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Selective Removal of Toxic Metals like Copper and Arsenic from Drinking Water Using Phenol-Formaldehyde Type Chelating Resins

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Abstract: The concentration of different toxic metals has increased beyond environmentally and ecologically permissible levels due to the increase in industrial activity. More than 100 million people of Bangladesh and West Bengal in India are affected by drinking ground water contaminated with arsenic and some parts of India is also affected by poisoning effect of copper, cadmium and fluoride. Different methods have been evolved to reduce the arsenic concentration in drinking water to a maximum permissible level of 10 $\mu\text{g/L}$ where as various methods are also available to separate copper from drinking water. Of the proven methods available today, removal of arsenic by polymeric ion exchangers has been most effective. While chelating ion exchange resins having specific chelating groups attached to a polymer have found extensive use in sorption and pre concentration of Cu^{2+} ions. Both the methods are coupled here to separate and preconcentrate toxic metal cation Cu^{2+} and metal anion arsenate (AsO_4^-) at the same time. We have prepared a series of low-cost polymeric resins, which are very efficient in removing copper ion from drinking water and after coordinating with copper ion they act as polymeric ligand exchanger, which are efficiently removing arsenate from drinking water. For this purpose Schiff bases were prepared by condensing *o*-phenylenediamine with *o*-, *m*-, and *p*-hydroxybenzaldehydes. Condensing these phenolic Schiff bases with formaldehyde afforded the chelating resins in high yields. These resins are loaded with Cu^{2+} , Ni^{2+} , and Fe^{3+} ions. The resins and the polychelates are highly insoluble in water. In powdered form the metal ion-loaded resins are found to very efficiently remove arsenate ion from water at neutral pH. Resins loaded with optimum amount of Cu^{2+} ion is more effective in removing arsenate ions compared to those with Fe^{3+} ion, apparently because Cu^{2+} is a stronger Lewis acid than Fe^{3+} . Various parameters influencing the removal of the arsenate ion from drinking water to a concentration level below 20 $\mu\text{g/L}$ are studied.

Keywords: Chelating resins, Metal ion uptake, Elution, Arsenate separation.

Introduction

The concentration of toxic metal ions like Cu(II), Cd(II), As(III), As(V), Pb(II), Ni(II) and U(VI) *etc.* has increased beyond environmentally and ecologically sustainable levels due to natural phenomenon as well as anthropogenic impact. It has resulted in severe contamination of ground and surface water. The poisoning effect of toxic metals from contaminated drinking water has evolved as one of the major health hazards in the 21st century^{1,2}. The adverse health effects caused by copper, mercury and arsenic poisoning are far more catastrophic than any other natural calamity through out the world in recent times. Especially in the developing countries, water and soil degradation generated by industrial effluents has been a serious issue³. An estimated 120 million people are at risk of poisoning effect of arsenic in Bengal Delta (parts of Bangladesh, Nepal, and West Bengal), Taiwan, the USA, Chile, and Argentina. Many people are also suffering from different health hazards due to poisoning effect of copper, lead, and mercury⁴. Extraction of these metal ions is a tedious process as they are associated with a variety of complex species present in the natural aquatic systems. Again copper, lead, nickel, cadmium and uranium are present as cations such as Cu²⁺, Pb²⁺, Cd²⁺ and UO²⁺ in ground and surface water while arsenic is present as anions like AsO₄⁻ and AsO₃⁻. 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 cations⁵⁻⁸. The Schiff bases having multiple coordination sites are known to form complexes with transition metal ion readily⁹⁻¹¹ present in a polymeric matrix they are expected to show affinity selectivity towards the metal ions at an appropriate pH. We have reported the synthesis, characterization and capacity studies of a number of phenol-formaldehyde type resins containing different Schiff base moiety¹²⁻¹⁶. These resins were found to react readily with several metal cations^{17,18}. It is also a challenge to evolve a cost effective arsenic removal technology which could reduce arsenic concentration below 10 µg/L from ground water. In this respect a lot of research has been carried out and technologies developed. Many technologies have been evolved for arsenic removal from ground water. Of the proven methods available today, polymeric ligand exchanger (PLE) is best and most innovative available technology (BAT) for removal of As(V).

In this paper, we have tried to combined both the above idea to separate and preconcentrate toxic metal cation Cu²⁺ and metal anion arsenate(AsO₄⁻) at the same time. Because the ground water in some part of India contaminated with both copper and arsenic¹⁹. Here, we are report the synthesis of three phenol-formaldehyde type resins containing *o*-phenylenediamine functionalities and their metal ion uptake capacity towards metal ion such as Cu²⁺, Ni²⁺ and Fe³⁺. 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.

Experimental

The starting materials such as *o*-, *m*-, *p* - hydroxybenzaldehyde (*o*-, *m*-, *p*- HB), *o*-phenylenediamine (*o*-PD) (Aldrich, U.S.A) were further purified by distillation or recrystallization from ethanol. The sulfate and/or nitrate salts of Cu²⁺, Ni²⁺, and Fe³⁺, potassium dihydrogen arsenate (KH₂AsO₄), formaldehyde and all other chemicals and solvents were of AnalaR/GR grade (Merck/BDH, India) and used as received. The buffer used to control the pH of the solution was acetic acid - sodium acetate (pH 3.42 - 6.5), ammonium hydroxide - ammonium chloride (pH 7.8 - 10).

Synthesis of Schiff base, resin and polychelates of resin

The Schiff base monomers *o*-, *m*-, *p*- hydroxybenzaldehyde- ethylenediamine (*o*-, *m*-, *p*-HB-*o*-PD) were synthesized by reacting 0.01 mol of *o*-phenylenediamine (*o*-PD) with 0.02 mol of *o*-, *m*-, *p*- hydroxybenzaldehyde dissolved in 20 mL of ethanol in presence of 0.5 g of anhydrous sodium acetate. The mixture was refluxed for 1h at 60 °C. The Schiff base *o*-HB-*o*-PD was formed within 10 minutes of reaction. The formation of *m*- and *p*-HB-*o*-PD required refluxing the mixture for 1 h. The contents were poured into ice cold water, allowed to stand for one hour, filtered and dried at 70 °C. The color of the isolated Schiff bases *o*-, *m*-, *p*-HB-*o*-PD were yellow, metallic grey and yellowish brown respectively (Figure 1). They were thoroughly washed in water, ethanol and air-dried. In the further steps, the Schiff bases were condensed separately with formaldehyde (HCHO) solutions in 1:2 molar ratios in ethanolic medium using few drops of 0.01 M NaOH solutions as catalyst and the mixture was refluxed in oil bath at 120-130 °C for 2 h (Figure 2). The insoluble resin was filtered, washed repeatedly with distilled water and dried at 70 °C. To prepare the polychelates, to 100 mg of the dry resin (100 mesh, ASTM) suspended over methanol, 10 mL of metal salt (0.15 M) in water was added. The mixture was stirred for 2 h at 40 °C. It was filtered, washed in distilled water followed by petroleum ether and dried at 70 °C.

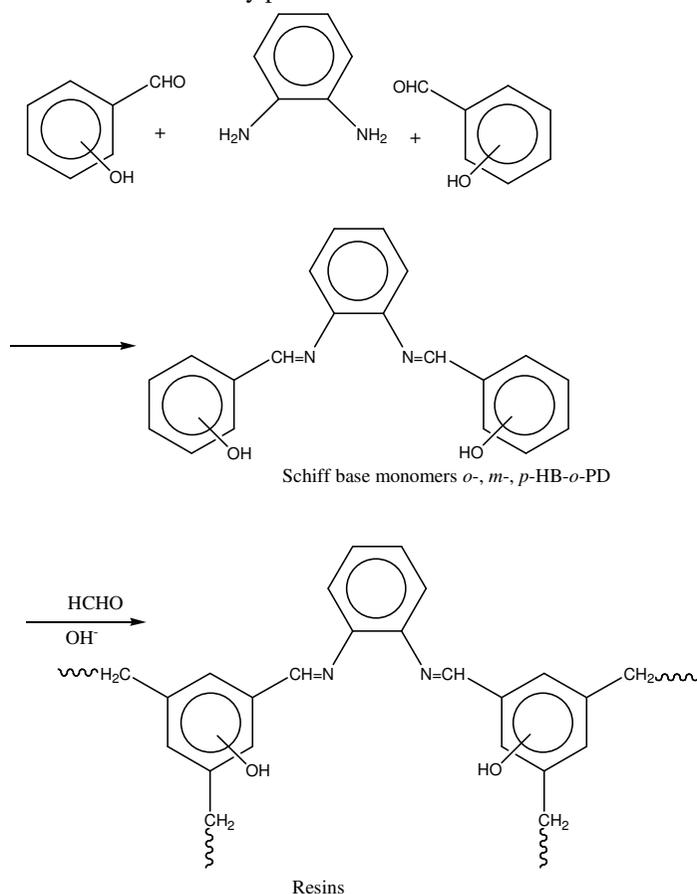


Figure 1. Schematic representation of synthesis of resin.

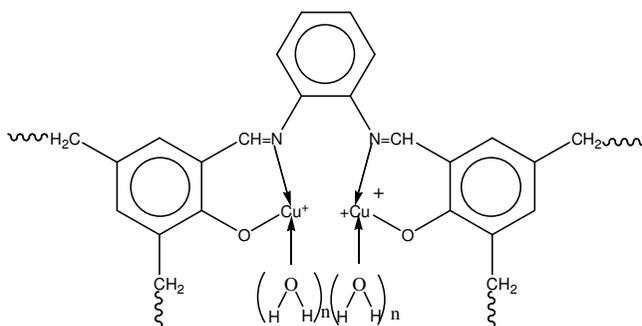


Figure 2 Structure of polychelate.

Procedure for metal ion uptake experiments

The metal ions uptake studies were done employing batch techniques. 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), thiocyanate method for Fe(III) and dimethylglyoxime method for Ni(II) after proper dilution, if necessary²⁰.

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 ($[\text{AsO}_4^{3-}] = 200 \mu\text{g/L}$), 100 mg of the copper polychelate of 100 mesh was added and shaken for a fixed time period in stoppered conical flasks at 30 °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 deionized water was used through all the experiments.

Results and Discussion

Metal ion uptake studies

Effect of contact time

The Cu(II), Ni(II) and Fe(III) solution were treated with the resin at natural pH of the solutions. The contact time was varied between 5 min to 24 h. The saturation time was obtained by plotting the percentage of metal ion against the contact time variation, keeping the initial metal ion concentration fixed (200 $\mu\text{g}/10 \text{ mL}$). In all the three resins, the rate of Cu(II)

adsorption is higher than that of Ni(II) and Fe(III) (Table 1). Several authors have noted the higher adsorption of Cu(II) over other metal ions^{21,22}. It is also found that *o*-HB-*o*-PD-HCHO is the most efficient resin for all the metal ions. It takes 80, 49.9, 48.8% of Cu(II), Ni(II), Fe(III) respectively at 24 h in natural pH of the solution. The order of adsorption efficiency of the resin is *o*-HB-*o*-PD-HCHO >> *m*-HB-*o*-PD-HCHO > *p*-HB-*o*-PD-HCHO. It could be explained on the basis that due to structural features of the above resins, the azomethine nitrogen and/or phenolic oxygen forms stable complexes on the above order. Because as we move from *ortho* to *para* complex the distance between azomethine nitrogen and phenolic oxygen increases.

Table 1. Effect of contact time.

Metal ion concentration [M]=200 µg /10 mL, Resin quantity=100 mg, Resin size=100 mesh, tempt =30 °C, pH=5.7

Resin	Metal ions	% metal ion adsorbed at different time intervals					
		0.1667	0.5	1	2	4	24
<i>o</i> -HB- <i>o</i> -PD-HCHO	Cu ²⁺	71.5	76	76.5	76.8	77.2	80
	Ni ²⁺	6	11.2	18.5	35	46.4	49.9
	Fe ³⁺	0	9.7	10	33	46.5	48.8
<i>m</i> -HB- <i>o</i> -PD-HCHO	Cu ²⁺	58	65.5	66.4	67	68.2	70
	Ni ²⁺	2	15	17.5	25.4	36.8	44
	Fe ³⁺	0	5	16.4	24	34.5	40.5
<i>p</i> -HB- <i>o</i> -PD-HCHO	Cu ²⁺	47	53.8	54	55.6	58	59
	Ni ²⁺	0	6.8	18.5	20.9	29.7	31
	Fe ³⁺	0	3.5	10.5	18.7	26.3	28.9

Effect of pH

The effect of the reaction medium on the extent of adsorption of Cu(II) and Ni(II) was studied using buffers in the pH range of 3.42-5.89 for Cu²⁺, 3.42- 8.9 for Ni(II) and 3.42- 9.0 for Fe(III) (Figure 3a-c). The metal ions are precipitated as hydroxides beyond the above pH ranges. 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. Because in lower pH, the coordinating groups get protonated²³. Dev and Rao have reported enhanced adsorption of metal ions with increase²⁴ in the pH. In our case, the optimum pH of the adsorption of Cu(II), Ni(II) and Fe(III) ions were 5.89, 8.9 and 9.0 respectively^{24,25}. It is also observed that the metal ion uptake percentage was higher in case of *o*-HB-*o*-PD-HCHO resin than the other two resins. However, all the three resins showed higher affinity towards Cu(II) than Ni(II) and Fe(III) .

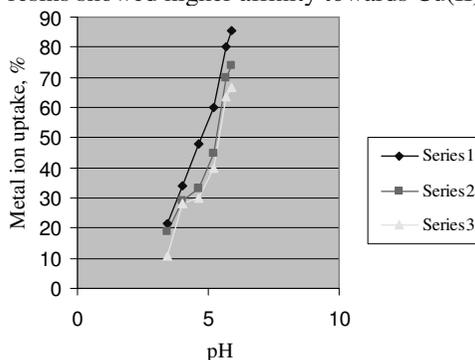


Figure 3(a). Uptake of Cu(II) ions by the resins with increasing pH.

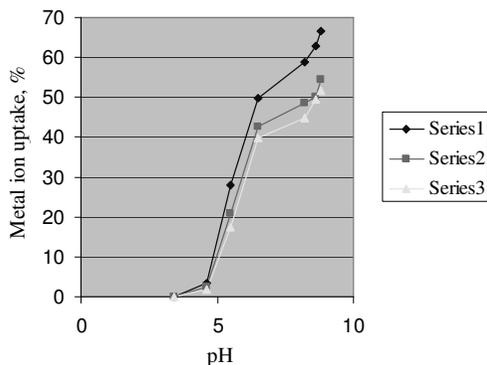


Figure 3(b). Uptake of Ni(II) ions by the resins with increasing pH.

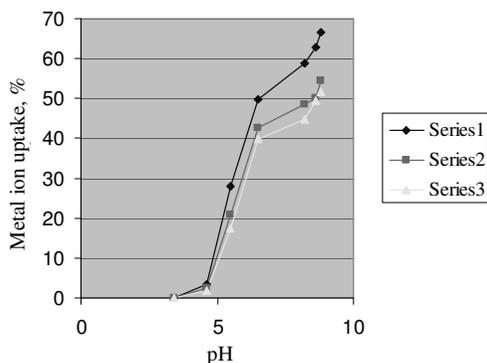


Figure 3(c). Uptake of Fe(III) ions by the resins with increasing pH.

Series 1. For *o*-HB-*o*-PD-HCHO

Series 2. For *m*-HB-*o*-PD-HCHO

Series 3. For *p*-HB-*o*-PD-HCHO

Effect of metal ion concentration

The effect of metal ion concentration on the uptake behavior of the resins was studied in the metal ion concentration range 50-500 $\mu\text{g/mL}$. It was observed that with increase in concentration of the metal ion, the amount of adsorption also increased up to a certain stage, after which there was no further increase in amount of metal ion adsorption. Many authors reported similar observations²⁶. This could be attributed to the saturation of the available coordinating sites in the resin with the metal ion. The adsorption coefficient, k_{ad} , of the resins for the uptake of Cu(II) was computed from Freundlich adsorption isotherm.

$$\log (x/m) = \log k_{\text{ad}} + 1/n \log C \quad (1)$$

where, 'C' is the concentration of the metal ion in mmol, 'm' is the weight of the resin in gram, 'x' is the metal ion adsorbed by the resin in mmol and 'n' is a constant. For all the resins the value of k_{ad} and 'n' were found out and presented in Table 2. High k_{ad} values were observed in all cases, which indicated that the equilibrium for metal ion adsorption was attained at a fast rate. Blasius and coworkers²⁸ have reported the adsorption constant for Mo^{6+} and W^{6+} and slow adsorption rate of the metal ion was associated with low k_{ad} values^{27,28}.

Table 2. Effect of variation of metal ion concentration on adsorption behavior of resins and Freundlich adsorption isotherm data.

Metal ion: Cu(II), Resin quantity: 100 mg, Sorbent size: 100 mesh, Temperature: 30 °C, Contact time: 24 h, pH=5.7

Resin	[Cu(II)] µg/10 mL	[Cu(II)] mmol (C)	log C	[Cu(II)] Adsorbed µg	[Cu(II)] Adsorbed mmol (x)	log x/m	K _{ad}	1/n
<i>o</i> -HB- <i>o</i> -PD- -HCHO	50	0.00008	-4.0969	46	0.0007	-2.1549	7.888	0.729
	100	0.00016	-3.7958	88	0.0014	-1.8538		
	150	0.00024	-3.6197	127.5	0.002	-1.6989		
	200	0.00031	-3.5086	160	0.0025	-1.602		
	300	0.00047	-3.3279	200	0.0031	-1.5086		
	500	0.00079	-3.1023	230.5	0.0036	-1.4436		
<i>m</i> -HB- <i>o</i> -PD -HCHO	50	0.00008	-4.0969	43	0.00067	-2.1739	5.662	0.706
	100	0.00016	-3.7958	78	0.0012	-1.9208		
	150	0.00024	-3.6197	110.5	0.0017	-1.7695		
	200	0.00031	-3.5086	125	0.0019	-1.7077		
	300	0.00047	-3.3279	178.6	0.0028	-1.5528		
	500	0.00079	-3.1023	206.5	0.0032	-1.4948		
<i>p</i> -HB- <i>o</i> -PD -HCHO	50	0.00008	-4.0969	41.5	0.00065	-2.187	2.6	0.6
	100	0.00016	-3.7958	74.5	0.00117	-1.9318	91	26
	150	0.00024	-3.6197	116.9	0.00184	-1.7351		
	200	0.00031	-3.5086	107.5	0.00169	-1.7721		
	300	0.00047	-3.3279	135.6	0.00213	-1.6716		
	500	0.00079	-3.1023	181.8	0.00286	-1.5436		

Effect of added salt

Effect of the cations like Na⁺, K⁺ and Mg²⁺ on the adsorption behavior of the resin towards Cu(II) was observed. It is done by treating 100 mg of all the resins with 200 µg per 10 mL of the Cu(II) in presence of the above alkali and alkaline earth metal ion solution at the natural pH of the solution for 24 h. It was observed that the presence of alkali and alkaline earth metal ions and the accompanying anion have negligible effect on the adsorption behavior of the resins (Table 3). Hence, the resin could be used to remove Cu(II) ion from saline and non-saline water rich in these above cations. Hodgkin and Eibl²⁹ prepared a Cu²⁺ - selective (sirez - Cu) from phenol-formaldehyde and piparazine and the selective capacity for Cu²⁺ was studied in the pH range 3-10.5. They observed that, the alkali and alkaline earth metals were not retained by the resin in this range. Dev and Rao²⁴ also reported the same observation as we are report in this paper.

Table 3. Effect of added salt on the adsorption of Cu(II) ion by the resin.

Metal ion: Cu(II), [Cu(II)]: 200 µg/10 mL, Resin quantity: 100 mg, Sorbent size: 100 mesh, Temperature: 30 °C, pH:5.7, Contact time: 24 h.

Resin	Cu(II) uptake			
	In absence of added salt	In presence of added salt		
		Na ⁺	K ⁺	Mg ²⁺
<i>o</i> -HB- <i>o</i> -PD-HCHO	80	79.8	79.5	79.2
<i>m</i> -HB- <i>o</i> -PD -HCHO	70	69.6	69.6	69.0
<i>p</i> -HB- <i>o</i> -PD -HCHO	59	58.6	58.5	58.3

Separation

To know the adsorption efficiency of the resins in a competitive environment where both Cu(II) and Fe(III) ions are present, two set of experiments were carried out. In the first set of experiment 10 mL of solution containing 200 µg each of Cu(II) and Fe(III) was treated with 100 mg of the resins at varying pH (Table 4). It was found that in the pH range 3.42-4.63 all the resins exclusively adsorb Cu²⁺ ion while in the pH range 4.63-5.89 all the resins adsorb high percentage of Cu²⁺ with many fold increase in the k_d value along with a small amount of Fe³⁺ and most efficient among all the resin is *o*-HB-*o*-PD-HCHO. Mendez and Pillai³⁰ have reported a resin which is highly selective for Cu²⁺ over UO₂²⁺ and VO₂²⁺ above pH 3.

Table 4. Separation of Cu(II) from a mixture of Cu(II) and Fe(III) at varying pH.

Metal ion: [Cu(II)]=[Fe(III)]: 200 µg/10 mL, Resin quantity: 100 mg, Sorbent size: 100 mesh, Temperature: 30 °C, Contact time: 24 h, pH:5.7.

Resin	pH	Cu(II)		Fe(III)	
		Uptake, %	K_d	Uptake, %	K_d
<i>o</i> -HB- <i>o</i> -PD-HCHO	3.42	15	17.64	0	0
	4.0	33.5	50.37	0	0
	4.63	42.5	73.91	0	0
	5.2	57.5	135.29	12.5	14.28
	5.5	71.7	215.31	15	17.64
	5.89	83.4	502.4	20.0	25.0
<i>m</i> -HB- <i>o</i> -PD-HCHO	3.42	15.5	18.34	0	0
	4.0	27	36.98	0	0
	4.63	31.7	46.41	0	0
	5.2	35.9	56.0	9.7	10.74
	5.5	65.3	188.18	13.2	15.20
	5.89	69.7	230.03	18.5	22.64
<i>p</i> -HB- <i>o</i> -PD-HCHO	3.42	9.7	10.74	0	0
	4.0	23.7	31.06	0	0
	4.63	25.5	34.22	0	0
	5.2	33.5	50.37	0	0
	5.5	55.8	126.24	10.2	11.35
	5.89	62.8	168.81	12.5	14.28

In the second set of experiment, 10 mL of the solution containing a fixed amount of Cu²⁺ (200 µg/ 10 mL) and varying amounts of Fe³⁺ (100-400 µg/ 10 mL) was treated with 100 mg of the resins at affixed pH for 24 h (Table 5). It was seen that at pH 5.89, all resins take up Cu²⁺ quantitatively and the adsorption of Fe³⁺ was negligible. Again the most efficient resin is *o*-HB-*o*-PD-HCHO. Therefore it can be concluded that in a competitive environment where both Cu(II) and Fe(III) are present these resins are quantitatively adsorb Cu(II) over Fe(III) and forms effective metal complex with Cu(II) ions.

Arsenate adsorption studies

Literature survey shows that most of the work on metal-loaded polymers used for separation of arsenate has been done with Fe(III), but these sorbents cannot be effectively used for drinking water treatment³¹⁻³³. Because all observation shows that only at low pH As(V) can be removed. Again, because of the weak Lewis acid characteristic of ferric ions, the amount of Fe³⁺ loaded was low. Moreover, the loaded iron was nearly completely stripped off the hosting resin during regeneration and reloading of Fe³⁺ was necessary after each cycle of operation. Realizing the critical drawbacks of Fe³⁺ ions, Raman and Sengupta³⁴ prepared a

PLE by loading Cu²⁺ onto a weak base chelating resin (known as DOW 2N) with 2-picolylamine groups. Since Cu²⁺ is a much stronger Lewis acid than Fe³⁺, according to the Irving and Williams³⁵ order. So a much greater metal-loading capacity was observed. The copper loaded DOW 2N showed orders of magnitude greater selectivity for arsenate and selenate in the presence of competing sulfate ions than commercial SBA resins³⁶. Here we used the Cu(II) polychelate of the most efficient resin *o*-HB-*o*-PD-HCHO as polymeric ligand exchanger (PLE) and studied the arsenate adsorption capacity of it. Also compared the result with the arsenate adsorption capacity of the Fe(III) polychelate of the same resin. The metal polychelates were synthesized using the metal nitrate salts. We have also observed similar result as Raman and Sengupta³⁴ which is discussed below.

Table 5. Separation of Cu(II) from a mixture of Cu(II) and Fe(III) with increasing Fe(III) concentration at fixed varying pH.

Resin quantity: 100 mg, Sorbent size: 100 mesh, Temperature: 30 °C, Contact time: 24 h, pH:5.89

Resin	[M] µg/10 mL		Metal ion uptake %	
	Cu(II)	Fe(III)	Cu(II)	Fe(III)
<i>o</i> -HB- <i>o</i> -PD-HCHO	200	100	84.2	0
	200	200	83.4	20.0
	200	400	55	24.7
<i>m</i> -HB- <i>o</i> -PD -HCHO	200	100	71.8	0
	200	200	69.7	18.5
	200	400	40	19.7
<i>p</i> -HB- <i>o</i> -PD -HCHO	200	100	64.6	0
	200	200	62.8	12.5
	200	400	35.1	16.4

Equilibrium time

To determine the equilibrium time for the adsorption of arsenate ions 100 mg, 100 mesh of the polychelates *o*-HB-*o*-PD-HCHO -Cu(II), *o*-HB-*o*-PD-HCHO -Fe(III) were treated with metal salt solutions (2 µg/10 mL) at the 7.0 pH of the reaction mixture. The contact time was varied between 5 min to 24 h. Comparing the arsenate adsorption capacity of the PLEs, it is observed that the arsenic uptake efficiency of *o*-HB-*o*-PD-HCHO-Cu(II) polychelate is significantly higher than that of *o*-HB-*o*-PD-HCHO-Fe(III). The former PLE is able to take 80.2% of arsenate ion at 24 h in natural pH of the solution while the later only adsorbs 52.8% of arsenate (Table 6). The reason for such an observation could be attributed to the concurrent Lewis acid-base interactions between arsenate and the immobilized Cu²⁺ ions at the sorbent-sorbate interface. Under the experimental conditions, monohydrogen arsenate (HAsO₄²⁻) is considered as predominant arsenate species. HAsO₄²⁻ is a divalently charged, bidentate ligand and stronger lewis base. Consequently, interactions between arsenate and the immobilized Cu²⁺ ions involve both LAB interaction (or inner-sphere complexation) and ion pairing (or electrostatic interactions) (Figure 4). It is noteworthy that LAB interaction also enhances the electrostatic interactions between arsenate and the loaded Cu²⁺ 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 Fe³⁺ *o*-HB-*o*-PD-HCHO -Fe(III) has comparatively lower arsenate adsorption capacity than *o*-HB-*o*-PD-HCHO-Cu(II).

It was also observed that competing ions like sulphate has negligible effect on the arsenate adsorption. Though sulfate is also a divalently charged ligand, it is a much weaker Lewis base than the arsenate. Therefore interactions between sulfate and the Cu²⁺ ions is predominantly ion

paring. Therefore *o*-HB-*o*-PD-HCHO-Cu(II) offered much greater affinity for arsenate over sulfate. Again in case of SBA resins, the commercial SBA resins³⁶, 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 reported by Zhao *et al.*³⁶ by performed similar experiments over DOW 3N-Cu PLE.

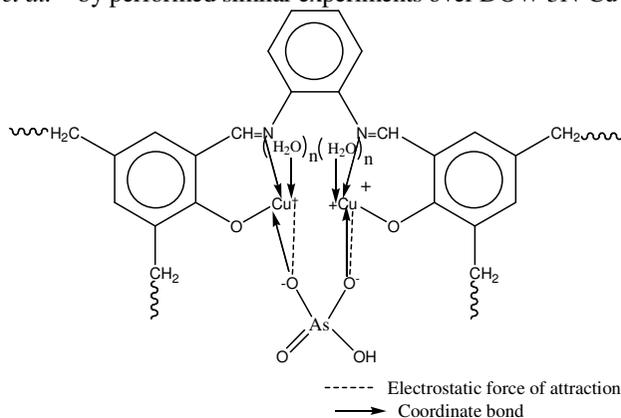


Figure 4. Structure of *o*-HB-*o*-PD-HCHO-Cu(II).

Table 6. Effect of contact time for arsenate adsorption studies.

[HAsO₄²⁻] = 200 μg/L, polychelate = 100 mg, sorbent size = 100 mesh, temp = 30 °C, pH = 7.0.

Contact Time, h	AsO ₄ ³⁻ ion uptake %	
	<i>o</i> -HB- <i>o</i> -PD-HCHO-Cu(II)	<i>o</i> -HB- <i>o</i> -PD-HCHO-Fe(III)
0.1667	0	0
0.5	21.3	8.5
1.0	45.5	17.1
2.0	59.0	29.5
4.0	72.5	41.7
24.0	80.2	52.8

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 (H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻) 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 *o*-HB-*o*-PD-HCHO-Cu(II) increased till pH 7.0 and then decreased but for *o*-HB-*o*-PD-HCHO-Fe(III) with increase in pH the arsenate adsorption capacity decreased (Table 7).

Sharp declination was observed in case of *o*-HB-*o*-PD-HCHO -Cu(II) after the pH range 8.0. Figure 5b 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 $\text{H}_3\text{AsO}_4 < \text{H}_2\text{AsO}_4^- < \text{HAsO}_4^{2-} < \text{AsO}_4^{3-}$. At $\text{pH} < 4$ the much less adsorbable H_2AsO_4^- or H_3AsO_4 is the predominant arsenate species, which cannot stand the competition of divalently charged sulfate anions. As a result, no As uptake is likely in the low pH range as observed in Figure 5(a-b). 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 sulfate, arsenate must be converted to the more adsorbable HAsO_4^{2-} species.

Table 7. Effect of pH for arsenate adsorption studies.

$[\text{HAsO}_4^{2-}] = 200 \mu\text{g/L}$, polychelate = 100 mg, sorbent size = 100 mesh, temp = 30 °C, contact time = 24 h.

pH	AsO_4^{3-} ion uptake %	
	<i>o</i> -HB- <i>o</i> -PD-HCHO-Cu(II)	<i>o</i> -HB- <i>o</i> -PD-HCHO-Fe(III)
3.42	0	67.3
4.63	24.0	61.0
5.5	63.5	56.3
7.0	79.9	52.7
7.8	57.8	45.1
8.2	33.2	28.6
8.8	8.7	18.9

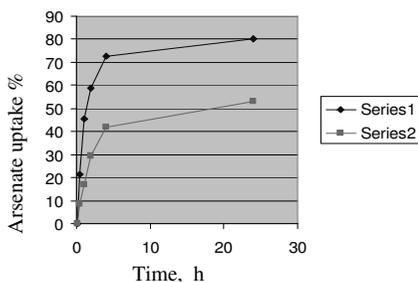


Figure-5(a). Effect of contact time on arsenate adsorption.

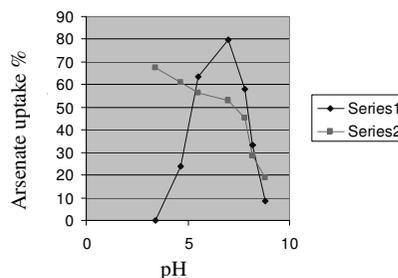


Figure- 5(b). Effect of pH on arsenate adsorption.

Series 1. For *o*-HB-*o*-PD-HCHO-Cu(II)
 Series 2. For *o*-HB-*o*-PD-HCHO-Fe(III)

Conclusion

It can be concluded that the phenolic Schiff base resins containing *o*-phenylenediamine are very efficient for uptake of various cations of heavy metals like copper, nickel and iron *etc.* Again the copper polychelates of *o*-HB-*o*-PD-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 the toxic 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 and arsenic, *etc.*

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