Selective Removal of Toxic and Heavy Metal Ions like Arsenic and Copper from Drinking Water by Using Novel Chelating Resins Immobilized on Silica Gel

Debasis Mohanty[1],*, Sandhyarani Acharya[2], and Shashadhar Samal[3]

[1]Dhenkanal College, Dhenkanal-759001, Odisha, India
[2] KMBB College of Engineering & Technology, Daleiput, Khurda, India
[3] S.B. Rath Govt. (Auto) Women's College, Berhampur, India

ABSTRACT

A new resin (*o*-HB-DAP-HCHO) obtained by condensing the Schiff base of *o*-hydroxybenzaldehyde-2, 6-diaminopyridine (*o*-HB-DAP) with formaldehyde(HCHO) was used as polymeric ion exchange resin for separation and preconcentration of metal ions. The metal ion uptake studies were determined by spectrophotometry. To increase the efficiency of the resin it was immobilized on silica gel. By the impregnation of silica gel more coordinating sites are exposed to metal ions. The adsorption behaviour of the impregnated resins towards Cu (II), Ni (II), and Fe (III) was studied by batch as well as column techniques with the variation of different parameters. The conditions for separation of Cu (II) from a Cu (II)/Ni (II) mixture were ascertained. The resin showed more effectiveness in the adsorption process towards Cu (II) ions in both competitive and non-competitive conditions. Copper and iron polychelate of the resins are used as polymeric ligand exchanger to remove arsenate from drinking water. A comparative study was done between the copper and iron PLE. Various parameters influencing the removal of the arsenate ion from drinking water were studied.

Key words: Chelating resins, Metal ion uptake, Immobilization, arsenate adsorption.

Corresponding author:

INTRODUCTION

In recent times the surface as well as ground water is contaminated with toxic metal like arsenic, mercury and uranium and heavy metal like copper, nickel and iron beyond environmentally and ecologically sustainable limits due to both natural phenomenon and human endeavours. The health hazards caused by toxic or heavy metals from contaminated drinking water are far more disastrous than any other natural calamity throughout the world in this era [1, 2]. Nearly 120 million people of Bangladesh, Nepal, West Bengal, Taiwan, the USA, Chile, and Argentina are susceptible to poisoning effect of arsenic [1-4], while many people in other places are also suffering from various health hazards due to prolonged use of water excessively contamination with other toxic or heavy metals like mercury, uranyl, copper, and lead [5]. Concentrations of dissolved arsenic in many areas of Bengal Delta exceed over 200 µg/L, while the maximum permissible arsenic concentration according to WHO and US EPA is 10 µg/L. Similarly according to WHO standards maximum permissible copper, mercury, iron, nickel concentrations are 1 mg/L, 2 µg/L, 300 µg/L, 20 µg/L respectively [6]. Due to contribution of industrial waste the concentration of above metal ions exceeds many areas beyond the permissible limits.

Separation of these toxic or heavy metal ions from drinking water source is very difficult and complex process. Because copper, lead, nickel, cadmium and uranium are present as cations such as Cu^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+} and UO_2^{2+} in ground and surface water while arsenic is present as anions like AsO_4^{3-} and AsO_3^{3-}. Therefore different methods and mechanism are required to separate them from water. Chelating ion exchange resins having specific chelating groups attached to a polymer have found extensive use in sorption and pre concentration of metal cations [7-10]. Similarly of the proven methods available today, polymeric ligand exchanger (PLE) is best and most innovative available technology for removal of arsenic anions. PLE is a metal polychelate of chelating ion exchange resins. The Schiff bases having multiple coordination sites are very good chelating ligands and form complexes with transition metal ion readily [11-13]. Present in a polymeric matrix they are expected to show affinity selectively towards the metal ions at an appropriate pH. Again these chelating resins enhance the pre concentration factor to a greater extent when successfully adsorb into a solid adsorbent [14, 15]. We have reported the synthesis, characterization and capacity studies of a number of phenol-formaldehyde type resins containing different Schiff base moiety and study their metal uptake behaviour [16-21]. We have also used some of the Cu (II) and Fe (III) polychelates of these resins as PLE for removal of AsO_4^{3-} from drinking water [22].

Here we are using a phenol-formaldehyde type chelating resin (*o*-HB-DAP-HCHO) prepared by condensing the Schiff base of *o*-hydroxybenzaldehyde-2, 6-diaminopyridine (*o*-HB-DAP) with formaldehyde (HCHO) (Figure-1). The resin reacted readily with several metal ions but the metal ion uptake from dilute aqueous solution was low. Most of the available coordination sites on the resin matrix were inaccessible to the metal ions. This led to a slow rate of adsorption. To expose relatively more coordinating sires, the resin was immobilized on silica gel. This resin-impregnated silica gel was found to be very effective in preconcentration of metal ions like Cu (II), Ni (II), and Fe (III) from dilute aqueous solutions (Figure-2). The idea is to

use the polymeric chelating resin to separate heavy metal cations like Cu^{2+}, Fe^{3+} and Ni^{2+} from the drinking water and simultaneously the metal polychelates of the resin can be used as polymeric ligand exchanger to remove arsenate from drinking water. In this paper, we are reporting adsorption of metal ions such as Cu^{2+}, Ni^{2+}, and Fe^{3+} from dilute aqueous solutions both in competitive and non-competitive conditions with the variation of contact time, pH and temperature is investigated. The chelating materials were used for the removal of metal ions from industrial waste and drinking water samples. Copper and iron polychelate of the resins are used as polymeric ligand exchanger to remove arsenate from drinking water. A comparative study was done between the copper and iron PLE.
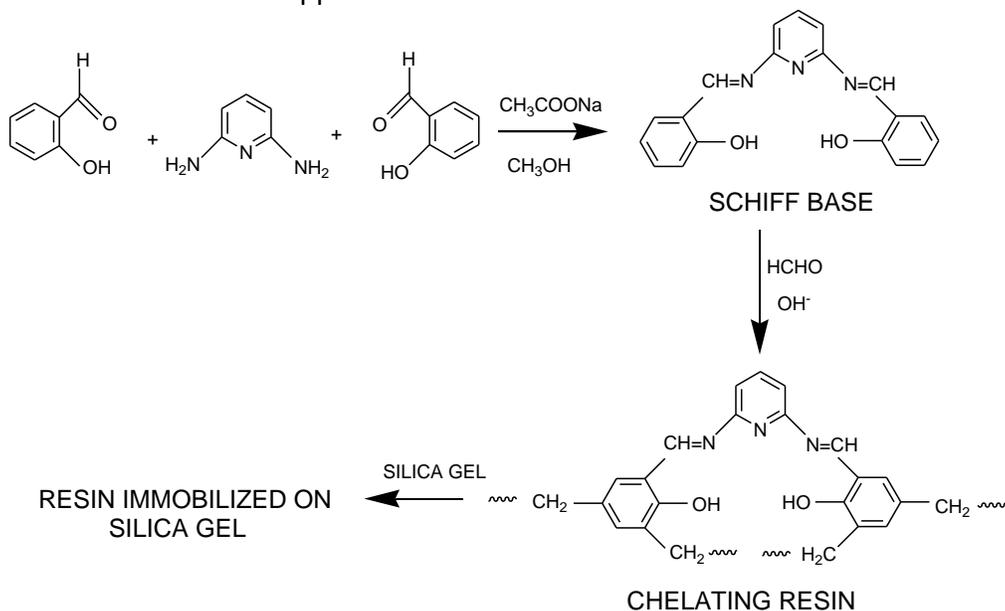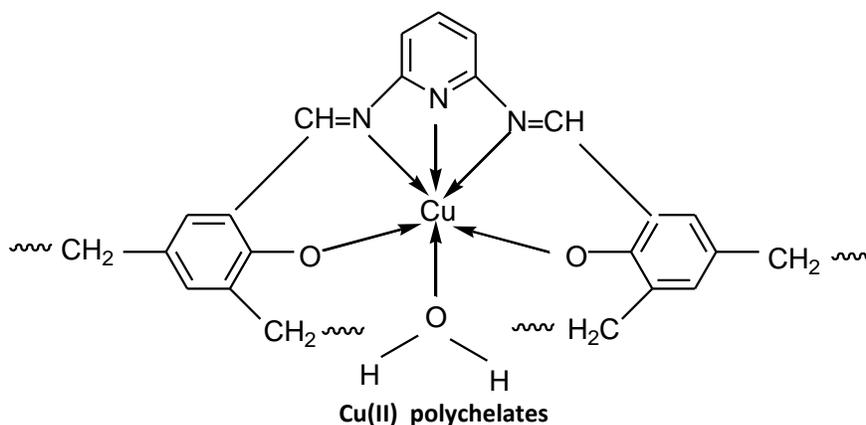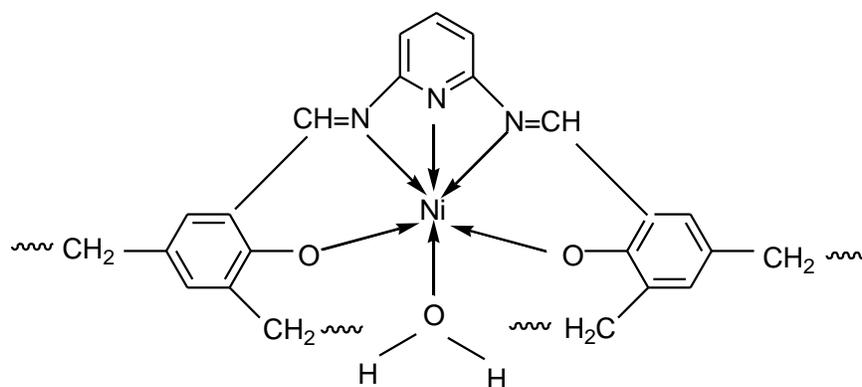

Figure – 1 : Structure of Schiff's Base and the resin

Cu(II) polychelates

Ni (II) polychelates
Figure – 2: Structure of polychelates of Cu(II) and Ni(II)

MATERIAL AND METHODS

Materials

The starting materials such as *o*- Hydroxybenzaldehyde (*o*-HB), 2, 6-Diaminopyridine (DAP) (Aldrich, U.S.A) were further purified by distillation or recrystallization from ethanol. The Sulphate and nitrate salt of Cu (II), Ni (II), Fe(III), formaldehyde and all other chemicals and solvents were of Anal R / GR grade (Merck / BDH, India) and use as received. Doubly distilled deionised water was used for the preparation of the solutions. The standard stock solution was prepared by dissolving an appropriate amount of Cu^{2+}, $Ni2^{+}$, Fe^{3+}, Co^{2+} and UO_2^{2+} salts in deionised water. Working solutions were prepared by appropriate dilution of the stock solutions. The buffer used to control the pH of the solution was acetic acid – sodium acetate (pH 3.42 - 5.89), disodium hydrogen phosphate – potassium dihydrogen phosphate, (pH 5 – 8) ammonium hydroxide – ammonium chloride (pH 8 – 10).

Instrumentation

The estimation of metal ion concentration in dilute aqueous solution was made using a Systronic digital spectrophotometer model 116. The pH of the solution was measured in a Systronic digital pH meter model 335 equipped with a combined glass-calomel electrode. The concentration of arsenic was determined by a two-channel atomic absorption/flame emission spectrophotometer model AA-8500 Mark II.

Metal ion uptake

The metal ions uptake studies were done employing both batch and column techniques.

Batch technique

In the batch technique, a suspension of the resin in the metal solution of known volume and concentration was taken in stopper glass bottles (100 ml.) and shaken for a definite time period at the shaking rate of 200 rpm. The pH of the solution was adjusted using suitable buffer. The resin was filtered off, and thoroughly washed with demineralized water. The metal ion concentration in the filtrate and washing were estimated colorimetrically using neocuprion method for Cu(II), dimethyl glyoxime method for Ni(II), and thiocyanate method for Fe(III) after proper dilution, if necessary [23].

The experiments were carried out in duplicate each time. The percentage of metal ion adsorbed by the resin and the distribution coefficient, K_d, were calculated using the following relations:

$$\text{Metal ion uptake (\%)} = \frac{W_i - W_f}{W_i} \times 100 \qquad \text{--- (1)}$$

Where, W_i = µg of metal ion in solution initially present

W_f = µg of metal ion present in the filtrate and washings

$$\text{Distribution coeff., } K_d \text{ (mL/g)} = \frac{\text{mmol of metal on the sorbent}}{\text{mmol of metal in solution}} \times \frac{\text{mL of solution}}{\text{gm. of resin}} \qquad \text{--- (2)}$$

Column technique

The resin particles were grounded to 0.1-0.2 mm. The glass column, (15 cm x 0.40cm i.d.) having stopcock and porous disk was used for the column operation. Five hundred milligram of resin was slurred in water and then poured into the column operation. The bed height of the column was approximately 15 mm. It was conditioned with 10-15 ml of pH 5.89 buffer. After each use the resin in the column was washed with large amount of water and stored in water for the next experiment. 50 ml of the sample solution of copper containing 500 µg of Cu (II) was buffered to desired pH. After 5-10 min, the solution was loaded to the column. The flow rate of the sample solution through the column was gravitationally performed at range of 0.5-3.0 ml min^{-1}. The flow rate of the sample was controlled using the stop cock of the column. After passage of the solution was finished, the column was washed with aqueous solution, adjusted to the working pH. The retained metal ions were eluted from the column by aid of dilute hydrochloric acid at 0.5 ml min^{-1} flow rate. The washing were analyzed to find out both the percentage of metal uptake and eluted from resin.

Desorption and reuse

Desorption of the metal ion was also carried out from the resin column. After loading the metal ion solutions onto the resin column at appropriate pH, the selected eluting agent was

run through the column by regulating the flow with the stopcock of the column. The desorption ratio (%) was calculated using the following expression.

$$\text{Desorption ratio(\%)} = \frac{\text{Quantity of metal ions desorbed to the eluting medium}}{\text{Quantity of metal ions adsorbed onto the sorbent}} \times 100$$

The adsorption-desorption cycle was repeated at least three times with the same resin to obtain a reliable result.

Arsenate adsorption studies

To 10 mL of the arsenate solution ($[AsO_4^{3-}]$ = 200 µg /L), 100 mg of the copper polychelate of 100 mesh was added and shaken for a fixed time period in stoppered conical flasks at $30^{o}C$. The contents of the flask were filtered off and the resin was thoroughly washed in demineralized water. The metal ion concentration in the filtrate and the washings was determined by a two-channel atomic absorption/flame emission spectrophotometer. To determine the optimum conditions for efficient uptake of arsenate ions by the copper polychelate, various parameters like contact time and pH were varied. Doubly deionised water was used through all the experiments.

RESULT AND DISCUSSION

Metal ion uptake study by batch technique

Effect of contact time

The Cu^{2+}, Ni^{2+}, and Fe^{3+} solution were treated with the virgin resin at natural pH of the solutions at $30^{o}C$. The contact time was varied between 5 min. to 24 hrs. It was found that 100mg of the resin of 100 meshes took 24 hr to remove a maximum of 65% of the Cu^{2+}, 33% of Ni^{2+}, and 23% of Fe^{3+} from 10 ml of each salt solution containing 200 µg of metal ion. Several authors have noted the higher adsorption of Cu (II) over other metal ions [24, 25]. On the other hand; the silica gel loaded with the same resin could adsorb Cu^{2+} at a much faster rate, the equilibrium being attained within 5 minutes. It could remove 88% of the Cu^{2+} ion from a 10 ml sample containing 2500 µg of metal ion at natural pH. Similarly the equilibrium time for adsorption of Ni^{2+}, and Fe^{3+} was 30 minutes and maximum of 50% of the metals could be adsorbed from a 10ml sample containing 2500 µg of metal ion at natural pH (Figure-3). B.S. Garg and co-workers have also noted that the time taken by the silica gel immobilized resin to attained equilibrium is 10 minutes in case of Zn, Fe and a Cu and 12 minutes in case of Co [26]. It can be concluded that metal ion adsorption efficiency of the virgin resin significantly increases by the immobilisation of silica gel (Figure-4).

Effect of pH

The effect of the reaction medium on the extent of adsorption of Cu^{2+}, Ni^{2+}, and Fe^{3+} was studied using buffers in the pH range of 3.42-5.89 for Cu^{2+}, 3.42- 8.9 for Ni^{2+}, and 3.42 - 9.0 for Fe^{3+} (Table). Increasing pH beyond the range resulted in precipitation of metal ions as hydroxides. The ease of coordination of the phenoxide ion over that of phenolic OH group and the enhanced basicity of the C = N nitrogen at higher pH are some factors for the resins to uptake high percentage of metal ions at higher pH. Since in lower pH, the coordinating groups get protonated [27]. Dev and Rao have reported enhanced adsorption of metal ions with increase in the pH [28]. It was found that at an optimum pH of 5.89, almost entire quantity of Cu (II) from a 10 ml sample containing 2500 µg of metal ion could be removed within 30 minutes. For nickel, at a pH of 8.9 a maximum of 84.5% metal ion could be adsorbed, while for iron a maximum of 83% metal ion was adsorbed at a pH 9.0. (Figure- 5).
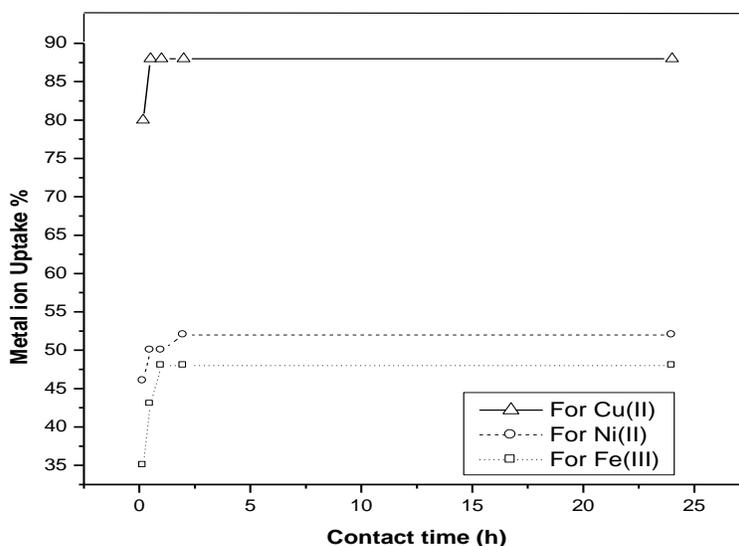

Figure – 3: Uptake of Cu^{2+}, Ni^{2+}, and Fe^{3+} ions by the resin immobilised on silica gel with increasing contact time.
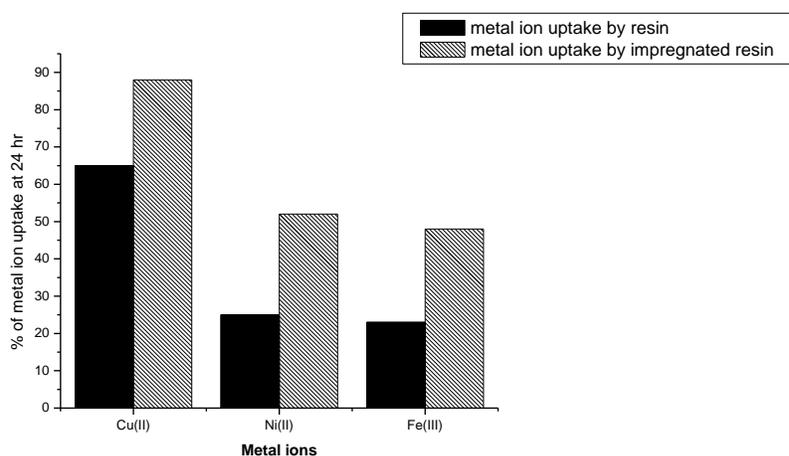
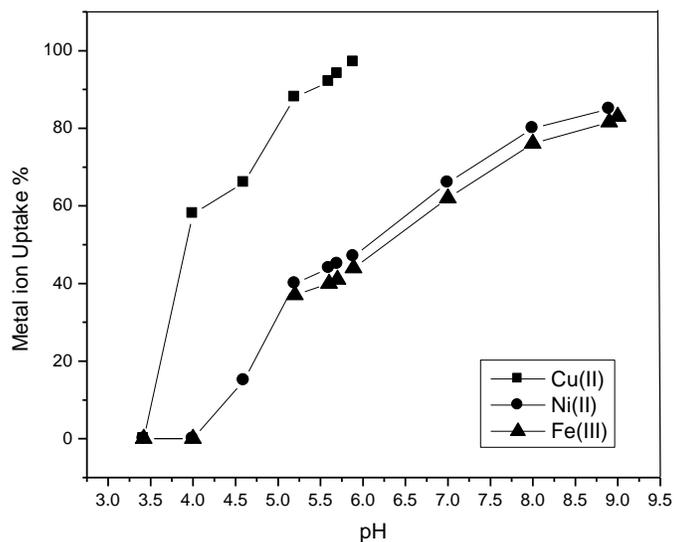**Figure-4: Comparison of % of Metal Ion Uptake between the virgin Resin and the resin immobilised on silica gel.**

Figure-5: Uptake of Cu^{2+}, Ni^{2+}, and Fe^{3+} ions by the resin immobilised on silica gel with pH variation.

Adsorption at competitive environment

The metal ion adsorption study of the chelating resins in the competitive environment was presented in table 1. For this study, 10 ml solution containing 2500 µg each of the Cu (II), Ni (II), and Fe (III) was treated with 100mg of the resin and the pH of the solution was varied between 3.42 and 5.89. It was noticed that, up to pH 4.9 no noticeable amount of Ni (II), and Fe (III) were adsorbed. Again, there is preferential adsorption of Cu (II) ions is noticed in comparison to the other metal ions. This is the optimum pH for the separation of Cu (II) ions in a competitive environment containing metal ions like Ni (II) and Fe (III). The distribution coefficient (K_d) is found to be maximum for Cu (II) ions. The higher value of K_d for Cu (II) indicating the higher adsorption efficiency for Cu (II) and faster adsorption rate among the metal ions [29, 30, 31]. Dev and Rao, in studying a polystyrenedivinylbenzene-based macro reticular resin functionalized with bis-(N,N'-salicylidine)1,3propanediamine Schiff-base ligand, observed that the resin could efficiently adsorb a number of metal ions [32]. However, the resin demonstrated nearly identical preference for both Cu^{2+} and Ni^{2+} among other metal ions. Ahuja and co-workers have also observed that Cu^{2+} can be separated from Cu^{2+}-Co^{2+} andCu^{2+}-Ni^{2+} mixtures at pH 5.5 [33].

In another experimental set up, the recovery of the metal ions were attempted in presence of the commonly present salts like $MgCl_2$, NaCl, KBr, $NaNO_3$, Na_2SO_4, and $NaHCO_3$ in water samples [Table 2]. A synthetic sample of water containing2500 µg per 10 ml of the Cu (II) ion in presence of the above alkali and alkaline earth metal ion was prepared and it was treated with 100 mg of the resin immobilized with silica gel at the natural pH of the solution for 24 hr. It was observed that the presence of alkali and alkaline earth metal ions and the accompanying anion have negligible effect on the adsorption behaviour of the resins thus, strengthening the

idea of recovery of the metal ions in saline and non-saline water samples. This is due to the fact that Na^+ K^+ Mg^{2+} ions are hard Lewis acids where as Cu^{2+} is a borderline Lewis acid. So Cu^{2+} showed more affinity to the Schiff bases than Na^+ K^+ Mg^{2+} etc. This can be explained with help of the Pearson HSAB concept [34]. Several authors also supported our observations [35, 36]. Hodgkin and Eibl prepared a Cu^{2+} - selective (sirorez – Cu) from phenol- formaldehyde and piparazine and the selective capacity for Cu^{2+} were studied in the pH range 3-10.5 [37]. They observed that, the alkali and alkaline earth metals were not retained by the resin in this range. Dev and Rao also reported the same observation as we are reporting in this paper [28].

Table- 1: Competitive sorption behavior.

pH	% LOADING					
	Cu(II)		Ni(II)		Fe(III)	
	Uptake (%)	K_d	Uptake (%)	K_d	Uptake (%)	K_d
3.42	0	0	0	0	0	0
4.0	52.5	110.52	0	0	0	0
4.6	62.8	168.81	0	0	0	0
4.9	69.7	230.03	0	0	0	0
5.2	83.4	502.4	14.5	16.95	10.5	11.73
5.89	95	1765.30	40.9	69.2	38.4	62.33

Metal ion: Cu(II), NI)II), Fe(III) [M] =2500 µg/10 mL, Resin quantity: 100 mg, Sorbent size: 100 mesh, Temperature: 30 ^{o}C,   Contact time: 24 h.

TABLE-2 : Effect of the added salt
[M (II)] =2500 µg / 10 ml, pH natural Temp. 30^{0}C, resin-loaded silica gel -100 mg, contact time – 30 min.

Metal ions immobilized on silica gel	In absence of the added salt	In presence of the added salt		
		Na^+	K^+	Mg^{2+}
Cu(II)	88	87.7	87.9	87.6

Metal ion uptake study by column technique

Adsorption by dynamic Conditions

The sorption behaviour at dynamic conditions can be related to the evaluation of its material properties for its subsequent use in industrial purpose. In the present case, the sorption/adsorption behaviour of the chelating resin *o*-HB-DAP-HCHO immobilized in silica gel for Cu (II) can be studied dynamically using column technique. For the study to conduct, two set of experiment were set. . In the first set of experiments, pH of the solution containing 500 µg of the metal ion in 50 ml of the solution was varied (Figure-6) while flow rate of the solution through the column was kept constant (0.5 ml min^{-1}). It was observed that at a pH 5.89, the column successfully retained nearly 79.0 % of the metal ion. Several authors choose the working pH 5-6 for maximum uptake of Cu (II) by resins in column operation study [38, 39]. In the next set of experiment, the pH of the solution was kept constant (pH-5.89), while the flow rate was varied (Figure-7). Again it was observed that at 0.5 ml min^{-1} flow rate, the resin was capable of retaining maximum amount of metal ions. Increasing the flow rate, however,

decreases the metal ion retention capacity of the resin. This is explained on the basis of the availability of the contact time in between the ligands and metal ions. With the increase of flow rate, the interaction between the coordinating groups and the metal ions decreases, results in the less adsorption. Hence, it can be concluded that such a resin may be found useful in recycle plant of recovering the metal ions in continuous column operation
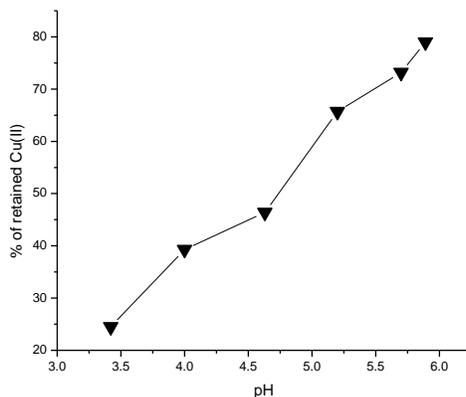

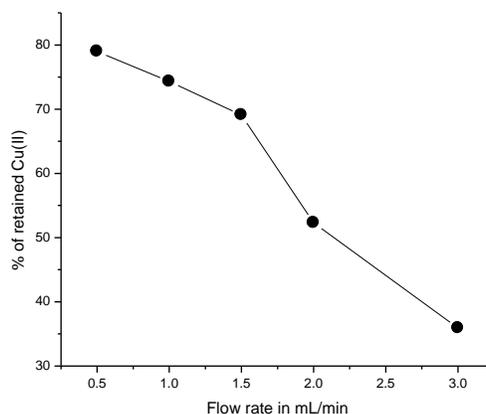**Figure-6: Study of adsorption behaviour in column operation with variation of pH of the medium**

Figure-7: Study of adsorption behaviour in column operation with variation of flow rate of metal ion solution

Elution of copper ion from the resin column

For the reusability of the chelating resin it is necessary to carry out the desorption process. For this study 1.0 mol/L of HCl is used as the eluting agent, It was found that about 50 ml of the eluant (1 mol/ L) is sufficient for the metal recovery process maintaining the flow rate of 0.5 ml/min. It is observed that elution was nearly 30-35 % of the absorbed metal ion from the resin but in case of resin immobilized on silica gel the elution was gone up to 94% in 2 cycles. It is also observed that with increase in the flow rate, the percentage of elution decreases. The breakthrough volume of Cu (II) ions from which the 75% of metal ion can be removed is 30 ml. From the above studies, it is concluded that, the chelating resin *o*-HB-DAP-HCHO immobilized in silica gel is specific for the quantitative removal of Cu (II) (100µg) ions at pH 5.89 using 1.0 gm of chelating resin on the column bed. (Figure-8). It was also found that the

stripped silica gel immobilized resin could be reused and after ten cycles of loading and stripping, the material did not lose its efficiency.
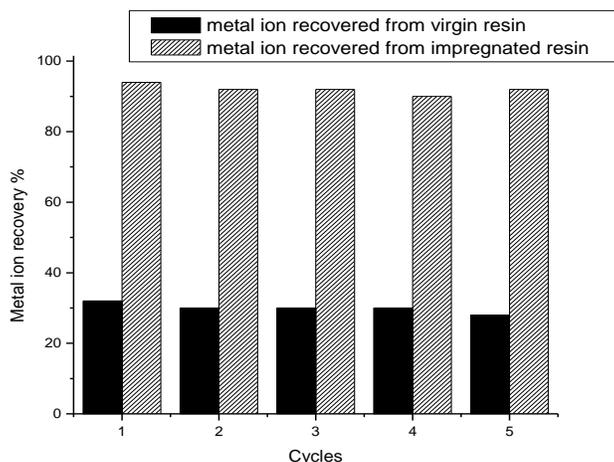

Figure-8: Comparison of elution of metal ion from virgin resin and impregnated resin.

Arsenate adsorption studies

It has been found that most of the work for arsenate separation from drinking water has been done using Fe(III) PLE, it cannot be effectively used for drinking water treatment [40,41, 42]. Because all observation shows that only at low pH As(V) can be removed. Again, since Fe(III) is a weak Lewis acid the amount of Fe^{3+} loaded was low and the loaded iron was almost completely stripped off the hosting resin during regeneration, Therefore reloading of Fe^{3+} was necessary after each cycle of operation. To overcome the critical drawbacks of Fe(III) loaded PLE, Ramana and Sengupta prepared a PLE by loading Cu^{2+} onto a weak base chelating resin (known as DOW 2N) with 2-picolylamine groups [43]. Since Cu^{2+} is a much stronger Lewis acid than Fe^{3+} which is in accord with the Irving and Williams order, a much greater metal-loading capacity was observed [44]. The copper loaded DOW 2N showed orders of magnitude greater selectivity for arsenate and selenate in the presence of competing sulphate ions than commercial SBA resins.

In this paper copper polychelates and iron polychelates of the chelating resin *o*-HB-DAP-HCHO immobilized in silica gel as polymeric ligand exchanger (PLE) for arsenic extraction is used. The metal polychelates were synthesized using the metal nitrate salts. We have also observed similar result as Raman and Sengupta which is discussed below.

Equilibrium Time

To determine the equilibrium time for the adsorption of Arsenate ions 100mg, 100 mess of the polychelates *o*-HB-DAP-HCHO -Cu(II), *o*-HB-DAP-HCHO -Fe(III) were treated with metal salt solutions (2µg/10mL) at the 7.0 pH of the reaction mixture. The above mixtures were taken in different conical flasks and stirred continuously with help of magnetic stirrer. The flasks were

removed after regular time intervals, the metal loaded resins filtered off and the metal ion concentration in the filtrate was measured.

Comparing the arsenate adsorption capacity of the PLEs, it is observed that the arsenic uptake efficiency of *o*-HB-DAP-HCHO -Cu(II) polychelate is significantly higher than that *o*-HB-DAP-HCHO -Fe(III). The former PLE is able to take 85.9 % of arsenate ion at 24 h in natural pH of the solution while the later only adsorbs 56.5 % of arsenate **(**Figure- 9**)**. The reason for such an observation could be attributed to the concurrent Lewis acid-base interactions between arsenate and the immobilized Cu^{2+} ions at the sorbent-sorbet interface. Under the experimental conditions, monohydrogen arsenate ($HAsO_4^{2-}$) is considered as predominant arsenate species. $HAsO_4^{2-}$ is a divalently charged, bidentate ligand and stronger Lewis base. Consequently, interactions between arsenate and the immobilized Cu^{2+} ions involve both LAB interaction (or inner-sphere complexation) and ion pairing (or electrostatic interactions), It is noteworthy that LAB interaction also enhances the electrostatic interactions between arsenate and the loaded Cu^{2+}ions.This is because the inner-sphere complexation occurs over a much shorter distance than outer-sphere complexation, and the electrostatic interactions within the much shortened distance are much stronger in accord with the Coulomb's law. But due to weak acid strength of Fe^{3+}, *o*-HB-DAP-HCHO -Fe(III) has comparatively lower arsenate adsorption capacity than *o*-HB-DAP-HCHO -Cu(II) (Figure 9).
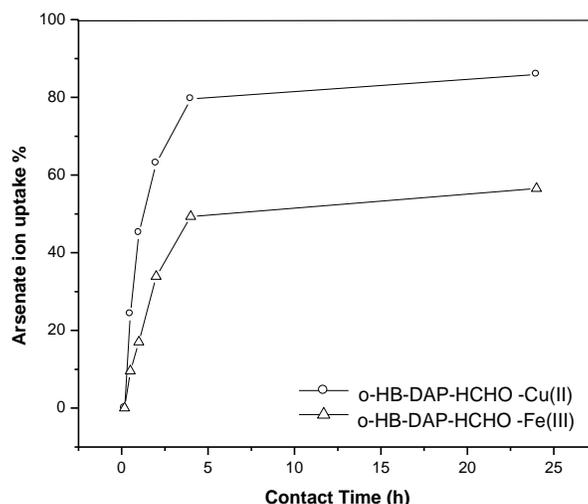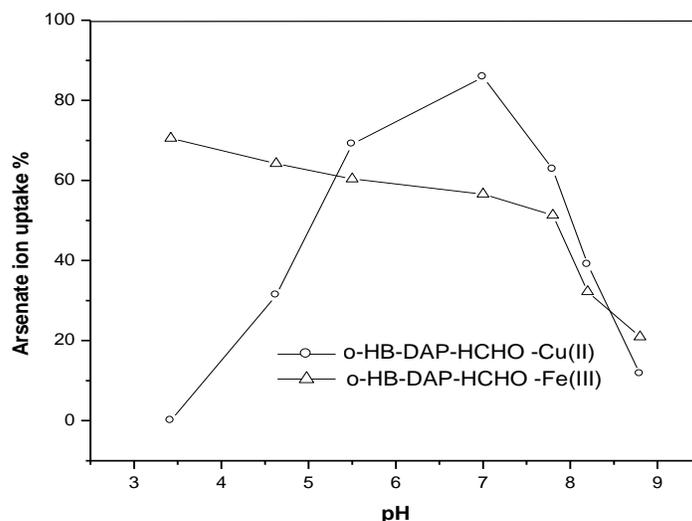

Figure-9: Effect of contact time on AsO_4^{3-}ion uptake of *o*-HB-DAP-HCHO polychelates

Figure-10: Effect of pH on AsO$_4^{3-}$ ion uptake of *o*-HB-MABT-HCHO polychelates

It was also observed that competing ions like sulphate has negligible effect on the arsenate adsorption. Though sulphate is also a divalently charged ligand, it is a much weaker Lewis base than the arsenate. Therefore interactions between sulphate and the Cu^{2+} ions is predominantly ion paring. Therefore *o*-HB-DAP-HCHO -Cu(II) offered much greater affinity for arsenate over sulphate. Again in of case SBA resins, the commercial SBA resins, take up anions predominately through electrostatic interactions, i.e., the ligand strength of an anion does not play a role in sorption affinity. Therefore, SBA resins are not selective for arsenate. Similar observations were observed by Zhao *et al.* by performing similar experiments over DOW 3N-Cu PLE.

Effect of pH

As in any ion exchange process, the PLE's selectivity for various competing ligands can be strongly influenced by solution pH. Solution pH can affect the PLE's. As uptake in two different aspects. First, solution pH governs the speciation of arsenate, resulting in arsenate species (H$_3$AsO$_4$, H2AsO4$^-$, HAsO$_4^{2-}$, and AsO$_4^{3-}$) of different ionic charges and ligand strength. Second, the hydroxyl anions become aggressively formidable competitors for the ligand exchange sites as solution pH goes up.

The effect of pH of the reaction medium on the extent of adsorption was studied extensively. The extent of adsorption of the PLEs was investigated using buffers in the pH range 3.42-8.8. It is observed that with increase in pH the arsenate adsorption capacity of *o*-HB-DAP-HCHO -Cu(II) increased till pH 7.0 and then decreased but for *o*-HB-DAP-HCHO-Fe(III) with increase in pH the arsenate adsorption capacity decreased (Figure 10). Sharp declination was observed in case of *o*-HB-DAP-HCHO- Cu(II) after the pH range 8.0. Figure 10 indicates that the optimal arsenate uptake occurs in the pH range of 6.0–8.0, with the peak uptake being at pH

7.0.At pH <4 or >10 there was virtually no uptake of arsenate observed. It is also interesting that As uptake started increasing at pH 4.0 almost in proportion to the increasing formation of the bidentate hydrogen arsenate species ($HAsO_4^2$). However, the As uptake dropped sharply as pH exceeded 8.0. Based on both ligand strength and ionic charge, the adsorbability of various arsenate species follows the sequence $H_3AsO_4 < H_2AsO_4^- < HAsO_4^{2-} < AsO_4^{3-}$. At pH<4 the much less adsorbable $H_2AsO_4^-$ or H_3AsO_4 is the predominant arsenate species, which cannot stand the competition of divalently charged sulphate anions. As a result, no As uptake is likely in the low pH range as observed in figure 10. The fact that the As uptake appears to be in proportion to the formation of $HAsO_4^{2-}$ in the pH range of 4.0 –7.0 agrees with the notion that to overcome the competition from sulphate, arsenate must be converted to the more adsorbable $HAsO_4^{2-}$ species.

CONCLUSION

Phenolic Schiff base of *o*-HB-DAP could be condensed with formaldehyde to produce chelating resin. But due to inaccessibility of most of the coordination sites on the resin matrix to the metal ion, the metal ion uptake percentage of the resin was very low. Therefore to expose relatively more coordination sites, the resin was immobilized on silica gel. It was found that resin impregnated with silica gel was efficiently removing very high percentage of Cu (II) and Ni (II) from dilute aqueous solution. It was also observed that at a particular pH Cu (II) can be separated from Cu (II)/Ni (II) mixture. Since the presence of alkali and alkaline earth metal ions and accompanying anion have negligible effect on the adsorption of the resin-impregnated silica, so the resin could be used to remove Cu (II) from saline and non-saline water rich in these above cations.

Further the copper polychelates of *o*-HB-DAP -HCHO can be used as a polymeric ligand exchanger for effective separation of arsenate from drinking water. So by the help of the resin and its polychelate simultaneously heavy cation Cu (II) and toxic anion arsenate can be separated from drinking water. Hence the resins and polychelates of the phenolic Schiff bases are very useful in combating poisoning due to toxic metal ions, such as, copper, cobalt, nickel, uranyl and arsenic, etc.

ACKNOWLEDGEMENTS

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