

## COMPARISON OF SIMPLE AND CHELATED AMBERLITE IR-120 FOR PRECONCENTRATION AND DETERMINATION OF Cu(II) FROM AQUEOUS SAMPLES

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**ABSTRACT.** In the present study, the efficiency of simple and chelating Amberlite IR-120 with  $\alpha$ -nitroso  $\beta$ -naphthol (IR- $\alpha$ N $\beta$ N) and with 8-hydroxy quinoline (IR-8HQ) has been compared for the removal of Cu(II) from aqueous solutions. The chelation was confirmed using different characterization techniques like SEM, TGA and FTIR. A number of experiments were carried out in batch system to determine the effect of different parameters on adsorption of Cu(II) like pH, contact time and sample volume. The results showed occurrence of maximum adsorption at pH 7 in 10 min with adsorption capacity of 71.5 mg g<sup>-1</sup> at 298 K. The adsorption followed pseudo second order kinetic model among the four kinetic models applied. Maximum desorption from IR-8HQ was obtained with a mixture of 4.0 M HCl and 0.5 M HNO<sub>3</sub>. Furthermore, IR-8HQ was found to be most selective adsorbent among three adsorbents investigated. The developed preconcentration procedure was successfully applied to spiked tap water and real samples.

**KEY WORDS:** Chelating adsorbent, Amberlite IR-120,  $\alpha$ -Nitroso  $\beta$ -naphthol, 8-Hydrox quinoline, Preconcentration

### INTRODUCTION

With the rapid development of industries, the environmental pollution along with the water pollution containing many toxic metals is important research focuses in terms of natural equilibrium and health of all organisms. To improve the quality and quantity, it is important to monitor the amount of trace metal ions in the samples of environmental importance and it has become a more demanding issue. Industries that introduce trace metals in the environment are predominantly metal sanitizing, paints and tinctures, metal extraction, batteries discharge and industrial effluents [1-3]. Copper is one of the heavy metals that tends to accumulate in the body and causes mucosal irritation, lung cancer, damage to capillary, kidney and liver and gastrointestinal symptoms such as diarrhea, abdominal pain, nausea, and vomiting [4]. Sources of copper in drinking water are mining, ores processes and from industries like chemical, fertilizer, textile dyeing, printing, and paper and pulp mills [5]. This makes the elimination of copper very important not only due its adverse effects on human health but also the probability of its reuse in many industries [6].

Different preconcentration procedures have been broadly used for removal of heavy metals and these include liquid-liquid or ion exchange extraction, coprecipitation, membrane separation and bio or chemical adsorption. Chelating ion exchange adsorption is one of the most nominal preconcentration methods due to its good mechanical stability, selectivity from a large aqueous volume, high enrichment factor, higher degree of interaction between adsorbate and adsorbent, high adsorption capacity for metal ions and regeneration of chelated resins. Therefore the demand of these chelated polymer resins for trace metal determination is increasing day by day. This is because; chelated polymer resins can be used for trace metal investigation mainly for water, biological and geological samples [7].

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Different chelated polymer resins have been used for preconcentration of trace metals. Among these the most widely used are chelated Amberlite XAD-2 [8], XAD-7 [9], XAD-16 [10], XAD-2000 [11] and in addition activated alumina [12], and activated carbon [13] have also been used. Many chelating ligands such as quinolone, 2-amino-2-thiazoline, pyridine and aminophosphonate have been broadly used for chelating polymer resins [14].

The chelated polymer resins with higher adsorption capacities can be prepared by taking chelating ligand of small size with populated functional group bound to a suitably cross-linked polymer. Due to the presence of different donor atoms on chelating ligands like oxygen, sulphur, nitrogen, these chelating ligands become more selective for adsorption of specific metal ion. The most widely used methods applied for preparation of chelated resins are either by simple adsorption of ligand on the polymer resin or by the intermediate functional group such as  $-N=N-$  by diazotization or  $-CH_2-$  by methylene chloride reaction. Chelating polymers synthesized by covalent bonds are much more resistant to external effects than those by simple adsorption [15].

Amberlite IR-120, a vinyl benzene polymer has good chemical, physical and thermal stability. It has high exchange capacity and good ion exchange kinetics. These specific characteristics make it a good resin for use as a solid support. In the present study Amberlite IR-120 has been functionalized with  $\alpha$ -nitroso  $\beta$ -naphthol and 8-hydroxy quinoline for preconcentration and determination of Cu(II) from aqueous samples and the results have been compared with the simple Amberlite IR-120.

## EXPERIMENTAL

### *Instruments*

For characterization of the adsorbents used for preconcentration, scanning electron microscope model JEOL-JSM-5910 (Japan), Perkin Elmer Diamond TG/DTA and FTIR spectrophotometer Pretige 21 Shimadzu (Japan) were used. For the analysis of Cu(II) Perkin Elmer AAnalyst 200 (USA) atomic absorption spectrophotometer was used.

### *Reagents and chemicals*

All chemicals and reagents used in this work were of analytical reagent grade purity and were manufactured by Merck, Germany. Chelating agent 8-hydroxy quinoline was obtained from Scharlau Chemie, USA, while Amberlite IR-120 was obtained from Across Organics, Belgium.

### *Solution preparation*

Stock 1000  $\mu\text{g mL}^{-1}$  copper standard solution was purchased from Merck. Working standards were prepared from this solution by dilution. Britton Robinson buffer solutions of pH 2-8 were prepared according to standard procedure [16] and were used for the adjustment of solution pH.

### *Chelation of Amberlite IR-120*

Chelation of Amberlite IR-120 was done according to the procedure given in literature [15] with little modifications. 20 g of Amberlite IR-120 (acid washed) was added to 80 mL mixture (3:5) of conc. nitric acid and sulphuric acid and was stirred for one h at 60 °C. The mixture was then poured into ice cold water, filtered and washed with distilled water many times until it was free from acid. Nitration was achieved at this step. Nitro group on the polymer was then reduced to amino by refluxing it in the presence of stannous chloride (40 g), conc. hydrochloric acid (50 mL) and distilled ethanol (60 mL) for 12 h at 70 °C. The resultant amino polymer was treated with 100 mL of 2 M hydrochloric acid for 30 min to remove stannous chloride and then washed with distilled water to remove excess of hydrochloric acid. The polymer was then suspended in 250 mL of an ice cold water and to this polymer was added 2 mL of 1 M hydrochloric acid

followed by the addition of 2 mL of 1 M sodium nitrite with constant stirring for 30 min for diazotization. The diazotized resin was filtered, washed with ice cold water and was then coupled with  $\alpha$ -nitroso  $\beta$ -naphthol ( $\alpha$ N $\beta$ N) by stirring it for 3 hours in 100 mL of 3%  $\alpha$ -nitroso  $\beta$ -naphthol solution prepared in distilled ethanol. After coupling the chelated resin was washed with ethanol to remove any unreacted  $\alpha$ -nitroso  $\beta$ -naphthol. Chelation with 8-hydroxy quinoline (8HQ) was also done using the same procedure. The proposed reaction mechanism is given in Figure 1.

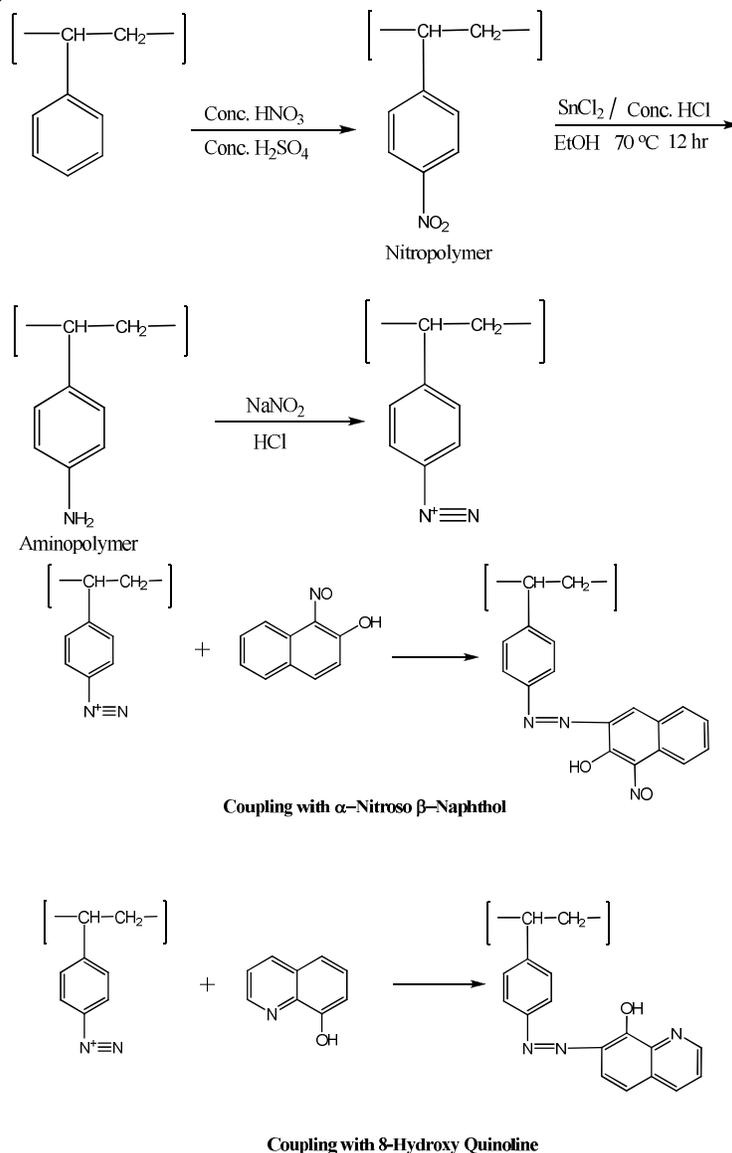


Figure 1. Proposed reaction mechanism for modification of Amberlite IR-120 with  $\alpha$ N $\beta$ N and 8HQ.

*Batch adsorption experiments using simple and chelated resins*

For the adsorption of Cu(II) from aqueous solutions, 100 mg of simple and chelated resins were taken in separate beakers. To each beaker 50 mL of  $10 \mu\text{g mL}^{-1}$  of Cu(II) solution was added. The pH of each solution was adjusted to the required pH by adding suitable volume of Britton Robinson buffer and was allowed to equilibrate for 60 min. Then it was filtered and the filtrate was collected in a 100 mL volumetric flask and diluted up to mark. Desorption of the adsorbed Cu(II) was carried out with 10 mL mixture of nitric acid and hydrochloric acid (0.5: 4 M). The residual metal ions concentration in the filtrates was determined using flame atomic absorption spectrophotometer (FAAS).

Adsorption capacity ( $q_e$ ) of Cu(II) and percent adsorption was calculated according to the Equation 1 and 2:

$$q_e = \left[ \frac{C_i - C_f}{m} \right] V \quad (1)$$

$$\% \text{ adsorption} = \left[ \frac{C_i - C_f}{C_i} \right] \times 100 \quad (2)$$

In Equation 1 and 2  $q_e$  is the amount of Cu(II) adsorbed on the adsorbent ( $\text{mg g}^{-1}$ ),  $C_i$  and  $C_f$  represent the initial and equilibrium concentrations of Cu(II) in  $\mu\text{g mL}^{-1}$ , respectively;  $V$  is the volume of Cu(II) solution (mL) and  $m$  is the amount of adsorbent (g).

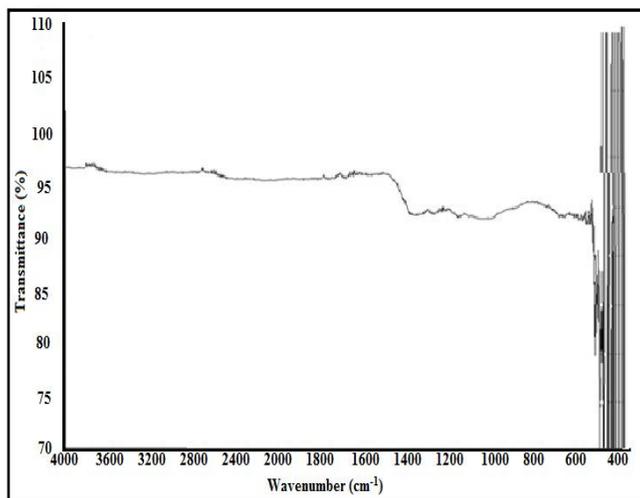
**RESULTS AND DISCUSSION**

Figure 2. FTIR spectrum of unmodified Amberlite IR-120.

*Characterization of simple and chelated IR- $\alpha$ N $\beta$ N and IR- $\delta$ HQ*

In order to confirm the chelation of Amberlite IR-120, various characterization studies using FTIR, SEM and TGA were conducted. The FTIR spectra of simple and chelated Amberlite were recorded and are shown in Figure 2 and 3, respectively. On comparing the spectra, it was clear that in case of chelated Amberlite IR-120, new IR bands have appeared. These bands are at  $1526\text{ cm}^{-1}$  for  $\nu(\text{N}=\text{O})$ ,  $1348\text{ cm}^{-1}$  for  $\nu(\text{N}-\text{H})$  and  $\delta(\text{N}-\text{H})$ ,  $1626$  and  $1383\text{ cm}^{-1}$   $\nu(\text{C}=\text{O})$  and  $1540\text{ cm}^{-1}$  for  $\text{N}=\text{N}$  group [17]. Thus FTIR analysis indicated the successful chelation of Amberlite IR-120.

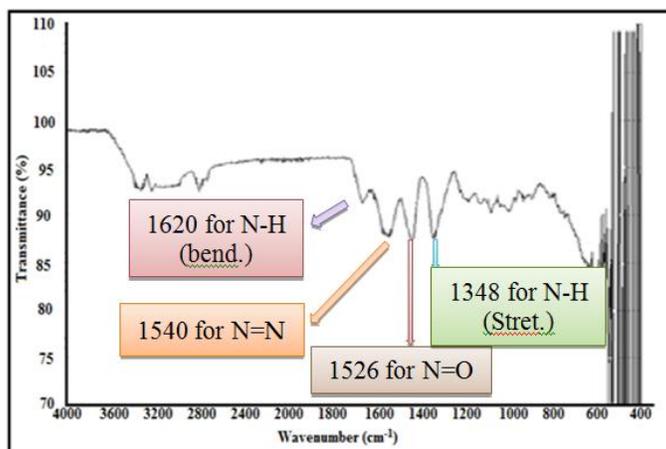


Figure 3. FTIR spectrum of modified Amberlite IR-120.

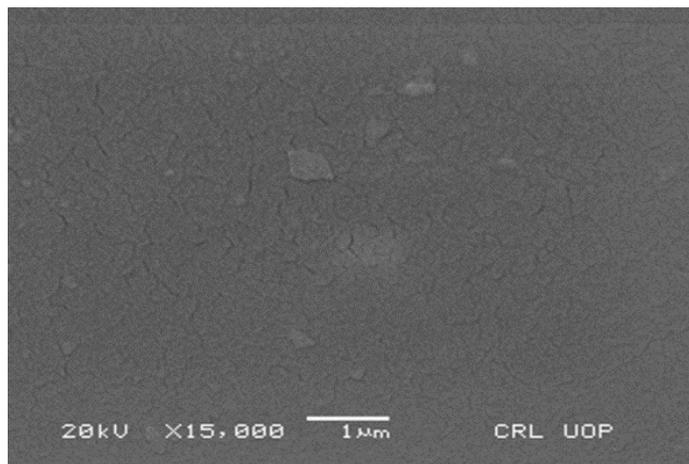


Figure 4. SEM of IR-120.

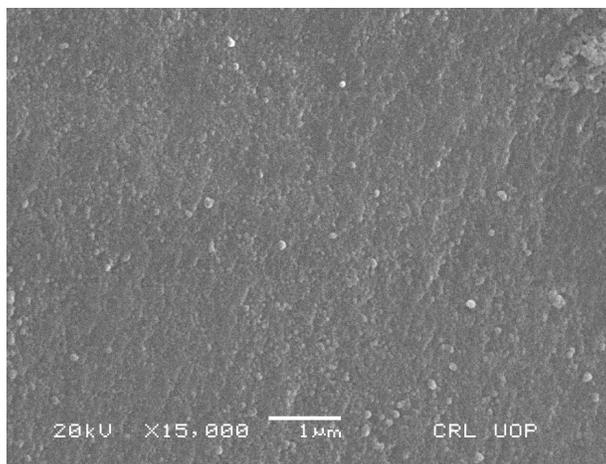


Figure 4a. SEM of IR-αNβN.

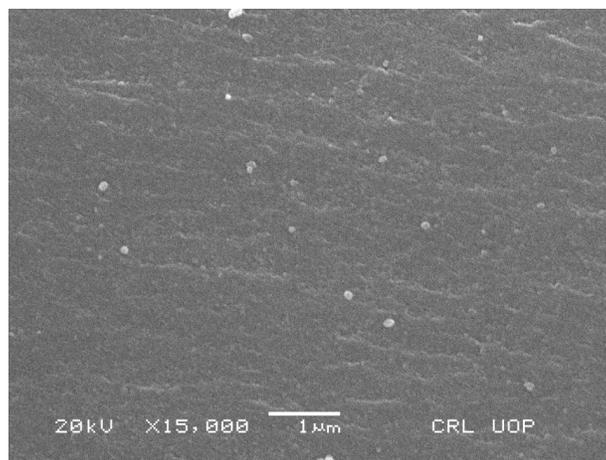


Figure 4b. SEM of IR-8HQ.

The surface morphology of simple and chelated Amberlite IR-120 was investigated by SEM at 15000X magnification. SEM images are shown in Figure 4, 4a and 4b. On comparing these images, it can be seen that the surface of Amberlite IR-120 has been modified and has become smoother after chelation with  $\alpha$ -nitroso  $\beta$ -naphthol and 8-hydroxy quinolone indicating the successful chelation.

The thermal stability of simple and chelated Amberlite IR-120 was investigated using TGA and is shown in Figure 5. The TGA curve of IR-120 showed two step mass losses up to 400 °C. In the first step the mass loss was 18% at 310 °C which may be due to the loss of adsorbed water. In the second step the mass loss was 52% with greater rate at 410 °C. In case of IR- $\alpha$ N $\beta$ N, the TGA curve showed two step mass losses. In the first step the mass loss was 20% at

300 °C and in the second step at 360 °C, the mass loss was 60%. Similarly the TGA curve of IR-8HQ showed two step mass losses. In the first step the mass loss was 20% at 380 °C and the mass loss in the second step was 40% at 450 °C. The TGA study shows that skeletal structure of IR-8HQ is strongly linked as compared to IR-120 or IR- $\alpha$ N $\beta$ N.

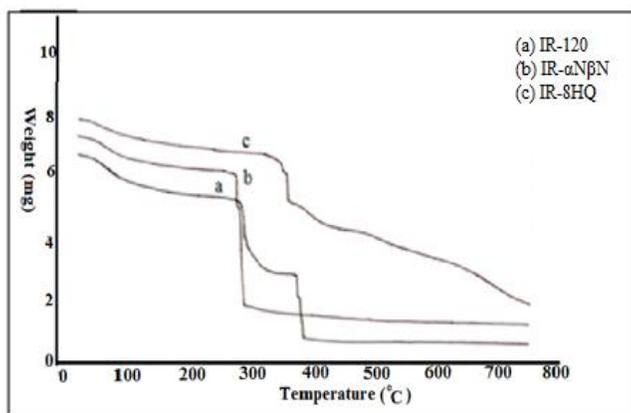


Figure 5. TGA of IR-120 (a), IR- $\alpha$ N $\beta$ N (b) and IR-8HQ (c).

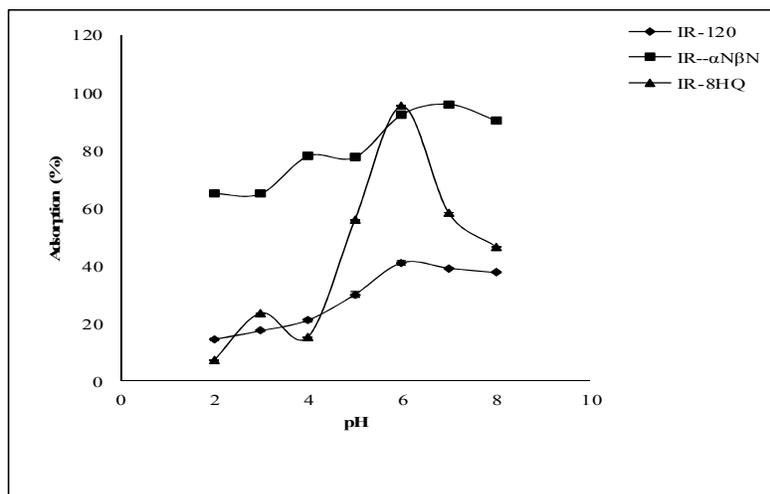


Figure 6. Effect of pH on % adsorption of Cu(II) from aqueous solution using IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

#### Effect of pH

The solution pH is an important factor which affects the adsorption phenomenon. In order to see the effect of pH on adsorption of Cu(II) on these three adsorbents, pH of the solution was varied from 2.0 to 8.0 using Britton Robinson buffer and the results are shown in Figure 6. The

adsorption process strictly depends upon solution pH. It can be seen from the figure that maximum adsorption, 41% and 95% was observed at pH 6 for IR-120 and IR-8HQ, respectively while in case of IR- $\alpha$ N $\beta$ N maximum adsorption (96%) was observed at pH 7. At lower pH, adsorption was less which may be due to competition between H<sup>+</sup> and the metal ion for the binding/exchange sites. The adsorption decreased at higher pH owing to the formation of hydroxide of the metal ions.

#### *Effect of contact time*

Contact time is another important parameter in adsorption process; therefore, the effect of contact time on adsorption behavior of Cu(II) was investigated in the range of 5 to 70 min and the results are shown in Figure 7. Generally, adsorption increases with increase in contact time and the same results were also observed with adsorption of Cu(II). This may be due to the availability of adsorption sites on adsorbent for the target metal ions. As the adsorption process continues, the adsorption sites become occupied and the adsorption process becomes slow. The adsorption of Cu(II) increased from 17.4% to 41.0% in 60 min for IR-120 and for IR-8HQ, adsorption increased from 38.5% to 95.3%. In case of IR- $\alpha$ N $\beta$ N, the rate of Cu(II) adsorption was quite fast as compared to other two adsorbents and adsorption reached to 97.8% in first 10 min which indicate that the chelation of Cu(II) with IR- $\alpha$ N $\beta$ N is faster as compared to IR-8HQ.

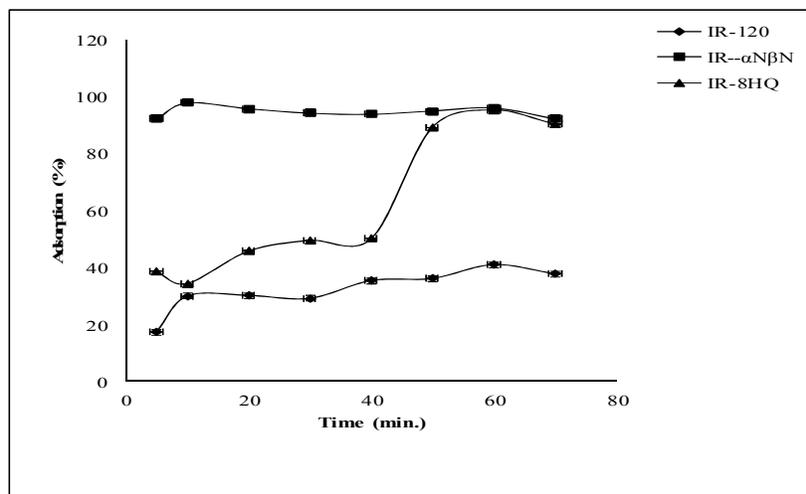


Figure 7. Effect of contact time on % adsorption of Cu(II) from aqueous solution using IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

#### *Adsorption kinetics*

The adsorption kinetic data of Cu(II) were fitted in four common kinetic models like pseudo first order, pseudo second order, intraparticle diffusion and Elovich equations. The model for pseudo first order is expressed by Equation 3:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where  $q_e$  is the amount of metal ion adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium,  $q_t$  is the amount of metal ions adsorbed ( $\text{mg g}^{-1}$ ) at any given time (min) and  $K_1$  is the pseudo first order reaction rate constant for adsorption ( $\text{min}^{-1}$ ). The model for pseudo second order is expressed with the help of Equation 4:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \tag{4}$$

where  $q_e$  is the amount of metal ion adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium,  $q_t$  is the amount of metal ions adsorbed ( $\text{mg g}^{-1}$ ) at any given time (min) and  $K_2$  is the pseudo second order reaction rate constant for adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

The constant values of first order kinetics  $K_1$ ,  $q_e$ ,  $R^2$  and the second order kinetics  $K_2$ ,  $q_e$  and  $R^2$  were calculated from the slope and intercept of linear line of each model respectively and are given in Table 1. It was observed that not only the correlation coefficient values of the pseudo second order model are higher than that of first order model but the  $q_e$  values of the second order are closer to the experimental  $q_e$  values. This suggests that the adsorption might be controlled by pseudo second order model.

Table 1. Kinetic parameters of Cu(II) adsorption using IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

Adsorbent	$q_e$ ( $\text{mg g}^{-1}$ ) (exp.)	Pseudo first order kinetic model			Pseudo second order kinetic mode			Intraparticle diffusion model			Elovich model		
		$K_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$K_{int}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	C	$R^2$	$\alpha$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )	$\beta$ ( $\text{g mg}^{-1}$ )	$R^2$
IR-120	1.14	0.020	0.616	0.809	0.072	1.21	0.959	0.091	0.323	0.878	0.398	4.69	0.866
IR- $\alpha$ N $\beta$ N	2.76	0.029	0.456	0.970	0.200	2.79	0.999	0.066	2.20	0.968	7.51E+4	6.35	0.981
IR-8HQ	2.45	0.038	2.325	0.826	0.012	3.20	0.885	0.276	0.123	0.938	0.349	1.62	0.840

Intraparticle diffusion is a kinetic model which is related to the transfer of adsorbate ions from its aqueous media to the pores of adsorbent. This model is generally expressed by the Equation 5:

$$q_t = K_{int} t^{1/2} + C \tag{5}$$

where C is the intercept and related to the thickness of the boundary layer and  $K_{int}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the intraparticle diffusion rate constant. The values of these constants were calculated directly from the intercept and slope of the graph and are given in Table 1. The plot of  $q_t$  versus  $t^{1/2}$  is not passing through the origin which indicates that intraparticle diffusion is not the controlling step during adsorption of Cu(II) on these three adsorbents and some other mechanisms are involved.

The Elovich kinetic equation is used to describe the kinetics of chemisorption on heterogeneous surfaces and is given by Equation 6:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{6}$$

where  $q_t$  is the amount of Cu(II) adsorbed ( $\text{mg g}^{-1}$ ) at time (t),  $\alpha$  and  $\beta$  are known as the Elovich coefficients,  $\alpha$  represents the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption ( $\text{g min}^{-1}$ ), respectively. The Elovich coefficients were calculated from the linear plot of  $q_t$  versus  $\ln(t)$ . It may be concluded from

kinetic data that pseudo second order kinetic model is a best choice to describe the experimental data as compared to other models.

#### *Adsorption isotherms*

The isotherm models were used to design the adsorption systems of the Cu(II). These models provide a relationship between the amount of Cu(II) adsorbed on the adsorbents and the concentration of Cu(II) in solution at equilibrium. The two most commonly used isotherms models Freundlich and Langmuir were applied to study the adsorption of Cu(II) on the three adsorbents. The Freundlich isotherm is used generally for non-ideal adsorption on heterogeneous surfaces and is expressed by Equation 7:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

The linear form of Freundlich equation is given in Equation 8:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

where  $K_F$  is the Freundlich adsorption isotherm constant ( $\text{mg g}^{-1}$ ),  $1/n$  ( $\text{g L}^{-1}$ ) and is a measure of the adsorption intensity or the heterogeneity factor whereas  $n$  is the measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of  $n$  is equal to unity, the adsorption is linear; if the value is below unity, the adsorption is chemical and if the value of  $n$  is above unity then adsorption is a favorable physical process.  $q_e$  is the amount adsorbed ( $\text{mg g}^{-1}$ ) and  $C_e$  is the equilibrium concentration ( $\mu\text{g mL}^{-1}$ ).

The Langmuir isotherm is used for monolayer adsorption on a homogeneous surface and is expressed with the help of Equation 9:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (9)$$

In a linear form, it is expressed by Equation 10:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (10)$$

where  $C_e$  is the equilibrium concentration ( $\mu\text{g mL}^{-1}$ ),  $q_e$  is the amount of solute adsorbed per gram of adsorbent,  $K_L$  and  $a_L$  are the Langmuir adsorption isotherm constants and are related to the maximum adsorption capacity ( $\text{L g}^{-1}$ ) and bonding strength ( $\text{L mg}^{-1}$ ), respectively. The theoretical monolayer adsorption capacity is  $Q_0$  and is numerically equal to  $K_L a_L^{-1}$ .

From the linear form of these isotherm models for Cu(II) adsorption on the three adsorbents, the constant parameters of these isotherms were calculated from the slope and intercept of the linear form of these equations and are given in Table 2. The  $n$  values are higher than unity, suggesting that adsorption of Cu(II) on the three adsorbents is a favorable physical process. Maximum adsorption capacities of IR-120, IR- $\alpha\text{N}\beta\text{N}$  and IR-8HQ were calculated from the linear form of Langmuir isotherm and were found to be 60.28, 73.89 and 71.50  $\text{mg g}^{-1}$ , respectively. It can be seen that IR- $\alpha\text{N}\beta\text{N}$  has maximum adsorption capacity as compared to the other two adsorbents. It may be concluded from these results that the adsorption data of Cu(II) on these three adsorbents were fitted into Langmuir isotherm model with high correlation coefficient ( $R^2 > 0.99$ ).

Table 2. Freundlich and Langmuir isotherm constants for the adsorption of Cu(II) using IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

Adsorbent	Freundlich model				Langmuir model			
	$K_F$ ( $\text{mg g}^{-1}$ )	$n$	$1/n$	$R^2$	$a_L$ ( $\text{L mg}^{-1}$ )	$K_L$ ( $\text{L g}^{-1}$ )	$Q_o$ ( $\text{mg g}^{-1}$ )	$R^2$
IR-120	0.220	4.37	0.299	1.000	3.77	227	60.3	0.993
IR- $\alpha$ N $\beta$ N	0.150	5.24	0.190	0.996	2.02	149	73.9	0.992
IR-8HQ	0.091	8.73	0.114	0.867	6.08	435	71.5	0.999

### Selectivity study

The selectivity study is very important because foreign ions if present along with the target metal ion may form complexes with the chelated adsorbent thus affecting the adsorption of target metal ion. Therefore, the selectivity of the simple and chelated adsorbents was evaluated by studying the effect of selected foreign ions in the range of 50 to 500  $\mu\text{g}$  under optimum conditions on adsorption capacity of the adsorbents for the target metal ion (Figure 8-10). It can be seen from Figure 9 that for IR-120, foreign ions are affecting the adsorption capacity of the resin whereas by chelation this interference can be minimized. In case of IR-120 the effect of interfering ions is minimal at lower concentration of foreign ions whereas it increases with increase in the amount of foreign ions. % adsorption of Cu(II) decreased up to 49, 50, 54, 44, 22, 49, 43, 51 and 49 in the presence of 500  $\mu\text{g}$  of K(I), Na(I), Mg(II), Ca(II), Cd(II), Co(II), Zn(II), Ni(II) and Fe(III), respectively. It can be seen from Figure 10 and 11 that adsorption capacity of IR- $\alpha$ N $\beta$ N and IR-8HQ was not affected by foreign ions at low concentration of these ions. With increase in concentration of foreign ions a slight decrease in the adsorption capacity was observed in case of IR- $\alpha$ N $\beta$ N while no effect or a very small decrease in adsorption capacity was observed for IR-8HQ. At very high concentration only Fe(III), Ni(II) and Ca(II) posed serious interference effect. In terms of % adsorption of Cu(II), it decreased up to 57, 59, 84, 71, 65, 69, 54, 70 and 69 in the presence of 500  $\mu\text{g}$  of K(I), Na(I), Mg(II), Ca(II), Cd(II), Co(II), Zn(II), Ni(II) and Fe(III) respectively in case of IR- $\alpha$ N $\beta$ N. Whereas in case of IR-8HQ, % adsorption of Cu(II) decreased up to 89, 88, 89, 83, 85, 89, 91, 79 and 49 in the presence of 500  $\mu\text{g}$  of K(I), Na(I), Mg(II), Ca(II), Cd(II), Co(II), Zn(II), Ni(II) and Fe(III), respectively.

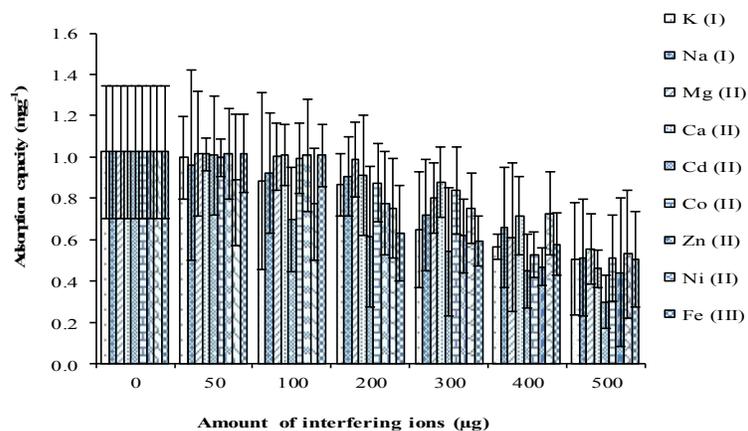


Figure 8. Effect of interfering ions on sorption capacity of Cu (II) using IR-120.

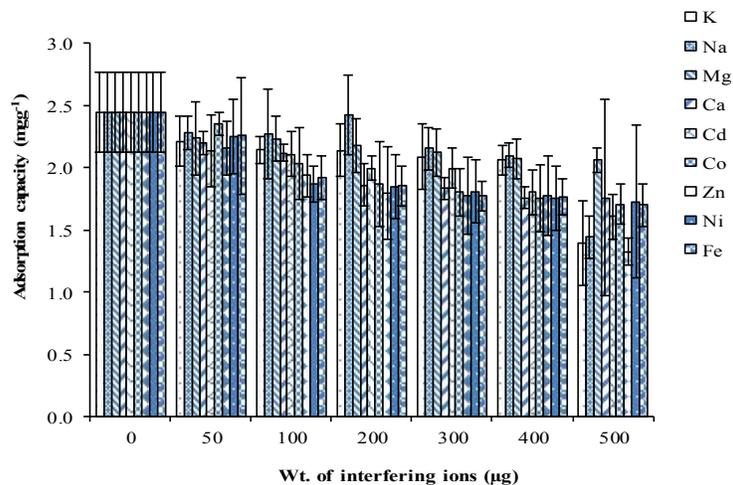


Figure 9. Effect of interfering ions on sorption capacity of Cu (II) using IR- $\alpha$ N $\beta$ N.

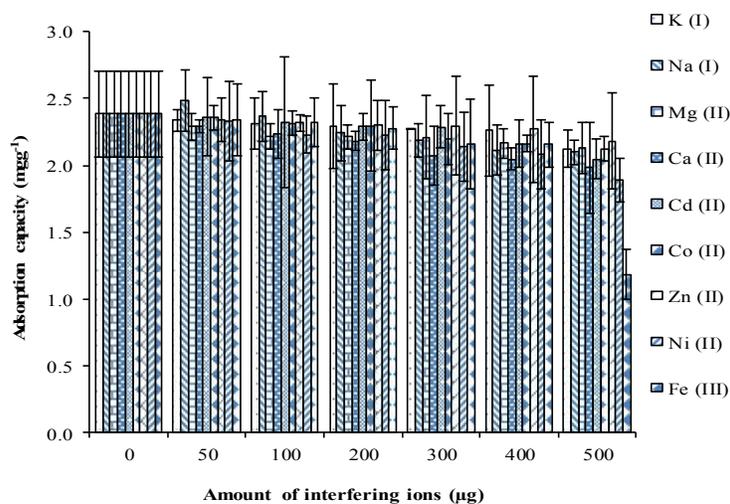


Figure 10. Effect of interfering ions on sorption capacity of Cu (II) using IR-8HQ.

#### Desorption studies

Desorption of the adsorbed metal ions is very important not only for preconcentration and subsequent determination of metal ion at trace level but also for the reuse of the adsorbents. For this purpose, various concentration of hydrochloric acid (0.4-5 M) and nitric acid (0.3-1.2 M) were tried and the residual concentration of Cu(II) was determined by FAAS. It can be seen from the Table 3 that desorption with HNO<sub>3</sub> and HCl was ineffective in case of unmodified IR-120 and IR- $\alpha$ N $\beta$ N while in case of IR-8HQ, 73% and 82% of Cu(II) was recovered with 1.2 M HNO<sub>3</sub> and 4 M HCl, respectively.

In order to completely desorb the adsorbed Cu(II), a mixture of HCl and HNO<sub>3</sub> was also tried in different ratios. The results are shown in Table 4. It can be seen from the table that maximum desorption (86%) was achieved with a mixture of 4 M HCl and 0.5 M HNO<sub>3</sub> (3:2) from Cu(II) loaded IR-8HQ. This indicates that for preconcentration and for the purpose of determination of Cu(II) at trace level, IR-8HQ is the best option.

Table 3. The effect of various eluents on % desorption of Cu(II) from IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

Eluents	Desorption (%)		
	IR- 120	IR- $\alpha$ N $\beta$ N	IR- 8HQ
0.3 M HNO <sub>3</sub>	29.5±0.07	7.12±0.04	41.9±0.01
0.5 M HNO <sub>3</sub>	16.9±0.04	23.2±0.02	74.9±0.04
0.7 M HNO <sub>3</sub>	16.0±0.06	10.8±0.09	42.5±0.02
0.9 M HNO <sub>3</sub>	25.0±0.08	10.2±0.02	47.6±0.03
1.0 M HNO <sub>3</sub>	11.8±0.02	13.0± 0.02	66.5±0.05
1.2 M HNO <sub>3</sub>	19.5±0.02	19.7±0.04	73.2±0.05
0.4 M HCl	65.3±0.09	10.3±0.04	53.8±0.01
0.6 M HCl	57.0±0.01	15.7±0.02	72.8±0.02
0.8 M HCl	20.4±0.02	23.0±0.04	73.5±0.02
1.0 M HCl	3.41±0.026	21.9±0.03	75.0±0.02
2.0 M HCl	56.4±0.02	14.6 ±0.09	73.4±0.04
3.0 M HCl	24.5±2.13	15.5±0.02	57.0±0.03
4.0 M HCl	18.5±0.04	14.9±0.09	82.0±0.05
5.0 M HCl	4.57±0.08	21.0±0.04	22.0±0.03

Table 4. Desorption of Cu (II) with mixture of HNO<sub>3</sub> and HCl from loaded IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

IR-120		IR- $\alpha$ N $\beta$ N		IR-8HQ	
HNO <sub>3</sub> : HCl (0.3 M : 0.4 M)	Desorption (%)	HNO <sub>3</sub> : HCl (0.5 M : 0.8 M)	Desorption (%)	HNO <sub>3</sub> : HCl (0.5 M : 4 M)	Desorption (%)
2 : 18	9.43±0.03	2 : 18	44.7±0.04	2 : 18	71.4±0.02
4 : 16	13.7±0.01	4 : 16	40.6±0.14	4 : 16	84.5±0.02
6 : 14	18.2±0.15	6 : 14	45.7± 0.09	6 : 14	66.9±0.01
8 : 12	14.3±0.17	8 : 12	45.2±0.04	8 : 12	86.1±0.06
10 : 10	56.5±0.06	10 : 10	44.4±0.15	10 : 10	61.0±0.02
12 : 8	55.2±0.02	12 : 8	31.7±0.06	12 : 8	48.0±0.01
14 : 6	6.04±0.02	14 : 6	40.2±0.02	14 : 6	69.0±0.03
16 : 4	5.63±0.01	16 : 4	38.6±0.02	16 : 4	63.4±0.03
18 : 2	10.8±0.02	18 : 2	41.2±0.04	18 : 2	39.7±0.02

The effects of shaking time on desorption of Cu(II) from IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ was also investigated in the range of 10 to 70 min. The optimum shaking time for desorption of Cu(II) from IR-120 was 50 min and for IR- $\alpha$ N $\beta$ N and IR-8HQ was 60 min. This indicated stronger bonding with chelated adsorbents as expected than with the simple one. Further it was observed that maximum extraction of Cu(II) occurred with IR-8HQ.

#### *Effect of sample volume on adsorption capacity and desorption*

For finding out the effect of sample volume, the total metal concentration (500  $\mu$ g) and the amount of adsorbent (0.1 g) were kept constant and the sample volume was varied from 50 mL to 500 mL. It was observed that the adsorption of Cu(II) decreases with increasing sample volume in case of IR-120 whereas an increase was observed for IR-8HQ and IR- $\alpha$ N $\beta$ N. A linear

increase in the adsorption capacity was observed for the IR-8HQ with increase in the sample volume.

Desorption of Cu(II) was also carried out using different volumes for each adsorbent under optimum condition. It was observed that minimum adsorption take place with increase in sample volume in case of simple Amberlite therefore maximum desorption was achieved with increase in sample volume.

The preconcentration factor was calculated for each adsorbent and is given in Table 5. From the table it can be seen that the maximum preconcentration factor of 50 was obtained for IR-8HQ with maximum desorption of Cu(II).

Table 5. Preconcentration factor for Cu(II) from IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

Initial sample volume (mL)	Final eluent volume (mL)	Preconcentration factor			Desorption (%)		
		IR-120	IR- $\alpha$ N $\beta$ N	IR-8HQ	IR-120	IR- $\alpha$ N $\beta$ N	IR-8HQ
50	10	5	5	5	65.3	45.7	86.1
100	10	10	10	10	100	44.8	100
150	10	15	15	15	100	59.8	100
200	10	20	20	20	100	54.3	100
300	10	35	35	35	100	66.5	100
400	10	40	40	40	100	71.7	100
500	10	--	50	50	0	100	100

#### Reusability of IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ

Reusability of the simple and chelated resins was studied for Cu(II) with suitable eluting solvents for three consecutive adsorption desorption cycles. IR-120 and IR- $\alpha$ N $\beta$ N cannot be reuse as % adsorption of Cu(II) decreases to 0.00 whereas IR-8HQ can be reuse five times with a little decrease in % adsorption of Cu(II).

#### Application/recovery studies of the method

The simple and chelated resins were used for the determination of Cu(II) in aqueous samples collected from river Jhelum and from the selected tube well and tap water. The aqueous samples were spiked with known concentration of Cu(II) and their adsorption and desorption was studied. The results are given in Table 6. The adsorption of Cu(II) was 38-42% for IR-120 and 92-96% for IR- $\alpha$ N $\beta$ N and IR-8HQ. It was observed that IR-8HQ is more efficient as compared to other two adsorbents with recovery of 86%.

Table 6. Real sample application for the preconcentration and determination of Cu(II) with IR-120, IR- $\alpha$ N $\beta$ N and IR-8HQ.

Sample	Spiked aqueous samples							
	$\mu\text{g mL}^{-1}$ added	$\mu\text{g mL}^{-1}$ found	Adsorption (%)			Desorption (%)		
			IR-120	IR- $\alpha$ N $\beta$ N	IR-8HQ	IR-120	IR- $\alpha$ N $\beta$ N	IR-8HQ
River Jhelum	5	5.22 $\pm$ 0.23	41.9 $\pm$ 0.71	95.50 $\pm$ 0.12	94.3 $\pm$ 0.32	56.9 $\pm$ 0.34	44.7 $\pm$ 1.04	85.9 $\pm$ 0.14
Tube well	5	5.26 $\pm$ 0.41	38.9 $\pm$ 0.13	96.1 $\pm$ 0.13	95.0 $\pm$ 0.23	46.5 $\pm$ 0.01	40.2 $\pm$ 0.42	86.0 $\pm$ 0.02
Tap water	5	4.89 $\pm$ 0.48	40.5 $\pm$ 0.25	92.3 $\pm$ 0.23	93.9 $\pm$ 0.13	50.5 $\pm$ 0.36	41.2 $\pm$ 0.35	86.6 $\pm$ 0.10

*Comparison with other adsorbents*

The efficiency of chelated Amberlite IR-120 with 8-hydroxyquinoline for removal of Cu(II) has been compared with other adsorbents given in literature and this comparison is given in Table 7. Although direct comparison of adsorption capacity of IR-8HQ adsorbent (present work) with other adsorbents is difficult since different experimental conditions are applied for different adsorbents. However it was found that the adsorption capacity of IR-8HQ is much higher than the other adsorbents already reported. This result indicates that IR-8HQ is one of the good adsorbents for the removal of Cu(II) from aqueous samples.

Table 7. Comparison of maximum adsorption capacity of different adsorbents for Cu(II).

Adsorbent	Maximum adsorption capacity (mg g <sup>-1</sup> )	Reference
Cationic resin TP 207	68.7	[18]
CT-8HQ	52.9	[19]
PTFE selective resin	39.84	[20]
Undaria pinnatifida	38.82	[21]
Granular activated carbon	38	[22]
Electric furnace slag	32.68	[23]
H-ePAN fibre mats	31.3	[24]
Chitosan	16.80	[23]
Ethylenediamine grafted silica	16.58	[24]
Peanut hulls	10.17	[24]
Hazelnut husk A.C.	6.645	[24]
Kaolinite	10.8	[25]
Anatase-type titaniumn	1.3	[25]
Phosphate rock	10.8	[25]
IR-8HQ	71.5	Present work

**CONCLUSIONS**

Simple and chelated Amberlite IR-120 with  $\alpha$ -nitroso- $\beta$ -naphthol (IR- $\alpha$ N $\beta$ N) and with 8-hydroxy quinoline (IR-8HQ) was compared for the removal of Cu(II) from aqueous solutions in batch systems. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) confirmed the successful chelation of adsorbents. Among the three adsorbents used IR-8HQ was found to be the best adsorbent for removal of Cu (II), preconcentration and in respect of its reusability. It was observed that the adsorption of Cu(II) was strictly pH dependent. The adsorption data followed Langmuir isotherm. Pseudo second order kinetic model was found to be the best choice as compared to the other kinetic models investigated for description of the data. For reusability of the adsorbents, desorption studies were conducted and maximum desorption (86%) was observed with a mixture of 4 M HCl and 0.5 M HNO<sub>3</sub> from IR-8HQ. The method was successfully applied to spiked tap water and real samples.

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