can be seen from Table 1 that uptake data is best described by second order equation.



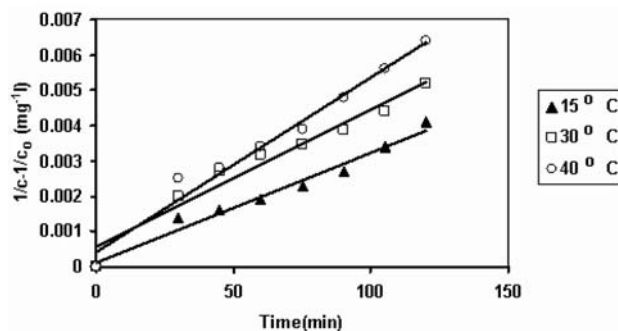
**Figure 4:** The kinetics data for Cu(II) uptake by MLCR particles at different temperatures. [Cu(II)] = 20 mg l<sup>-1</sup>; particle size = 635 μm.

The following integrated rate expression was used to calculate the ‘second order’ rate constants.

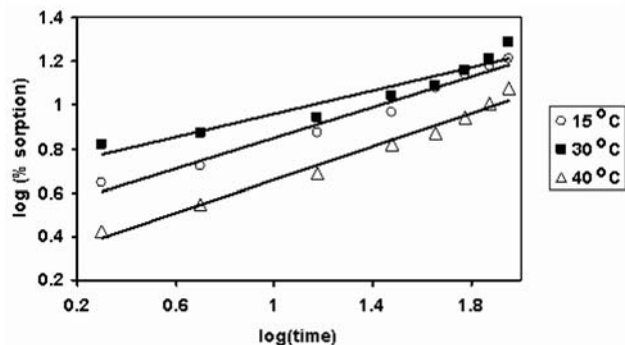
$$\frac{1}{C} - \frac{1}{C_0} = K_{ad}t \quad (1)$$

where  $C_0$  is the initial bulk concentration of the Cu(II) solution, and  $C$  is the concentration at time  $t$ . From the slopes of the linear plots, as depicted in the Fig.5, the adsorption coefficient ( $k_{ad}$ ) values at 15, 30 and 40 °C were calculated and found to be  $3 \times 10^{-5}$ ,  $4 \times 10^{-5}$  and  $5 \times 10^{-5}$  (l mg<sup>-1</sup> min<sup>-1</sup>) respectively. The almost linear nature of plots clearly indicates that Cu(II) uptake follows ‘second order kinetics’.

Owing to the porous nature of the sorbent particles, pore diffusion is also expected. Knocke and Hemphill<sup>26</sup> stated that since diffusion is an endothermic process, the



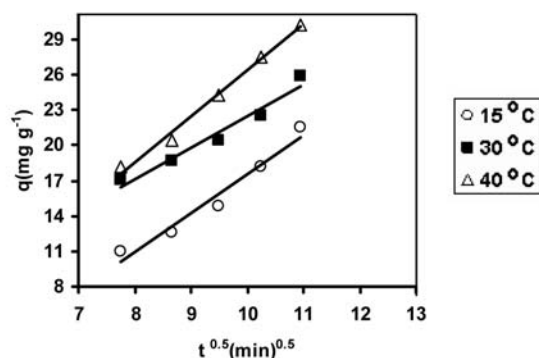
**Figure 5:** Second-order kinetic fit for Cu(II) uptake by MLCR particles at different temperatures. [Cu(II)] = 20 mg l<sup>-1</sup>; particle size = 635 μm.



**Figure 6:** Linear plots obtained between log (% adsorption) and log (time) for Cu(II) uptake by MLCR sorbent particles at different temperatures. [Cu(II)] = 20 mg l<sup>-1</sup>; particle size = 635 μm.

rate of adsorption will increase with an increased solution temperature when pore diffusion is the rate limiting step. So, in the present study, we may expect Cu(II) uptake process to be pore diffusion controlled. To further confirm this, graphs were plotted between log (% adsorption) and log (time) which yielded fair straight lines, (see Fig. 6) thus confirming the occurrence of intra-particle diffusion, which would be rate limiting step. Similar results have also been reported elsewhere.<sup>21</sup> The rate constants of intra-particle diffusion ( $k_{id}$ ) were calculated from the slopes of linear portion of the plots of amount adsorbed  $q$  (mg g<sup>-1</sup>) versus square root of time at three temperatures (see Fig. 7) using the Weber and Morris equation:<sup>27</sup>

$$q = k_{id}t^{0.5} \quad (2)$$



**Figure 7:** Plots to evaluate intraparticle diffusion coefficient  $k_{id}$  for sorption of Cu(II) into MLCR particles at different temperatures. [Cu(II)] = 20 mg l<sup>-1</sup>; particle size = 635 μm.

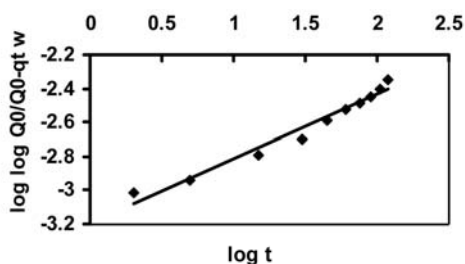
where  $k_{id}$  is the intraparticle diffusion coefficient. According to Weber and Morris equation, initial curve portion represents boundary layer sorption while slope of final linear portion is a measure of intra-particle pore diffusion. The values of  $k_{id}$  at 15, 30 and 40 °C were found to be  $170.2 \times 10^{-2}$ ,  $204.2 \times 10^{-2}$  and  $221.8 \times 10^{-2}$  (mg l<sup>-1</sup> min<sup>-0.5</sup>) respectively.

In order to confirm further the occurrence of intra-particle diffusion, the Bangham equation, as suggested by Rehman et al.<sup>1</sup> was applied to the sorption data in the following form:

$$\log \log \frac{Q_0}{Q_0 - q_t} = \log \frac{k_0 W}{2.303 V} + \alpha \log t \quad (3)$$

where  $Q_0$  is the initial concentration ( $\text{g dm}^{-3}$ ) of metal ions in the solution,  $V$  is the volume of sorbate solution ( $\text{dm}^{-3}$ ),  $W$  is the weight (g) of sorbent,  $q_t$  is the amount of metal ions sorbed ( $\text{g g}^{-1}$ ) at time  $t$ , while  $\alpha$  and  $k_0$  are constants.

Using the kinetic data for Cu(II) uptake at 30 °C, fair linear plot was obtained between  $\log \log Q_0 / (Q_0 - q_t)$  and  $\log t$  (see Fig. 8) which confirmed the validity of Bangham equation. The values of  $\alpha$  and  $k_0$ , as calculated from the slope and intercept of the linear plot, were found to be 0.3781 and  $3.6 \times 10^{-3}$  respectively. The linear nature of plot indicated intra-particle diffusion.

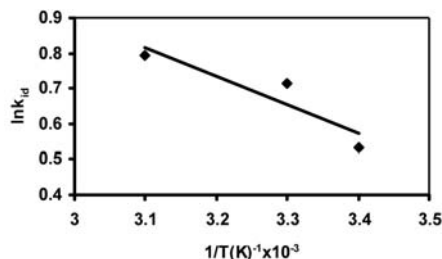


**Figure 8:** Linear plot obtained by fitting dynamic Cu(II) uptake data in Bangham equation to confirm intraparticle diffusion at 30 °C. [Cu(II)] = 20  $\text{mg l}^{-1}$ ; particle size = 635  $\mu\text{m}$ .

The energy of activation was determined from the slope of the Arrhenius plot of  $\ln k_{ad}$  versus  $1/T$  (see Fig. 9) and was found to be 6.78 ( $\text{kJ mol}^{-1}$ ). The relatively lower value suggests that Cu(II) sorption takes place by an activated or a diffusion controlled process. In addition, positive value suggests that sorption is favoured by rise in solution temperature.

### 3. 5. Sorption Isotherm

The effect of temperature on the equilibrium sorption of Cu(II) onto MLCR particles was studied at 15, 30, 40 °C in the concentration range of 20 to 100 ( $\text{mg l}^{-1}$ ) and the equilibrium uptake data was fitted in the rearranged Freundlich isotherm equation.<sup>19</sup> The adsorption isotherm

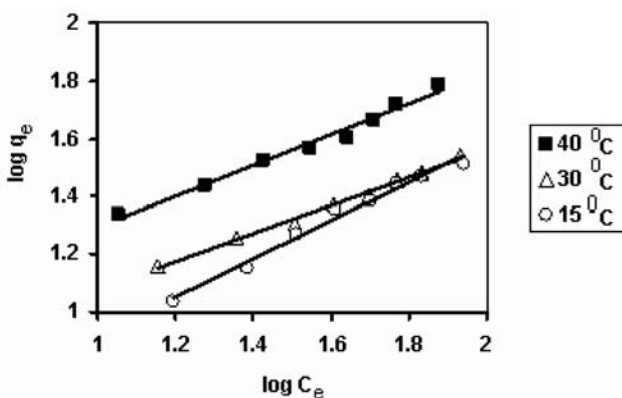


**Figure 9:**  $\ln k_{ad}$  versus  $1/T$  plot for evaluation of activation energy. [Cu(II)] = 20  $\text{mg l}^{-1}$ ; particle size = 635  $\mu\text{m}$ .

indicates how the sorbate molecules are distributed between the liquid phase,  $C_e$  ( $\text{mg l}^{-1}$ ) and the solid phase,  $q_e$  ( $\text{mg g}^{-1}$ ). The linearized Freundlich equation may be given as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

where  $q_e$  is the amount of Cu(II) sorbed per unit weight of sorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration of sorbate solution ( $\text{mg l}^{-1}$ ),  $K_F$  is a measure of sorption capacity and  $1/n$  is sorption intensity. The values of  $K_F$  and  $1/n$ , as obtained from the intercept and slope of the linear plots (see Fig. 10) and also evaluated from the regression analysis have been shown in Table 2. It is clear that the values obtained from experimental linear plots are in close agreement with the regression values, thus indicating the suitability of the Freundlich isotherm on the experimental sorption data. In addition, the magnitude of the exponent  $n$  gives an indication of the favorability and capacity of



**Figure 10:** Freundlich isotherms plots for equilibrium sorption of Cu(II) into 635  $\mu\text{m}$  sized MLCR particles at different temperatures.

**Table 2:** Values of Freundlich constants  $K_F$  and  $1/n$  obtained from equilibrium sorption data of Cu(II) uptake by MLCR sorbent particles at different temperatures.

Temperatures (C°)	Values obtained from			
	Experimental plots		Regression analysis	
	$K_F$	$1/n$	$K_F$	$1/n$
15	1.782	0.6659	1.787	0.6651
30	3.900	0.4862	3.915	0.4852
40	5.799	0.5313	5.798	0.5313

the sorbent/sorbate system. It has been reported<sup>23</sup> that 'n' values, between 1 and 10, represent favorable sorption conditions. In this study, the values of n at different temperatures namely 15, 30, 40 °C were found to be 1.50, 2.85, 1.88 respectively thus suggesting beneficial sorption for the system. Finally, the suitability of Freundlich isotherm in the present study is also indication of the heterogeneous nature of the sorbent surface. This may simply be supported by the argument that surface of MLCR particles contains entrapped magnetite nanoparticles as well as exchangeable cations of resin matrix.

In order to confirm the nature of the sorption process, the equilibrium sorption data was also applied to the Dubinin-Radushkevich (D-R) isotherm model. The D-R equation<sup>26</sup> is:

$$C_{ad} = C_m \exp(-B \varepsilon^2) \quad (5)$$

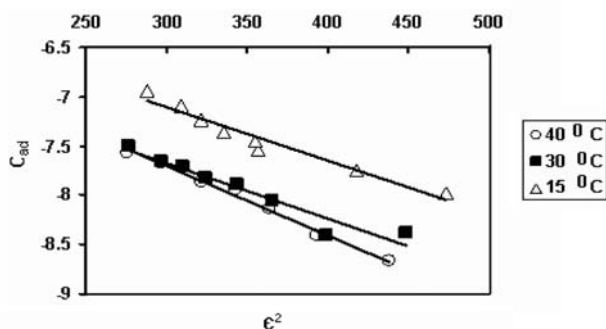
where  $C_{ad}$  is the amount of Cu(II) sorbed,  $C_m$  is the maximum amount of Cu(II) that can be sorbed under the optimized experimental conditions, B is a constant with dimensions of energy, and  $\varepsilon$  is Polanyi potential which is expressed as  $\varepsilon^2 = RT \ln(1+1/C_e)$  where R is a gas constant in ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ), T is the absolute temperature in (K) and  $C_e$  is the equilibrium concentration of Cu(II) in solution. The obvious linearized D-R isotherm is:

$$\ln C_{ad} = \ln C_m - B\varepsilon^2 \quad (6)$$

when  $\ln C_{ad}$  values were plotted against  $\varepsilon^2$ , straight lines were obtained (see Fig.11.) The computed values of B, as obtained from the slope of the linear plots, were found to be -140.6, -166.2, -174.9 ( $\text{kJ mol}^{-1}$ ) at 15, 30, 40 °C respectively. Finally, the mean sorption energy (E) was calculated as:

$$E = 1/\sqrt{-2B} \quad (7)$$

which is the free energy transfer of one mole of solute from infinity to the surface of the MLCR particles. The numerical values of E, as evaluated from equation (7), we-



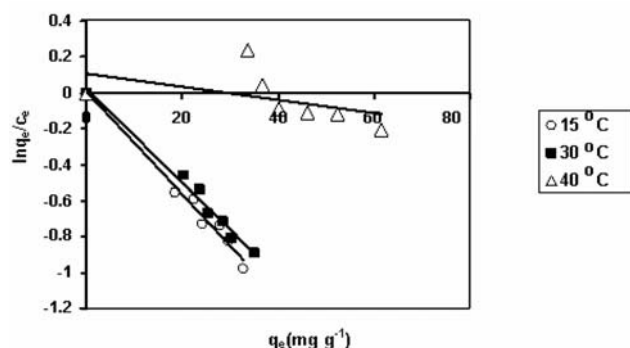
**Figure 11:** Dubinin-Radushkevich isotherm plot for the evaluation of constant B for Cu(II) uptake by 635  $\mu\text{m}$  sized MLCR particles at different temperatures.

re 8.47, 9.45, and 9.6 ( $\text{kJ mol}^{-1}$ ) respectively. Since these values lie in the range of 8–16 ( $\text{kJ mol}^{-1}$ ), the sorption process seems to be mainly governed by ion-exchange mechanism/chemisorption.

### 3. 6. Evaluation of Thermodynamic Parameters

Thermodynamic parameters were calculated from the variation of the thermodynamic distribution coefficient  $k_o$  with change in temperature. The values of  $k_o$  were determined by plotting  $\ln q_e/C_e$  versus  $q_e$  and extrapolating the linear plot to zero  $q_e$  as shown in Fig. 12. The standard free energy,  $\Delta G^0$  was calculated using the expression

$$\Delta G^0 = -RT \ln k_o \quad (8)$$



**Figure 12:**  $\ln q_e/C_e$  versus  $q_e$  plots for evaluation of thermodynamic constant  $k_o$  for sorption of Cu(II) into 635  $\mu\text{m}$  sized MLCR particles at different temperatures.

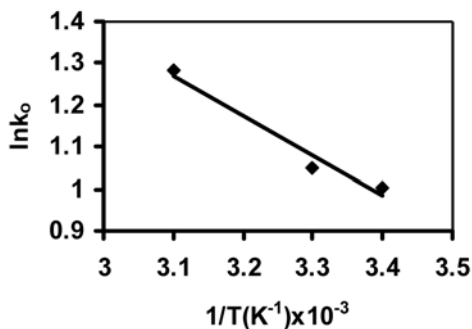
Finally standard enthalpy change  $\Delta H^0$  and entropy change  $\Delta S^0$  were calculated using the slope and intercept of the linear Vant Hoff plot respectively, using the relation:

$$\ln k_o = \Delta S^0/R - \Delta H^0/RT \quad (9)$$

The plot of  $\ln k_o$  versus  $1/T$  has been depicted in Fig. 13. All the values have been shown in Table. 3. It is clear that  $\Delta G^0$  is negative and decreases with temperature, thus indicating that better removal is obtained at higher temperature. The positive value of  $\Delta H^0$  confirms the endothermic nature of the adsorption process. The positive value of

**Table 3:** Various thermodynamic parameters obtained for sorption of Cu(II) ions by MLCR particles at different temperatures.

Temperature (K)	$K_c \times 10^3$	$\Delta G^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^0$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
288	2.1	-5.02		
303	20.6	-51.89	7.97	35.29
313	107.9	-280.78		



**Figure 13:**  $\ln k_0$  versus  $1/T$  plots to evaluate  $\Delta H^\circ$  and  $\Delta S^\circ$  for Cu(II) uptake onto MLCR particles.

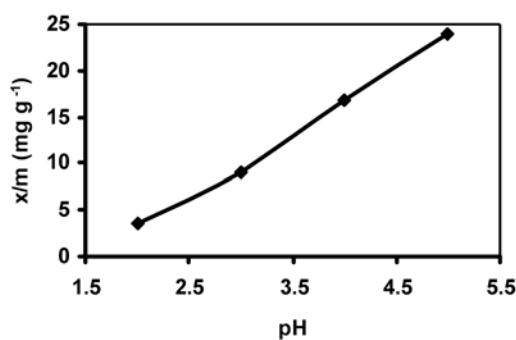
$\Delta S^\circ$  also indicates the increased randomness during sorption process.

### 3. 7. Effect of pH on Cu(II) Sorption

The effect of pH of the sorbate solution on Cu(II)-uptake was investigated by agitating definite quantity of sorbent in sorbate solutions of different pH, in the range of 1.0 to 6.0. It was observed that the amount of Cu(II) sorbed in mg per g of sorbent (i.e.  $x/m$ ) increased with pH of the solution (see Fig. 14). This may be explained by the fact that at lower pH, there exists an appreciable concentration of  $H^+$  ions that compete with the already existing  $Cu^{2+}$  ions for available binding sites. This results in decrease in the Cu(II)-uptake. However, with the increase in pH of the sorbate solution, the numbers of  $H^+$  ions is decreased and hence more sites are now available for Cu(II) uptake. This causes an enhancement in the sorption of Cu(II) ions. Here it is also worth mentioning that the pH of sorbate solution could not be raised above 6.0 due to observed precipitation of Cu(II) as hydroxide.

### 3. 8. Desorption Studies

MLCR particles, loaded with Cu(II), were put in distilled water as well as in HCl solutions of different concentrations, in the range 0.02 M to 0.10 M, for a period of



**Figure 14:** Effect of pH of the sorbate solution on metal uptake at 30 °C.  $[Cu(II)] = 20\ mg\ l^{-1}$ ; particle size = 635  $\mu m$

24 hours. The percent desorption was found in the range of 0.013 to 0.046, thus suggesting almost negligible desorption. This indicates that adsorption of Cu(II) onto MLCR is governed mainly by chemical forces. The almost negligible desorption also supports our presumption of extremely low desorption while fitting the uptake data on 'second order kinetics.'

### 3. 9. Mechanism of Uptake

On the basis of the results of the desorption study, as mentioned above, a probable mechanism for  $Cu^{2+}$  uptake by MLCR particles can be worked out as shown below:

- When MLCR particles are put in Cu(II) solution, there occurs ion-exchange process between  $Na^+$  ions present within the MLCR particles (i.e. exchangeable cations of resin) and  $Cu^{2+}$  ions present in the sorbate solution. So, this ion-exchange mechanism seems to be responsible for Cu(II)-uptake.
- In addition, within the resin matrix, these Cu(II) ions may also co-ordinate with the electron rich oxygen of magnetite nanoparticles.

Therefore, we see that nature of sorbent is heterogeneous which is also supported by the fact that uptake data was well fitted to the Freundlich isotherm which is usually applied for the sorbent with heterogeneous surface.

## 4. Conclusions

From the above study it is concluded that magnetite-loaded cation resin (MLCR) particles are the appropriate sorbent material for magnetic separation of Cu(II) from aqueous solutions. The sorbent particles can easily be removed from the sorbate solution by using moderate magnetic field. This opens the possibilities of using this novel sorbent material in industries for effective removal of toxic metals from industrial effluent.

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## Povzetek

Pri treh temperaturah (15, 30 in 40 °C) smo raziskovali adsorpcijo Cu(II) iz vodnih raztopin na nanodelcih magnetita, vgrajenih v komercialno dostopno kationsko smolo Seralite SRC-120. Izkazalo se je, da adsorpcijo lahko opišemo s Freundlichovo adsorpcijsko izotermo, hitrost procesa pa najbolje ponazori hitrostni zakon 2. reda. Domnevamo, da gre v preiskovanem sistemu za kemisorpcijo, kar potrjuje tudi uspešna aplikacija Dubinin-Radishkevicheve izoterme. Količina adsorbiranega Cu(II) je odvisna od pH raztopine sorbata in doseže maksimalno vrednost pri pH = 6.0. Presenetljiva pa je ugotovitev, da gre za endotermen proces, ki ga spremlja povečanje entropije.