Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Dey, R. K. , Patnaik, Tanushree , Mohapatra, Neelkamal and Samal, S.(2007) 'Removal of Heavy Metal Ions using New Chelating Material Containing N, O, and S Donor Sites', Separation Science and Technology, 42: 16, 3593 — 3608

To link to this Article: DOI: 10.1080/01496390701515045

URL: http://dx.doi.org/10.1080/01496390701515045

Separation Science and Technology, 42: 3593–3608, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701515045

Removal of Heavy Metal Ions using New Chelating Material Containing N, O, and S Donor Sites

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Abstract: A new chelating material (AT-PHE-HCHO) was synthesized by reacting 2-aminothiazole-phenol (AT-PHE) azodye and formaldehyde (HCHO) in an alkaline medium. The materials were characterized by elemental analysis, FT-IR and ^{1}H-NMR spectroscopic studies. The chelating material was used for the adsorption of Cu(II), Zn(II), Mn(II), and Cr(III) from dilute aqueous solutions with variation of adsorption parameters. The adsorption was described quantitatively by fitting the equilibrium data to the Freundlich isotherm. The thermodynamic parameters ΔS and ΔH were calculated to be $86.02\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $-126.9\ \mathrm{KJ\ mol^{-1}}$, respectively. The metal adsorption followed the sequence $\mathrm{Cu(II)} > \mathrm{Zn(II)} \sim \mathrm{Cr(III)} > \mathrm{Mn(II)}$. The material was used for the removal of metal ions from synthetic as well as real samples.

Keywords: Adsorption, isotherms, chelating, removal

Received 29 January 2007, Accepted 30 April 2007

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INTRODUCTION

Removal of toxic heavy metal ions from water bodies is essential to reduce metal related environmental pollution control problems (1). Water pollution with heavy metals is primarily related to the anthropogenic inputs from various industrial wastes (2). Water soluble ions or compounds of heavy metals get readily absorbed into living organisms and they can bind to the vital cellular components such as structural proteins, enzymes, and nucleic acids, thus, clearly interfering with the body's physiological functioning (3). The use of functionalized polymers for separation and preconcentration of various metal ions from aqueous solutions has been discussed extensively in various available literatures (1–4). Solid phase extraction of metal ions using insoluble functionalized polymers is preferred mainly due to their operational flexibility, ease of formation of complexes with high metal to polymer bond energies, specific and fast complexation kinetics, and above all reusability of the polymeric ligand (5). Azo compounds have been used in the spectrophotometric determination of metal ions due to their strong ability to form complexes with a variety of metal ions (6). For example, pyridylazo-naphthol (PAN) and pyridylazo-resorcinol (PAR) act as terdentate ligands complexing with metals through a hydroxyl oxygen atom, a pyridine nitrogen atom, and one of the azo group nitrogen atoms (1). In thiazolylazo-naphthol (TAN), thiazolylazo-resorcinol (TAR), thiazolylazo-4-hydroxytoluene (TAC), and benzothiazolylazo-4-hydroxytoluene (BTAC), the nitrogen atom of the thiazole ring is bonded to a metal ion rather than to a pyridine nitrogen atom (1, 7). Incorporation of functional compounds in a suitable polymer matrix offers a methodology for using the excellent metal coordination properties of functional compounds while maintaining their structural integrity by combination with a polymeric material (8). Such kinds of materials can find numerous potential applications for the removal of toxic heavy metal ions from dilute aqueous solutions as well as industrial wastes (9–12).

While synthesizing chelating materials, the choice of ligands always plays an important role in achieving selectivity. A recently published report showed usefulness of polymeric materials containing benzimidazolylazo, and imidazolylazo in a polystyrene bed for separation of various toxic metal ions like Hg(II), Ag(I) and Pd(II) in trace quantities from geological, medicinal, and environmental samples (13).

The present investigation reports the synthesis of a new chelating material from the reaction of azodye of 2-aminothiazole-phenol and formaldehyde. Adsorption of metal ions such as Zn(II), Cu(II), Mn(II), and Cr(III) from a dilute aqueous solution was studied in both competitive and non-competitive conditions with variation of adsorption parameters such as pH, temperature, and time. The chelating material was used for the removal of metal ions from wastewater and drinking water samples. The synthetic methodology adopted here offers a new adsorbent material for industrial use and the material is expected to find widespread applications for toxic/heavy metal removal from water bodies.

MATERIALS AND METHODS

Instrumentation

The FTIR spectra were recorded in the range 4000–500 cm^{-1} using Bruker spectrophotometer and KBr phase. The ^1H NMR (BrukerDRX300) spectra were run in $DMSOd_6/CDCl_3$ solvent. The elemental analysis was performed using Carlo Erba 1108 elemental analyzer. Estimation of metal ions was done using a Shimadzu atomic absorption spectrophotometer (AAS) (model AA-680) equipped with a single element hollow cathode lamp and an air-acetylene burner. The instrument parameters were those recommended by the manufacturer. The wavelength (nm) selected for the analytes were as follows: Mn 279.5, Cr 357.9, Cu 324.8, and Zn 213.9. The pH of the solution was measured in a Systronic Digital pH meter model 335 equipped with a combined glass-calomel electrode.

Reagents

The starting materials such as 2-Aminothiazole (AT), (Merck), phenol (PHE), formaldehyde (HCHO), (Merck/BDH, India, AnalR grade) were used as received. Doubly distilled water was used for the preparation of solutions. Standard solutions of AAS grade Cu, Cr, Zn, and Mn (CDH, India) were used for the preparation of the calibration curve in atomic absorption spectrophotometer and estimation of metal ions was done according to the standard procedures (14). pH of solutions were maintained using buffers (15). Solutions of Cu(II), Cr(III), Mn(II), and Zn(II) were prepared from respective reagent grade nitrate or chloride salts by dissolving them in double distilled water.

Synthesis of Chelating Material

The synthesis of the chelating material, as outlined in reaction scheme (Fig. 1), was performed in two different steps. In the first step, AT was reacted with PHE to yield AT-PHE, which was allowed to react with formaldehyde in the subsequent step to produce the final chelating material AT-PHE-HCHO. In a typical procedure, 10.0 g of 2-aminothiazole was dissolved in 120 mL of 6 mol L^{-1} H_2SO_4 solution. To this solution, 3.0 g of sodium nitrite ($NaNO_2$) in 20 mL of water was added in a dropwise manner while the temperature of the reaction medium was maintained in between 0–4°C for nearly 45 minutes (solution 1). For the coupling

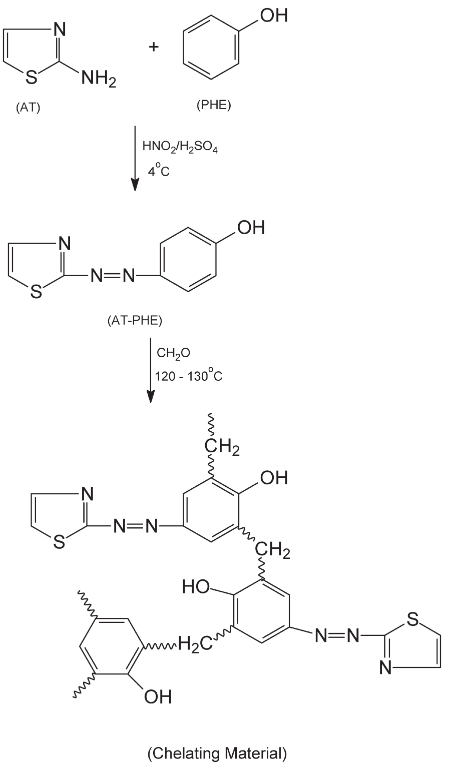

Figure 1. Reaction scheme.

reaction, 9.4 g of phenol was added to 20 mL of 1.0 mol L^{-1} Na_2CO_3 solution in a separate conical flask and the mixture was cooled to nearly 0°C (solution 2). The solution 2 was subsequently added drop-wise to the solution 1 with continuous stirring. The reaction mixture was allowed to stand overnight in a cooled condition (nearly 4°C) and after 24 h the precipitation (AT-PHE) was filtered and recrystallized with isopropyl alcohol.

The synthesis of the final chelating material was done following a procedure in which 5.0 g of AT-PHE was suspended over 50.0 mL of water at 40°C with the addition of a few drops of dilute sodium hydroxide solution. Formaldehyde solution (37% v/v) was added in 1:2 molar ratios and the mixture was refluxed in an oil bath at 120–130°C for 2 h. The insoluble chelating material, so formed, was filtered off and washed thoroughly with enough quantity of demineralized water, and finally dried at 70°C. The dried material (AT-PHE-HCHO) was powdered, suspended in water at pH 4.0 for 24 h, filtered, washed with large excess of water, and finally dried at 70°C.

Metal Adsorption Studies

The metal adsorption studies were carried out using batch equilibration technique. The suspension of the chelating material in the metal solution of known volume and concentration was kept for different time periods, from 0.5 h to 24 h, as per necessity, under constant shaking condition. After the fixed time interval, the chelating material was filtered off and thoroughly washed with double distilled water. The metal ion concentration in the combined filtrate and the washing was estimated using AAS. The percentage of the extraction of metal ions was calculated from the difference between the metal concentration of aqueous solution before and after the contact time period/equilibration. The amount of metal sorbed per unit mass of sorbent (Q, mmol g^{-1}), distribution ratio (D, mL g^{-1}) was calculated according to the following equations:

$$Q = (C_o - C_e)V/m \quad D = Q/C_e$$

Where, C_o, and C_e are the initial concentration and final equilibrium concentration of metal ions (mmol L^{-1}), respectively. "V" is the volume of the solution in dm^3, and "m" is the mass (in g) of the chelating material.

In the column operation study, a glass column (15 cm height × 0.40 cm internal diameter) having a stopcock and porous disk was used. 2.0 g of the chelating material (60–120 mesh sizes slurred in water) were poured into the column and the column was conditioned with buffer solution. The metal ion solution was run through the column and the gravity-driven flow of the solution was controlled with regulating stopcock. After each use the column was washed with water and stored in water for the next experiment.

RESULTS AND DISCUSSION

Characterizations

The synthesized chelating material (AT-PHE-HCHO) was a colored solid, and found to be soluble in various organic polar solvents such as DMF, DMSO, and THF. The material showed poor solubility in methanol, benzene, toluene, and remained insoluble in water. The experimental percentage of C, N, and S were found to be 47.7, 12.5, and 10.8, respectively. The intrinsic viscosity of the chelating material, determined from Huggin's Plot using DMSO as solvent, was found to be 0.203 dL g^{-1}.

The infrared spectra of the synthesized AT-PHE and AT-PHE-HCHO showed the O-H stretching frequency at 3422 cm^{-1}. The N=N stretching frequency observed at 1468 cm^{-1} in AT-PHE, appeared as a sharp band at 1460 cm^{-1} in the corresponding final chelating material AT-PHE-HCHO. The Ph-O frequencies observed at 1245 and 1248 cm^{-1} for AT-PHE and

AT-PHE-HCHO, respectively. In all synthesized materials, the aromatic (C=C) stretching frequencies were registered in the region 1598–1496 cm^{-1}. Peaks observed at 2925 and 1502 cm^{-1} in AT-PHE-HCHO indicated the CH stretching frequencies of -CH_2- group of formaldehyde moiety. Upon coordination with Cu^{2+} metal ion, the Ph-O vibration in AT-PHE-HCHO was shifted to 1224 cm^{-1}. The aromatic C=C stretching frequency was also registered shifting to 1502 cm^{-1}, indicating the metal coordination with the available ligands (16, 17).

The ^1H NMR spectra of the synthesized compounds are presented in Fig. 2. The compound AT-PHE registered the aromatic proton peaks in the region 6.9–7.8 ppm. The peaks observed at 6.9 ppm assigned to the proton positioned ortho to the phenolic O-H group and the peaks at 7.7 ppm was assigned to the protons ortho to the N=N. Upon condensation with formaldehyde, the spectral pattern changed and a new set of peaks appeared in the range 4.6–4.7 ppm, which was assigned to the bridging -CH_2- groups present in AT-PHE-HCHO (18).

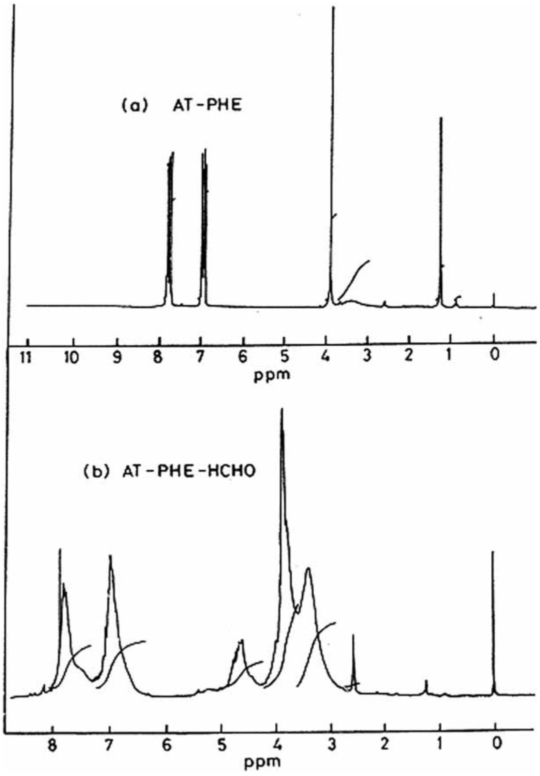

Figure 2. ^1H NMR spectra of (a) AT-PHE (b) AT-PHE-HCHO.

Effect of pH

The influence of pH upon the metal adsorption properties, presented in Fig. 3, was studied in the range 2.5–7.5 using a buffer. A contact time period of 6 h was maintained to ensure maximum adsorption of metal ions by the adsorbent material, which is taken as the equilibrium condition. The adsorption of Cu(II), Zn(II), and Cr(III) was found to be more than Mn(II). It was observed that an increase in the pH of the medium favored higher adsorption of metal ions, which could be attributed to the ease of protonation of available coordination sites at low pH of the medium. The adsorption of metal ions followed the sequence Cu(II) $>$ Zn(II) $\sim$ Cr(III) $>$ Mn(II). The high adsorption of Cu(II) may be explained on the basis of the fact that Cu(II) could act as an intermediate Lewis acid, thus exhibiting a strong tendency to form complexes with ligands containing N-donor atoms with intermediate base properties (19, 20). An adsorption experiment beyond pH 7.5 was discouraged due to the possibility of hydrolysis of metal ions.

Effect of Contact Time

The variation of contact time is shown in Fig. 4. It was found that the amount of metal sorbed per unit mass of the sorbent in case of Cu(II) and Zn(II) reached its maximum value within a contact time period of 30–50 min. However the adsorption process was relatively slow for both Cr(III) and Mn(II) for which the maximum adsorption was reached within a time period of 60–120 min. The observed metal chelating property of the

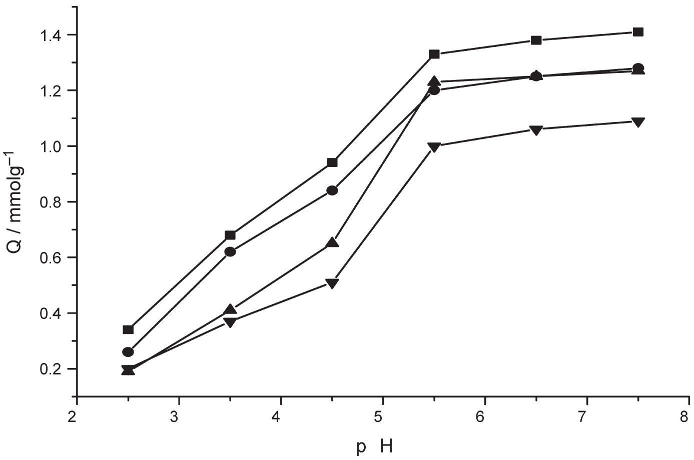

Figure 3. Effect of variation of pH of the medium. Quantity, 1.0 g; size, 100 mesh; temp., 27°C; contact time, 6 h, Relative Standard Deviation (R.S.D.) values varies between 0.32–0.47%, Cu(II): (■); Zn(II): (●); Cr(III): (▲); Mn(II): (▼).

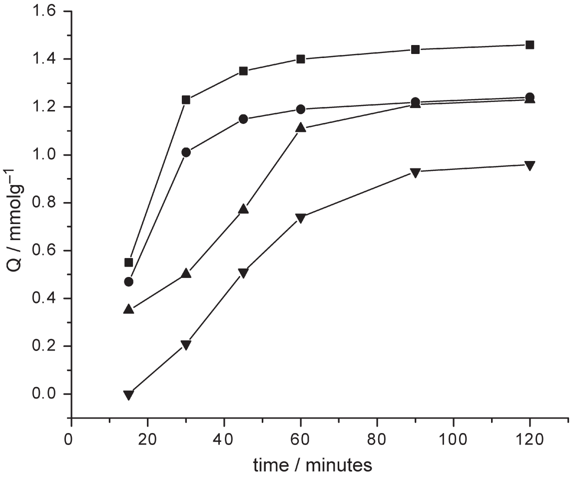

Figure 4. Effect of variation of contact time. Quantity, 1.0 g; size, 100 mesh; temp., 27°C; pH 5.8, R.S.D. values varies between 0.21–0.36%, Cu(II): (■); Zn(II): (●); Cr(III): (▲); Mn(II): (▼).

material could be explained on the basis of the presence of both nitrogen and sulfur atoms as the coordination sites in which the presence of sulfur in the moiety might favors the binding to the metal ions, followed by chelation via azo nitrogen atom (21). Apart from this, the sulfur containing groups are mainly soft bases and, therefore, it is reasonable to use the sulfur containing functional group materials for the removal of metal ions like copper, cadmium, and silver, which sometimes with change in oxidation states, behave as weak acids in solutions (1). In the present investigation, the observed result showed a higher adsorption of Cu(II) in aqueous solution in comparison to other metal ions taken for study at pH 5.8. But change in solvent medium and pH of the solution can stimulate other factors such as competition of metal ions to coordinate with the available ligands, which may also change the trend in adsorption behavior (22).

Effect of Temperature

The metal adsorption property of the chelating material for Cu^{2+} and Zn^{2+}, with variation of temperature of the medium, is presented in Fig. 5. A contact time period of 0.5 h was chosen. It was observed that an increase in temperature of the medium favors adsorption of metal ions by the chelating material. The reason may be attributed to the fact that high temperature offers the possibility of swelling of the chelating matrix in the presence of a solvent medium, therefore, the accessibility of the coordination sites to the metal ions could be more facilitated. However, increasing the temperature

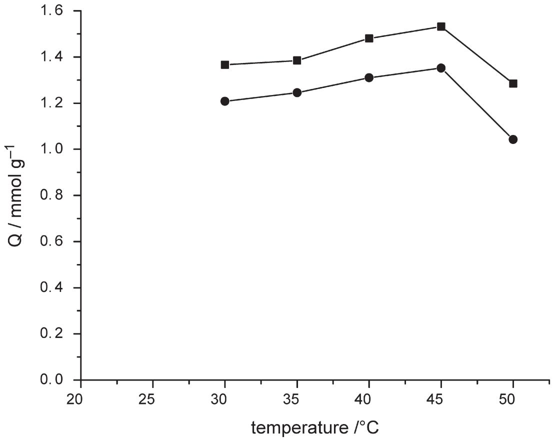

Figure 5. Effect of variation of temperature of the medium. Quantity, 1.0 g; size, 100 mesh; pH 5.8; contact time, 0.5 h; R.S.D. values varies between 0.12–0.25%, Cu(II): (■); Zn(II): (●).

beyond a certain limit, which in the present investigation was 45°C, leads to further desorption of metal ions from the coordination sites. The plot of log D versus 1/T (Fig. 6) shows a near linear relationship with a correlation coefficient of 0.9089. Using the equation, $\log D = -\Delta H/2.303RT + \Delta S/R$,

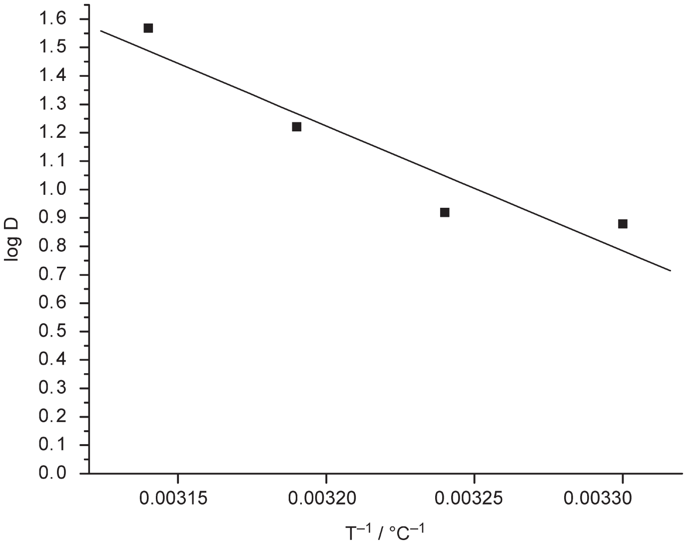

Figure 6. Plot of log D vs. 1/T. Quantity, 1.0 g; size, 100 mesh; pH 5.8, R.S.D. values varies between 0.56–0.65%, Metal ion: Cu(II).

the enthalpy (ΔH) and entropy (ΔS) parameters were calculated to be 84.02 kJ mol^{-1} and 126.9 J mol^{-1} K^{-1}, respectively.

Sorption Kinetics

The Freundlich adsorption isotherm was verified for sorption of Cu(II), Zn(II), and Cr(III) onto the chelating material. The Freundlich equation in linearized form can be written as:

$$\ln Q = \ln K_F + 1/n \ln C_e \tag{1}$$

where, "Q" is the adsorption capacity in mmol g^{-1}, "C_e" is the equilibrium concentration of metal ions in mmol mL^{-1}, "n" is the constant, "K_F" is the binding energy constant reflecting the affinity of chelating material to metal ions. The plot of lnQ versus lnC_e for Cu(II), as shown in Fig. 7, was found to be linear. The Freundlich equation for Cu(II): $\ln Q_{Cu}^{2+} = 0.9675. \ln C_e + 0.0913$; for Zn(II): $\ln Q_{Zn}^{2+} = 0.9376. \ln C_e + 0.1663$; and for Cr(III): $\ln Q_{Cr}^{3+} = 0.8116. \ln C_e + 0.4591$. The constant "$K_F$" and "n" were calculated to be 1.095, 1.180, 1.582 and 1.034, 1.066, 1.232, respectively, for Cu(II), Zn(II), and Cr(III). The values $1 < n < 10$ indicated the favorable adsorption of metal ions onto the chelating material (23). The correlation coefficients (R^2) for the Zn(II), Cr(III), and Cu(II) were found to be 0.9966, 0.9927, and 0.9986, respectively, indicating good fit of experimental data in Freundlich isotherm equation.

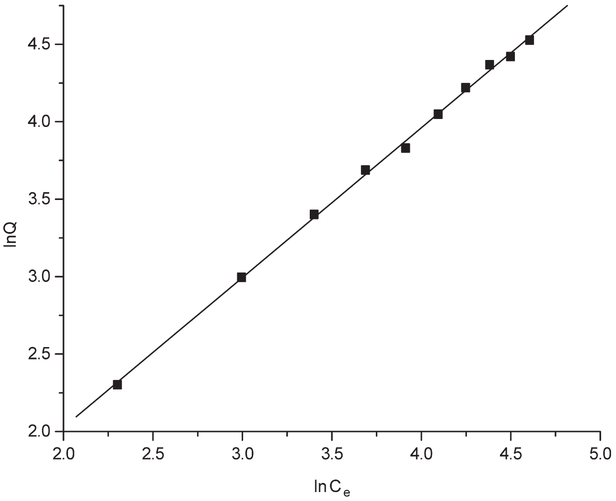

Figure 7. Verification of Freundlich adsorption isotherm. Quantity, 1.0 g; size, 100 mesh; contact time, 2.0 h; Metal ions: Cu(II).

Adsorption in Competitive Environment

The preferential adsorption of metal ions by the chelating material was determined in competitive environment. For this, the metal adsorption property, as shown in Fig. 8, was studied by taking a mixture of equimolar quantity of Cu(II), Zn(II), and Mn(II) with the variation of pH of the medium. It was observed that no quantitative adsorption of Mn(II) was noticed till pH 4.5. However, the preferential adsorption of Cu(II) was found to be more than other tested metal ions.

In a separate experimental set up, the recovery of Cu(II), Zn(II), and Cr(III) was attempted in the presence of salts of $MgCl_2$, $CaCl_2$, NaCl, KBr, $NaNO_3$, Na_2SO_4, and $NaHCO_3$ at the natural pH of the medium. These metal salts are commonly found in water sample. A synthetic sample of all above metal salts, as shown in Table 1, was prepared (24). The conductivity of the sample was measured to be 7.23 mS. 1.0 g of the chelating material was treated separately with 50 μg mL^{-1} of Cu(II), Zn(II), and Cr(III) containing the above interferents at ambient temperature (27°C). The amount of recovery of metal ions was found to be 78.0, 62.0, and 53.0%, respectively, for Cu(II), Zn(II), and Cr(III). This study also indicated little variation in metal adsorption behavior in the presence of alkaline and alkaline earth metal ions.

Column Studies

Study of metal adsorption properties in dynamic conditions can be related to the evaluation of material property for subsequent industrial use. In the present

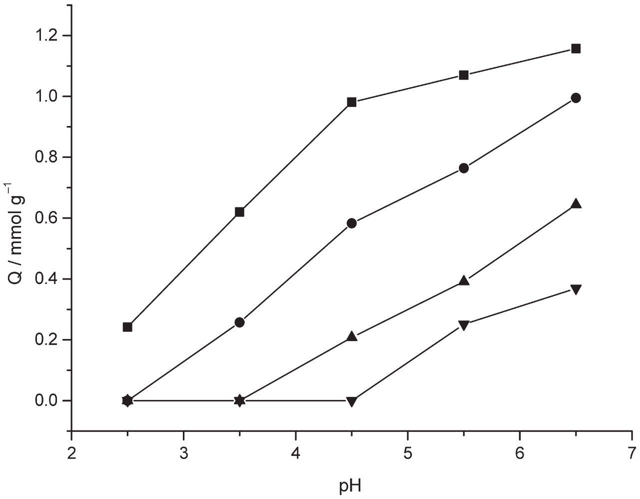

Figure 8. Competitive sorption behavior. Quantity, 1.0 g; size, 100 mesh; contact time, 2.0 h; R.S.D. values varies between 0.32–0.45%, Metal ions: Cu(II): (■); Zn(II): (●); Cr(III): (▲); Mn(II): (▼).

Table 1. Concentration of various metal ions in synthetic sample

Salts	Concentration mol L^{-1}
$MgCl_2$	4.1×10^{-2}
$CaCl_2$	4.1×10^{-2}
NaCl	4.0×10^{-2}
KBr	1.2×10^{-4}
$NaNO_3$	8.0×10^{-4}
Na_2SO_4	3.1×10^{-3}

case, the metal adsorption property of the chelating material was investigated in a dynamic condition, using column studies, for Cu(II) and Zn(II). Prior to the adsorption experiment, the filled column was conditioned with a buffer of pH 5.8. In the subsequent step, the metal solution (50 mL, 50 μg mL^{-1}) was loaded onto the column at 0.5 mL min^{-1} flow rate. The analytes were collected with the variation of flow rate in the range 0.5–2.0 mL min^{-1}. The percentage of retention of Cu(II) and Zn(II) was found to be 68.0 and 62.0, respectively, by maintaining a minimum flow rate of 0.5 mL min^{-1} for the collection of analytes. The adsorption of metal ion decreased with an increasing flow rate of the collection of analytes. This could be attributed to the availability of less contact time for material-metal ion interaction (22).

Following adsorption, desorption of metal ions from the loaded column was also attempted using 1.0 mol L^{-1} HCl solution as eluting agent. Previously, the column was packed with 1.0 g of the chelating material and subsequently loaded with copper metal ion (50 μg, 0.5 mL min^{-1} flow rate) with different feed volumes varying between 100–1000 mL. It was found that 40 mL of eluent (1.0 mol L^{-1}) was sufficient for quantitative recovery of Cu(II) from the chelating material. The flow rate was controlled gravimetrically (0.5 mL min^{-1}) using stopcock and it was observed that nearly 85.0% of the metal ions could be successfully eluted from the loaded column within two operation cycles. The effect of sample volume on the recovery of Cu(II) was shown in Fig. 9. However, increasing the flow rate of the eluting agent decreases the percentage of elution. The breakthrough volume of Cu(II) solution from which quantitative recovery of metal ion could be achieved was 15.0 mL. A maximum preconcentration factor of 62.3 could be achieved in case of Cu(II). Similarly, in case of Zn(II) metal ion, the breakthrough volume was found to be 20 mL and the maximum preconcentration factor was calculated as 45.1.

Extraction of Metal Ions from Industrial Waste

The metal removal property of the chelating material was also evaluated using industrial wastewater samples. Water samples from the nearby Paradeep

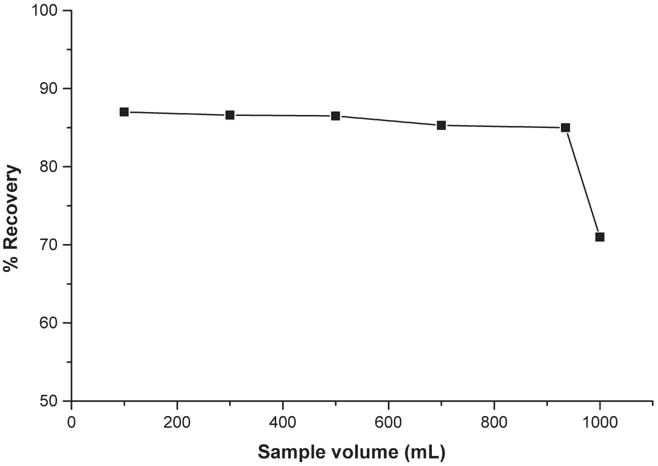

Figure 9. Effect of sample volume on the recovery of Cu(II).

industrial estate was collected in cleaned polyethylene bottles. The samples were filtered using micro filter paper (0.5 μm) to remove any solids and suspended materials. The quantitative estimation of Cu(II), Zn(II), and Cr(III) was done prior to the application of the chelating material for metal removal purpose. The adsorption of metal ions was carried out at the natural pH of the medium, which varies within 2.5–3.0, using a batch system. The removal of Cu(II) by the chelating material was found to be nearly 65.0%; however, no significant removal of Zn(II) and Cr(III) was noticed. Although the chelating material showed good adsorption property for metal ions such as Zn(II), Cr(III) in the synthetic laboratory sample in a non-competitive as well as a competitive environment. In case of a real industrial sample the situation could be different in which case the presence of other possible cations like iron, aluminum, etc., and the pH of the medium could significantly affect the metal adsorption properties. Some more study on this aspect is currently in progress and the present observation can be helpful in projecting the future experimental set up.

Concentration of Metal Ions from Spiked Natural Tap Water Sample

Water for domestic use is mainly drawn from ground water and surface waters. Ground water, extracted from aquifers below the water table, has long been an important source of domestic water. The water is then treated in a water treatment plant before entering the municipal water supply that is available as tap-water, which is often directly utilized as drinking water in developing countries like India. Treatment of water varies depending on the

Table 2. Removal of metal ion from spiked natural tap-water sample

Metal ion	Metal ion added (mg L^{-1})	Metal ion found (mg L^{-1})	Recovery, %
Cu(II)	0	0.43	—
	0.5	0.90	96.7
	1.0	1.33	93.0
Cr(III)	0	0.0	—
	0.5	0.43	86.0
	1.0	0.93	85.0
Mn(II)	0	0.10	—
	0.5	0.52	63.0
	1.0	0.91	70.9

Quantity of material, 1.0 g; size, 100 mesh; time of contact, 2.0 h.

quality of the water, but it generally involves filtration and chemical treatment. Water may also become contaminated during distribution. For example, the use of lead pipes between water mains and homes is the chief course of contamination of drinking water. Similarly, old copper pipes, metallic water taps, and joints, often contaminated the water with various metal ions like copper, chromium, and manganese. Therefore, water intended for drinking purpose, which is directly available from water taps, needs to be free from toxic/heavy metal contaminants.

In the present investigation, drinking water sample (1L) was collected from municipal tap-water sources in Ranchi the town of and spiked separately with Cu(II), Cr(III), and Mn(II) (0.5–1.0 mg L^{-1}) (Table 2). The suspension of the chelating material and metal ions were stirred for 2 h at ambient temperature (27°C). The unabsorbed metal ions were estimated by AAS. The result showed that more than 90% of Cu(II) removal from the spiked water sample could be possible; however, the removal of Cr(III) and Mn(II) was limited to nearly 70–80%. Since the preliminary results are encouraging, therefore, the chelating material could be developed as a small water traps for the removal of heavy metal ions.

CONCLUSIONS

A new synthetic chelating material was prepared from azodye of aminothiazole-phenol and formaldehyde in alkaline medium. The chelating material was characterized using FTIR and ^{1}H NMR techniques. The presence of multiple donor atoms like nitrogen and sulfur favored the removal of a number of cations such as Cu(II), Zn(II), Cr(III), and Mn(II) from dilute aqueous solution. The adsorption processes found to obey Freundlich adsorption isotherm model and the values constant "n" ($1 < n < 10$), indicated the favorable adsorption of metal ions onto the chelating material. The presence of diverse ions in the solutions imparted little effect on the adsorption properties of the material. A series of experimental parameter variations in laboratory conditions as well as the applications of the material in case of industrial sample and tap-water sample demonstrated the selective removal of Cu(II) in comparison to Mn(II) and Cr(III). In commensuration with the experimental observations, the material is expected to find a diverse range of suitable applications in the removal of heavy metal ions from contaminated aqueous samples.

ACKNOWLEDGMENTS

The authors wish to acknowledge financial support (Grant No.: F12-32/04) of University Grants Commission (UGC), New Delhi, to carry out the project work. Analytical results obtained from the Central Drug Research Institute (CDRI), Lucknow, are thankfully acknowledged.

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