Nickel and Copper Removal Study from Aqueous Solution Using New Cationic Poly[acrylamide/*N*,*N*-DAMB/*N*,*N*-DAPB] Super Absorbent Hydrogel

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ABSTRACT: A new cationic poly[acrylamide/*N*,*N*-diallyl morpholinium bromide/*N*,*N*-diallyl piperidinium bromide] super absorbent hydrogels (H1–H7) were prepared via microwave irradiated free radical cyclopolymerization using different composition. By the swelling study, hydrogel H1 is found to bear good swelling properties amongst all prepared hydrogels. The hydrogel H1 has been characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), and TGA analysis. A batch system was applied to study the adsorption of Ni(II) and Cu(II) from aqueous solutions by hydrogel H1. The effect of treatment time, pH of the medium, amount of adsorbent doses, and initial feed concentration of metal ion on adsorption of Ni(II) and Cu(II) from their solution were also investigated. Adsorption of Ni(II) and Cu(II) increases with the increase in treatment time, adsorbent doses, and initial feed concentration and decreases with the increase in pH of the medium. The desorption of metal ions were carried out using 1*N* HCl and 0.5*N* H_2SO_4. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2485–2493, 2011

Key words: cationic hydrogel; cyclopolymerization; adsorption; metal removal; Ni(II); Cu(II)

INTRODUCTION

Industrial wastewater is one of the major sources of environmental pollution. Among the environmental pollutions, heavy metals have gained relatively more significance due to their toxicity.[1] Heavy metals are released into the environment in a number of different ways, such as battery manufacturing, painting, printing, coal combustion, sewage wastewaters, automobile emissions, mining activities, tanneries, alloy industries, and the utilization of fossil fuels.[2] The removal and recovery of heavy metal ions from industrial wastewater has been a potential approach owing to economic and environmental factors. Conventional techniques used to remove heavy metals from wastewater including chemical precipitation, filtration, reverse osmosis, adsorption, electrochemistry, and ion exchange.[3] Most of these techniques are costly and ineffective, especially in removing heavy metal ions from wastewater.

The need for cost–effective, safe, and ability to carry out almost complete removal of heavy metal ions from wastewater has resulted in the development of new techniques such as polymeric adsorbents especially hydrogels. In recent years, many researchers along with our research group have worked on removal or retention of heavy metal ions using different hydrogels having different functional groups.[4–11]

Hydrogels are hydrophilic water insoluble polymers. Which can absorb enormous amount of water up to thousands of times their own weight. The swelling behaviors of superabsorbent polymers may be characterized by water adsorption.[12–14] The water imbibing capacity depends on the pH,[15,16] temperature,[17–20] ionic strength[19,20] of the swelling medium and on the network structure of macromolecular chains, such as hydrophilic functionality,[21–23] crosslinking density,[24–26] chain flexibility, osmotic potentials,[19,26] and free volume.[17]

The aim of present work is to prepare new cationic P[acrylamide (AAm)/*N*,*N*-diallyl morpholinium bromide (DAMB)/*N*,*N*-diallyl piperidinium bromide (DAPB)] superabsorbent hydrogels (H1–H7). The obtained hydrogel H1 were used as new adsorbent for the removal of Ni(II) and Cu(II) ions from aqueous solution and the effect of adsorption parameters, such as initial concentration, pH, adsorbent doses, and contact time on their adsorption properties were investigated. The plausible retention mechanism is as shown in below Scheme 1.

EXPERIMENTAL

Chemicals

Acrylamide (AAm) monomer, *N*,*N*-methylene bisacrylamide (MBAm) crosslinker, piperidine, allyl bromide,

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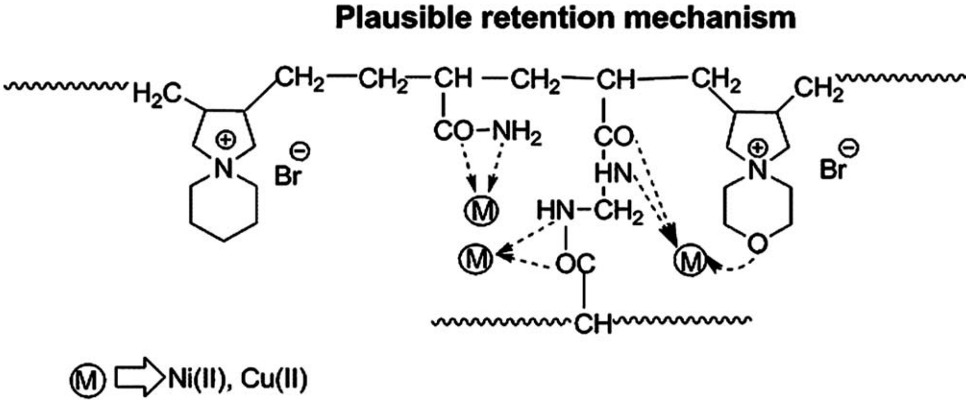

Scheme 1

and both the metal salts $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ were used of analytical grade. Initiator 2,2′-azobis (2-methyl propionamidine) dihydrochloride (V-50) were supplied by Aldrich (Steinheim, Germany). Double distilled water was used for hydrogel synthesis and the metal removal studies.

Instrument

Bruker Avance II 400 MHz NMR spectrophotometer was used to record the ^1H and ^{13}C-NMR spectra using D_2O as solvent. Fourier transform infrared (FTIR) spectra were recorded on Perkin-Elmer's spectrum GX FTIR spectrophotometer in the range of 400–4000 cm^{-1} via KBr pellet. Philips XL 30 ESEM Environmental Scanning Electron Microscope was used to observe the surface morphology. Perkin-Elmer PYRIS-1 Thermo Gravimetric Analyzer (TGA) was used to determine the thermal behavior of the hydrogel. Shimadzu-18A UV-Visible spectrophotometer.

Synthesis of *N,N*-diallyl morpholinium bromide

This was prepared by quaternization of *N*-allyl morpholine with allyl bromide as described elsewhere.[27]

Synthesis of *N,N*-diallyl piperidinium bromide

20 g, 1 mole of piperidine dissolved in 40 mL dry acetone was charged in a 250 mL three necked round bottom flask equipped with additional funnel. The flask was cooled in ice bath at 5°C. Then after (14.2 g, 0.5 mole) allyl bromide was added drop wise over a period of 30 min with constant stirring. The clear solution turned cloudy soon after addition of allyl bromide, indicating formation of the by product. After completion of the allyl bromide addition, the contents of the flask were discharged and then filter. The filtrate containing the intermediate product N-allyl piperidine was collected and returned to the flask. Then after 14.2 g (0.5 mole) of allyl bromide was again added slowly to the flask. Crystals of *N,N*-diallyl piperidinium bromide monomer precipitated out during the course of the allyl bromide addition and were recovered, after completion of the reaction, by filtration. The *N,N*-diallyl piperidinium bromide monomer was subsequently dried for 24 h in a vacuum oven. The melting point of compound is 215°C, yield 95%.

The synthesized monomer has been characterized by FTIR, ^1H, and ^{13}C-NMR spectroscopy.

FTIR

2967 cm^{-1} $=C{-}H$ stretching, 1634 cm^{-1} $C{=}C$ stretching, 1454 cm^{-1} CH_2 bending, 1276 cm^{-1} $C{-}N$ stretching, 899 cm^{-1}, and 973 cm^{-1} olefinic $C{-}H$ out of plane bending vibration.

^1H-NMR(δppm)

1.54–1.57 δ (2H,t), 1.78 δ (4H,s), 3.22–3.23 δ (4H,d), 3.79–3.81 δ (4H,d), 5.55–5.61 δ (4H,m), 5.84–5.96 δ (2H,m).

^{13}C-NMR (δppm)

19.25 ($CH_2{-}CH_2{-}N^+$), 20.59 ($CH_2{-}CH_2{-}CH_2{-}N^+$), 58.25 ($CH_2{-}N^+$), 60.90 ($CH_2{-}CH$), 123.95 ($CH{=}CH_2$), 128.58 ($CH{=}CH_2$).

Hydrogel synthesis

The P[AAm/*N,N*-DAMB/*N,N*-DAPB] hydrogels (H1–H7) were prepared via microwave irradiated free radical cyclopolymerization in the presence of MBAm as a crosslinker and V-50 as an initiator. Monomers, crosslinker, and initiator were mixed together in the appropriate molar ratio and dissolved in 9 mL of double distilled water in a 100 mL single neck round bottom flask under magnetic stirring. This mixture was stirred to give homogeneous solution. The flask was put in microwave and irradiated at 240 W for 2 min and at 280 W for 1 min. Then the flask was put in an oven at

TABLE I
Composition Detail and Swelling Characteristic of Studied Hydrogels

Hydrogel code	AAm mole	*N,N*-DAMB mole	*N,N*-DAPB mole	MBAM mole	V-50 mole	% Seq (in distilled water)
H1	1	1	1	0.06	0.04	11,550
H2	1	1	0.5	0.06	0.04	11,190
H3	1	0.5	1	0.06	0.04	9160
H4	0.5	1	1	0.06	0.04	9550
H5	1	0.5	1	0.06	0.04	8020
H6	0.5	1	0.5	0.06	0.04	9280
H7	0.5	0.5	1	0.06	0.04	8870

60°C for 5 h to reduce the residual monomer content in the gel. The polymerization reactions were carried out by varying the concentrations of P[AAm/*N,N*-DAMB/*N,N*-DAPB] hydrogels (H1–H7) and crosslinker in feed. The hydrogels (H1–H7) were immersed in double distilled water and kept for one day by changing the water at every 4 h of intervals. The swollen gel was immersed in acetone for about 4 h by replacing fresh acetone twice. Finally the gel was dried in air forced oven at 60°C to constant weight. The hydrogel sample code, composition detail, and swelling characteristics of the hydrogels are presented in Table I.

Swelling studies

To determine the % equilibrium swelling (%Seq)[7,28,29] of the P[AAm/DAMB/DAPB] hydrogels (H1-H7) in Figure 1, the gravimetric method was used. An accurately weighed hydrogel was put in a tea bag; immersed in a beaker containing 100 mL distilled water. After attaining the equilibrium, the tea bag was taken out and the excess water was removed by filter paper and then weighed accurately using an electronic balance (Citizen CX120, $d = 0.1$ mg).

The % equilibrium swelling of hydrogel was calculated using the following eq. (1).

$$\%\,\mathrm{Seq} = \frac{W\mathrm{eq} - W\mathrm{o}}{W\mathrm{o}} \times 100 \qquad (1)$$

Where Weq is the weights of swollen gel at equilibrium and Wo is the weight of dry gel.

Metal removal study

To explore the effect of influencing factors, such as contact time, pH, adsorbent doses, and the initial concentration of metal solution, a series of batch experiments were conducted. The entire adsorption experiments, the stock solutions were diluted to the required concentration. The adsorption experiments were performed by agitating specified (50 mg) amount of adsorbent (Hydrogel) in 50 mL of metal solutions of the desired concentrations at varying pH in a 100 mL stoppered conical flask. The pH of the solutions in the experiments was adjusted with 0.1 *N* HCl and 0.1 *N* NaOH. The reaction mixture was agitated at 200 rpm for a known period of time at 30°C in a Scigenics Orbitek mechanical shaker. After equilibrium, the concentrations of metal ions remaining in the solution were determined by a Shimadzu-18A UV–Visible spectrophotometer, using precalibrated curves. The amount of metal ions adsorbed on the hydrogel was calculated, based on the difference of the metal ions concentration in the aqueous solution before and after adsorption, according to the following eq. (2).[30]

$$Q = \frac{[C_0 \,—C_e]V}{W} \qquad (2)$$

Where Q (mg/g) is the amount adsorbed per unit mass of adsorbent at equilibrium, C_o and C_e denote the initial and equilibrium metal concentrations, respectively (mg/L), V is the volume of the solution (L), and W is the weight of the adsorbent used (g).

RESULTS AND DISCUSSION

In this study, cationic hydrogel was prepared by free radical solution polymerization of diallyl monomers (DAMB & DAPB) together with AAm (to increase the molecular weight) and crosslinker such

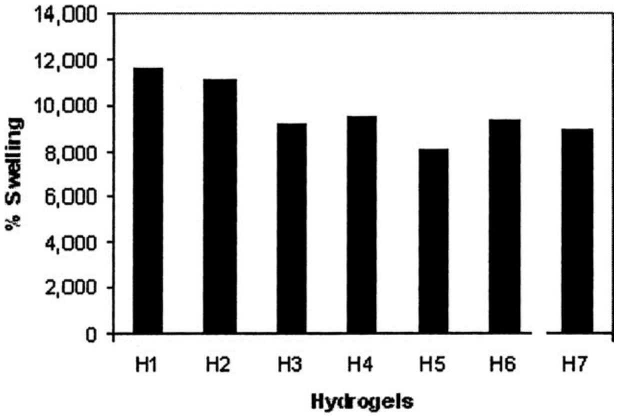

Figure 1 The % equilibrium swelling (%Seq) of the P[AAm/DAMB/DAPB] hydrogels (H1–H7).

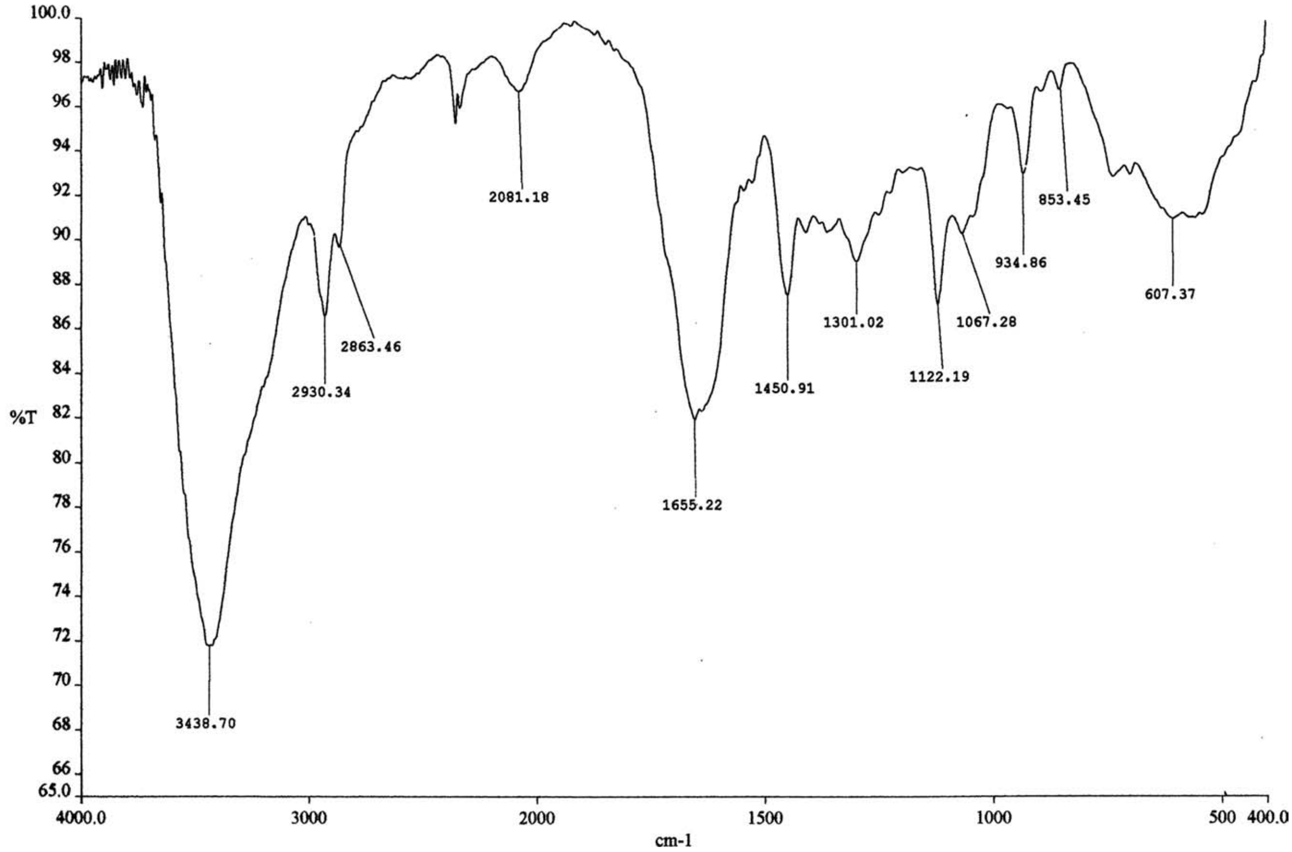

Figure 2 FTIR spectrum of P[AAm/DAMB/DAPB] hydrogel H1.

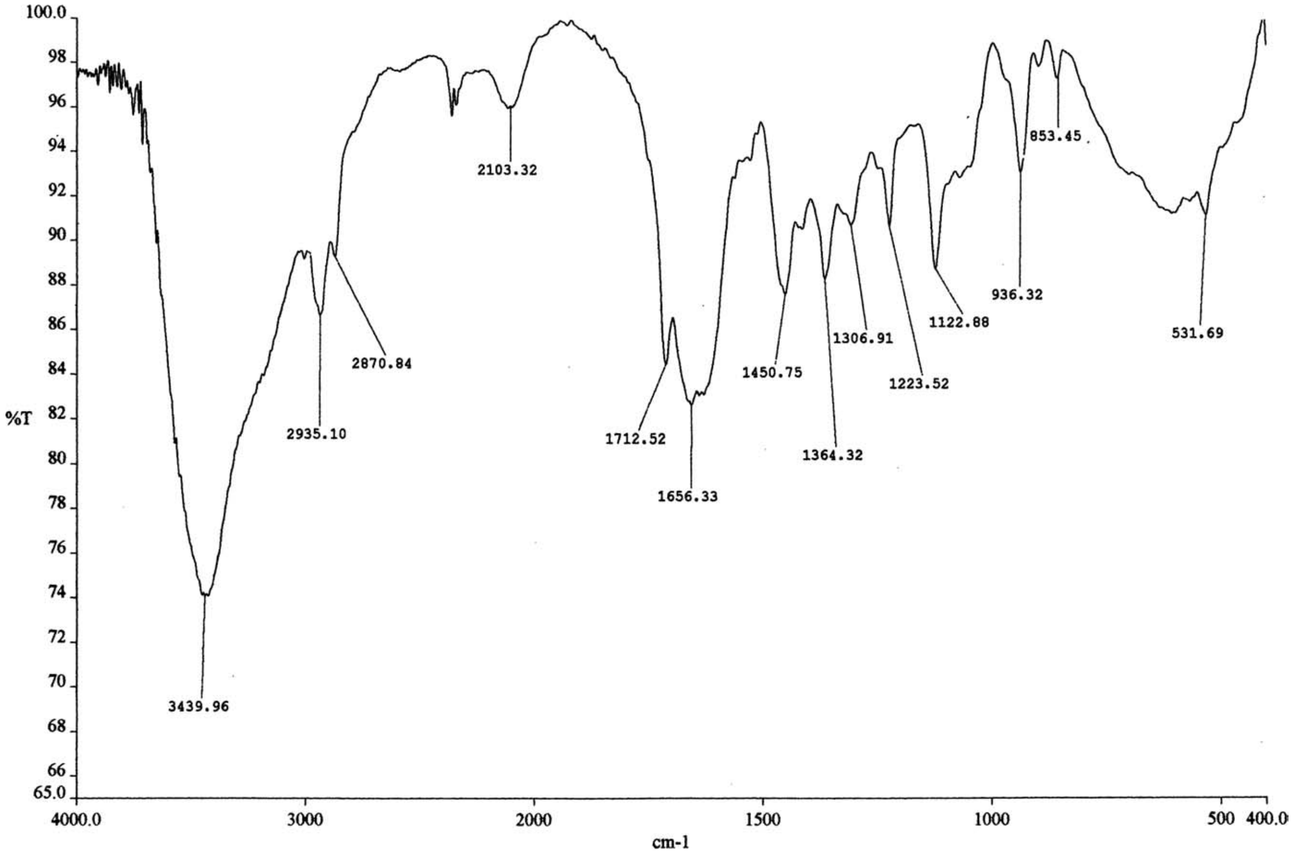

Figure 3 FTIR spectrum of Ni(II) chelated P[AAm/DAMB/DAPB] hydrogel H1.

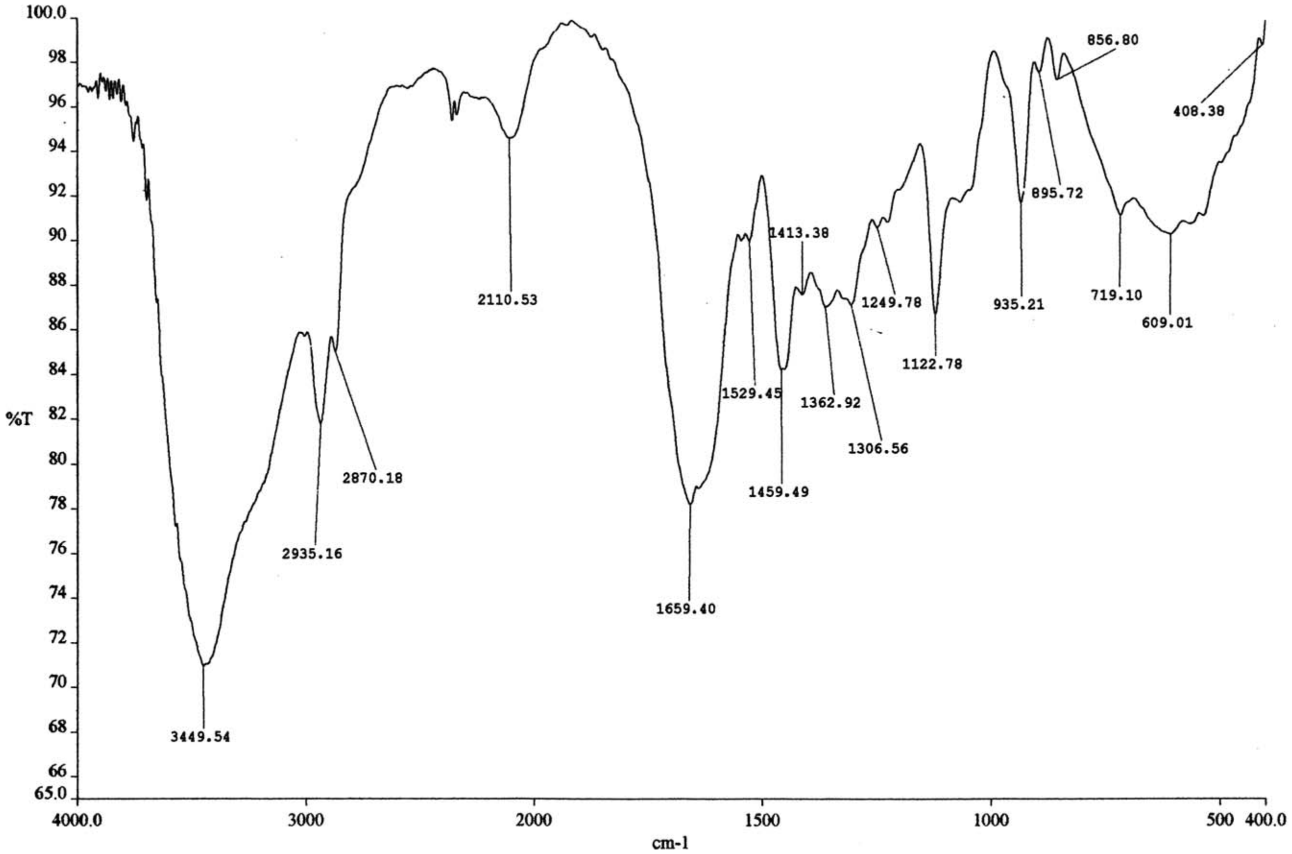

Figure 4 FTIR spectrum of Cu(II) chelated P[AAm/DAMB/DAPB] hydrogel H1.

as MBAm. The synthesized hydrogel has been characterized by FTIR, TGA, and their surface morphology was analyzed using SEM.

The infrared spectrum of P[AAm/DAMB/DAPB] hydrogel H1 with and without chelated metal ions was investigated, with the various spectra shown in Figures 2–4. Sample was thoroughly ground, mixed with KBr and mixture was kept for 2 days in vacuumed oven at 60°C. The spectrum does not reveal absorption bands characteristic of the stretching vibration of the double bond. Moreover, the absorption bands were found at 1122, 1450, 1655, 2930, and 3438 cm^{-1} characteristic vibrations of the following groups: C—O stretching, CH_2 bending, C=O stretching, C—H stretching and N—H stretching, of the amide group, respectively. In the FTIR spectra of Ni(II) and Cu(II) chelated hydrogels the absorption peak of N—H stretching at 3438 cm^{-1} is shifted to lower frequency at 3439 and 3449 cm^{-1}. The peaks in the region 800–400 cm^{-1} can be assigned to the M—O (Metal-Oxygen) stretching band. The absorption peak of C—H stretching at 2930 cm^{-1} is shifted to lower frequency at 2935 cm^{-1} in both the metal chelated IR spectra.

To investigate the thermal stability of the polymer-metal complex, TGA thermograms were taken for P[AAm/DAPB/DAMB] hydrogel H1 with and without metal ion adsorption. The thermal decomposition behavior of a polymer-metal complex depends on the macromolecular characteristics of the polymer base and the type of coordination geometry.[31] The relative thermal stabilities of the different hydrogels were assessed by comparing the weight loss in the temperature range 50–700°C. The TGA data furnished in Figures 5–7 show the nature of the thermograms of the P[AAm/DAPB/DAMB] hydrogel H1 and the hydrogel H1 with chelated metal ions. The wt % loss of P[AAm/DAPB/DAMB] hydrogel H1 shows three steps, whereas Ni(II) and Cu(II) chelated hydrogels shows four steps, respectively. The wt % loss at 200°C of P[AAm/DAPB/DAMB] hydrogel H1 is 13.52, whereas for Ni(II) and Cu(II) chelated hydrogels are 46.05 and 34.51, respectively. The decrease in the thermal stability in the initial stage of decomposition may be due to the water coordination to the Ni(II) and Cu(II) ions, which were lost, resulting in the higher weight loss in the initial stage of decomposition.[32] The morphology of P[AAm/DAPB/DAMB] hydrogel H1 was observed by SEM analysis and the SEM photographs are presented in Figure 8.

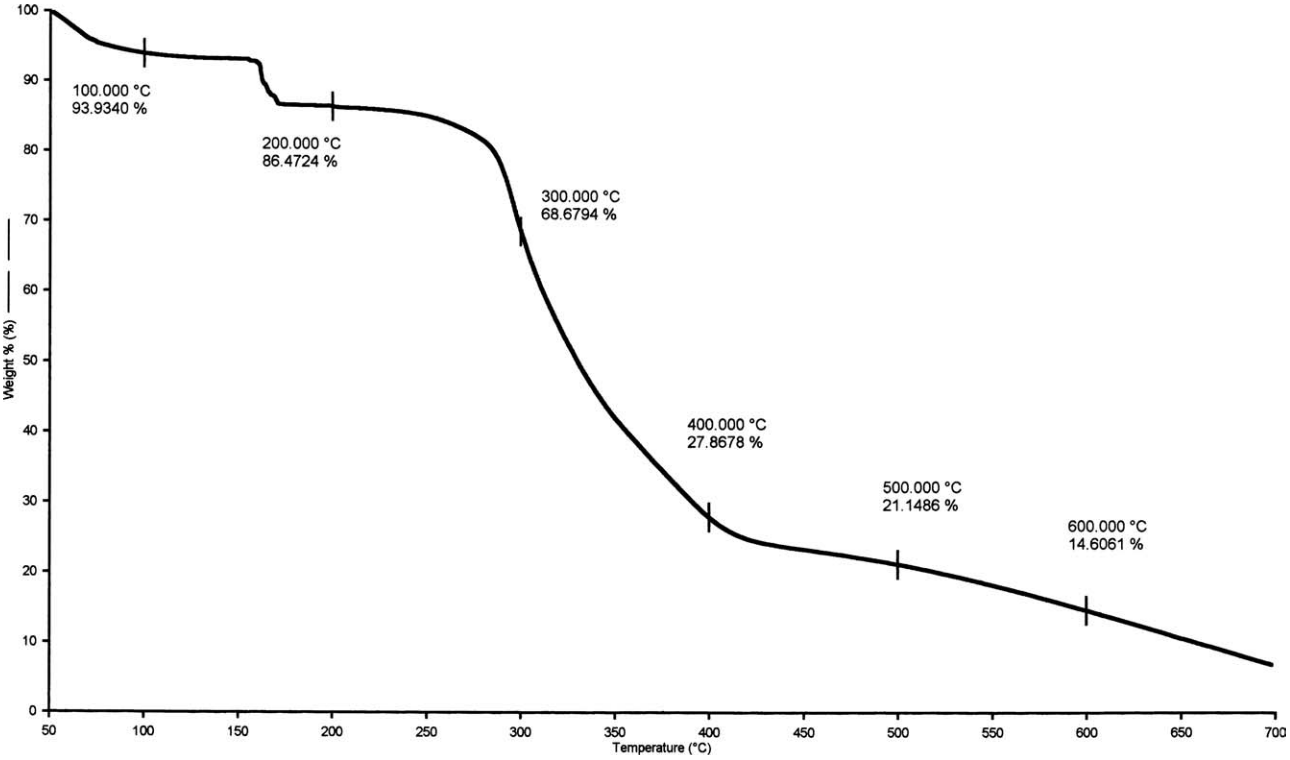

Figure 5 TGA thermograms of P[AAm/DAMB/DAPB] hydrogel H1.

Effect of initial feed concentration of metal ions

To explore the applicability of the copolymer hydrogel, it was informative to obtain knowledge on its sorption capacity and efficiency towards nickel and copper ions. This study was carried out by equilibrating a fixed amount of hydrogel with a series of metal ion solutions of gradually increasing

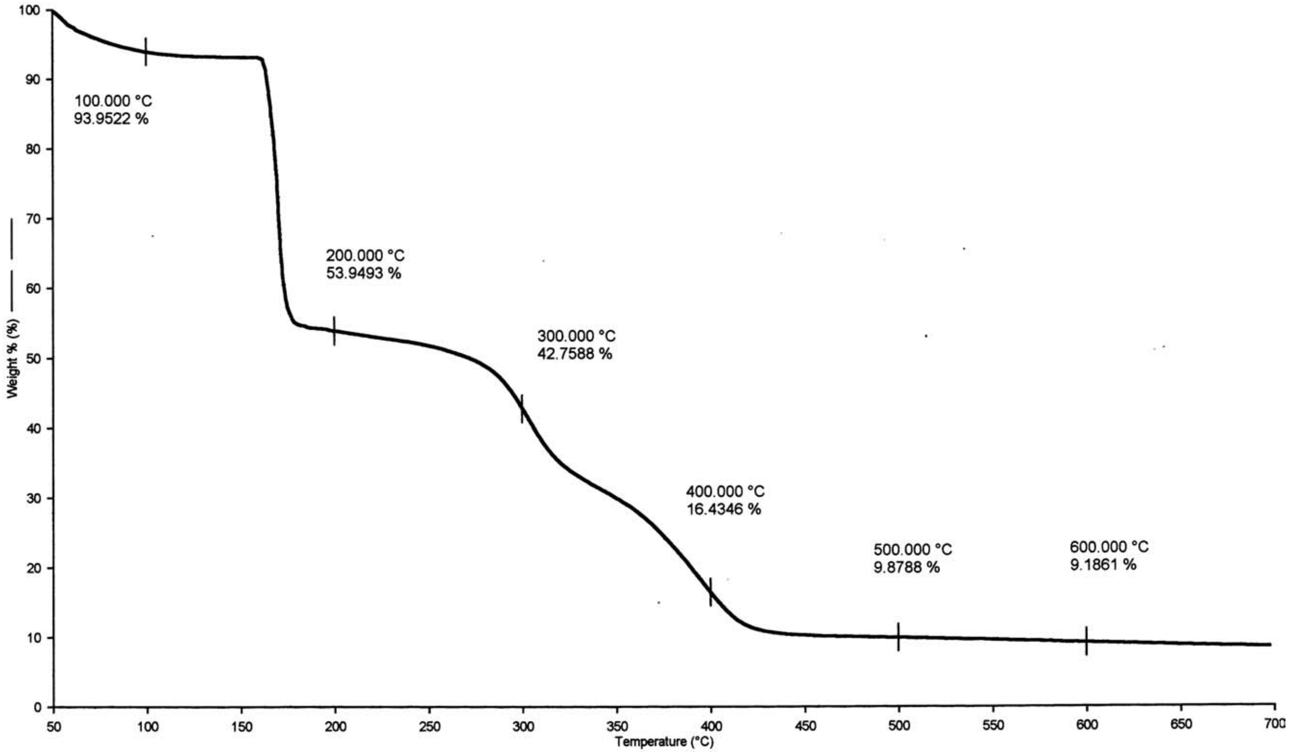

Figure 6 TGA thermograms of Ni(II) chelated P[AAm/DAMB/DAPB] hydrogel H1.

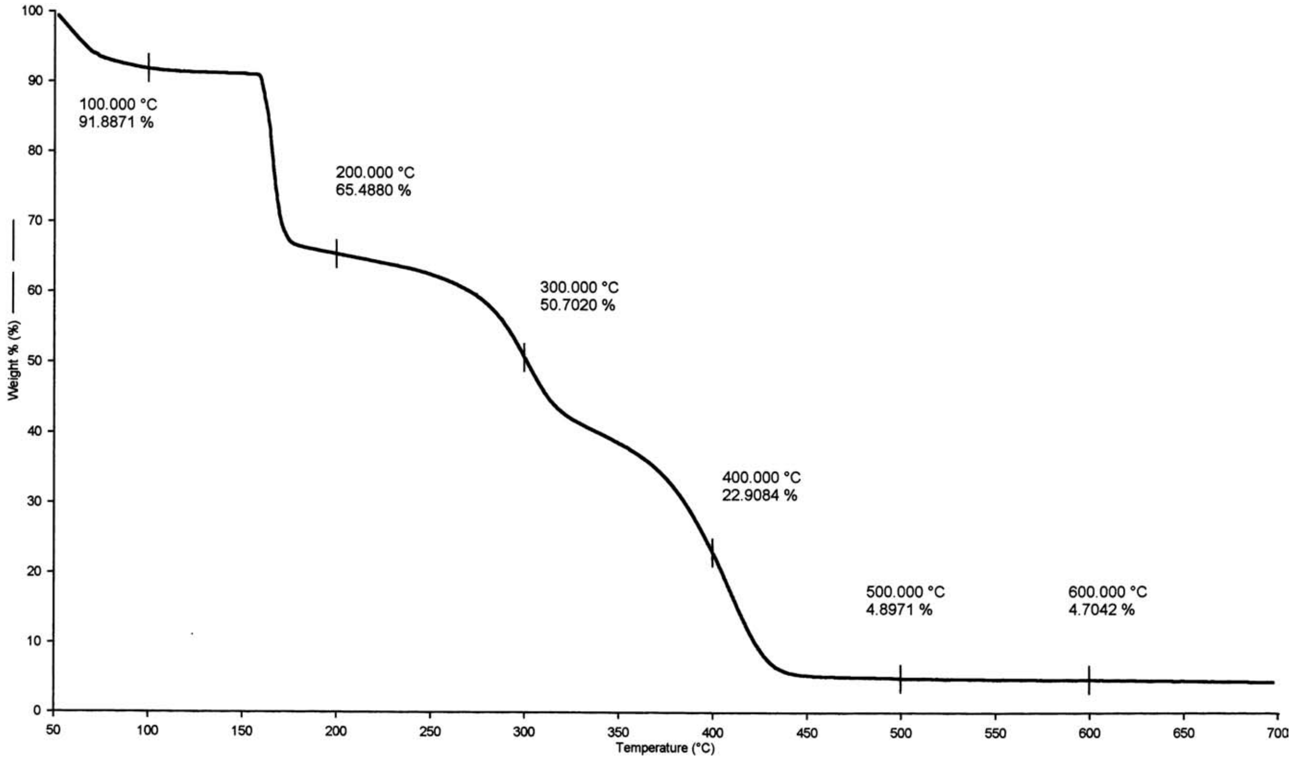

Figure 7 TGA thermograms of Cu(II) chelated P[AAm/DAMB/DAPB] hydrogel H1.

concentration. The sorption capacity is the maximum amount of metal ion removed from the solution when the chelating sites of the adsorbent are saturated. Figure 9 show the uptake profile of P[AAm/DAPB/DAMB] hydrogel H1 towards Ni(II) and Cu(II) ions with different initial feed solution concentration varying from 1100 to 2000 mg/L. Figure 9 clearly shows a dependence of the uptake profile on the initial metal ion concentration, i.e., increasing the concentration of metal ions results in increasing the amount of metal ions uptake to reach a maximum at a certain value then it tends to level off at higher feed solution concentration. The maximum adsorption of Ni(II) and Cu(II) was observed at 1800 mg/L.

Effect of pH

It is well known that the pH of the medium has a great effect on the performance of the chelating hydrogel because chelation of metal ion by polymeric ligands is highly dependent on the pH of the medium.[33] The pH of the medium has two kinds of influence on metal uptake: an effect on the solubility and speciation of metal ion in aqueous solution, and an

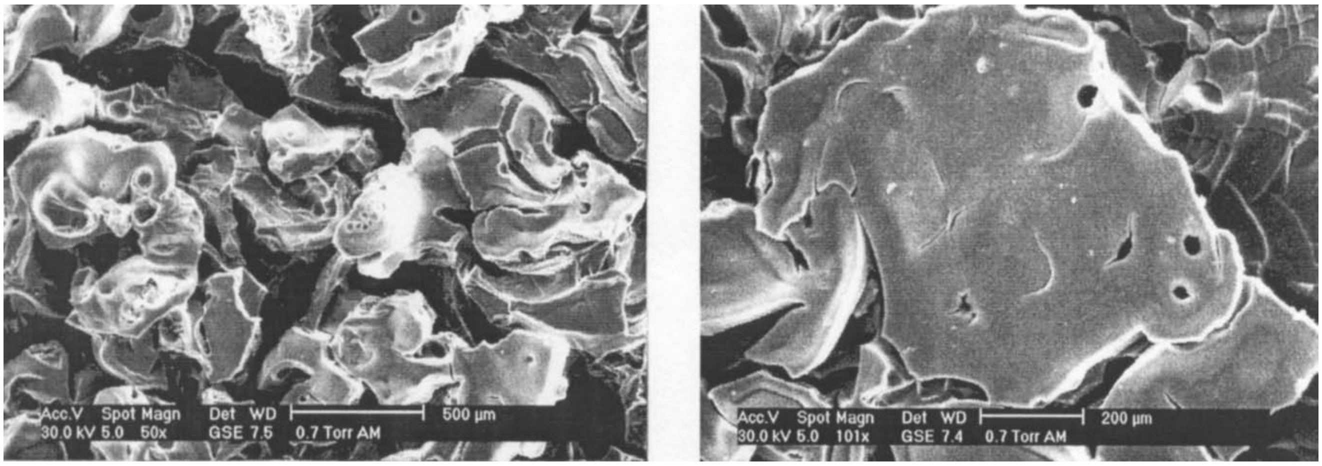

Figure 8 SEM photograph of of P[AAm/DAMB/DAPB] hydrogel H1.

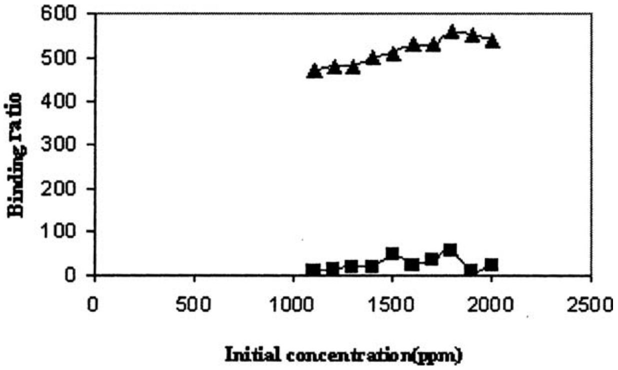

Figure 9 The uptake profile of P[AAm/DAMB/DAPB] hydrogel H1 towards (▲) Ni(II) and (■) Cu(II) ions with different initial feed solution concentrations.

overall charge of the ligands of the adsorbents.[34] To optimize the pH for maximum removal efficiency, experiments were conducted with 50 mL of 1800 mg/L of metal solution containing 50 mg of P[AAm/DAPB/DAMB] hydrogel H1 in the pH range 1 to 4 for copper and 1 to 5 for nickel at 30°C. This pH range is chosen because copper and nickel ions get precipitated above pH 4 and 5, respectively. The adsorption behavior of Ni(II) and Cu(II) ions on the P[AAm/DAPB/DAMB] hydrogel H1 at various pH values are presented in Figure 10(a,b), respectively.

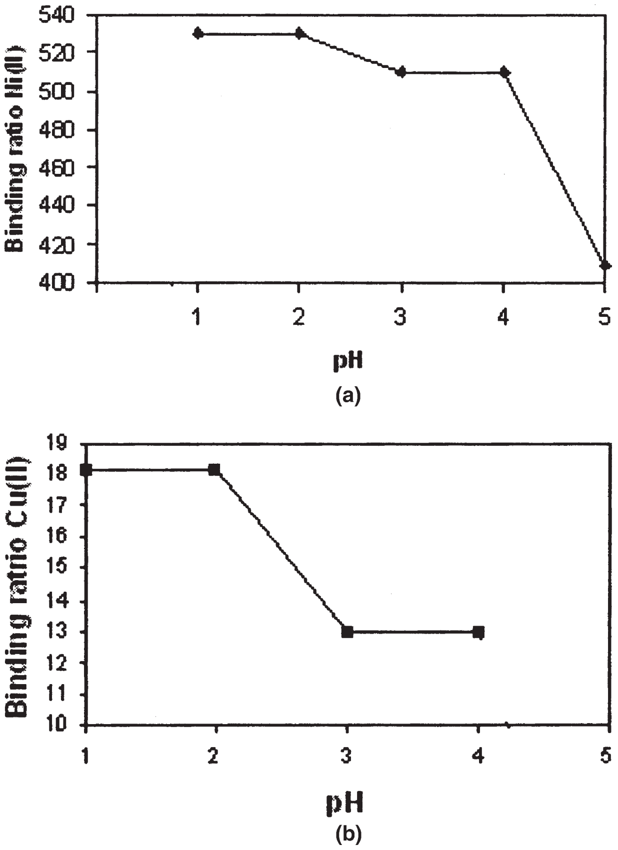

Figure 10 (a) The adsorption behavior of (◆) Ni(II) ions on P[AAm/DAMB/DAPB] hydrogel H1 at various pH values. (b) The adsorption behavior of (■) Cu(II) ions on P[AAm/DAMB/DAPB] hydrogel H1 at various pH values.

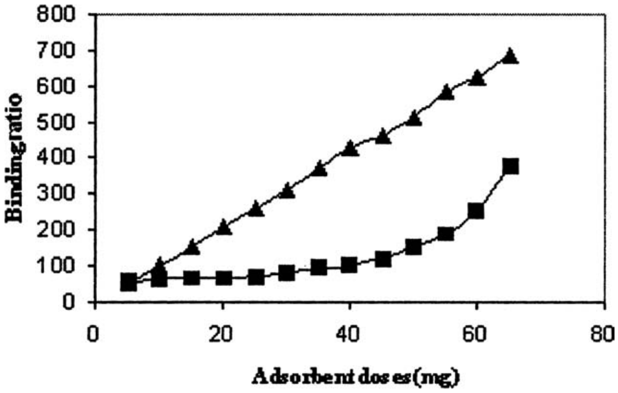

Figure 11 The adsorption behavior of (▲) Ni(II) and (■) Cu(II) ions on P[AAm/DAMB/DAPB] hydrogel H1 at various adsorbent doses.

Effect of adsorbent doses

The dependence of adsorption of Ni(II) and Cu(II) on the amount of P[AAm/DAPB/DAMB] hydrogel H1 is studied by varying the adsorbent doses from 5 to 70 mg, while keeping the volume (50 mL) and concentration (1800 mg/L) of the Ni(II) and Cu(II) metal solution constant. The results are shown graphically in Figure 11. It is apparent that the binding ratio (*Q*) increases rapidly with increase in the dose of adsorbent to reach a maximum at certain value and then, it tends to level off at higher adsorbent dose. The maximum binding ratio observed for Ni(II) and Cu(II) metal is 688.58 and 376.62 mg/g at 65 mg dose of adsorbent.

Effect of contact time

Time course metal ions chelation by hydrogel was investigated to determine the time at which equilibrium adsorption has occurred. In this experiment 50 mg of hydrogel was agitated with 50 mL solution

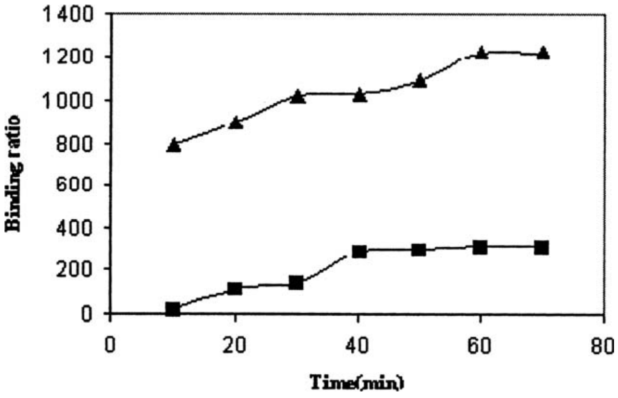

Figure 12 The time course adsorption of (▲) Ni(II) and (■) Cu(II) ions on the P[AAm/DAMB/DAPB] hydrogel H1.

TABLE II
Recycling Profile of P[AAm/DAMB/DAPB] Hydrogel H1 Towards Ni(II) and Cu(II) Ions

Cycle with 1 *N* HCl	Amount of chelated metal ions (mg/g)		Cycle with 0.5 *N* H_2SO_4	Amount of chelated metal ions (mg/g)	
	Ni(II)	Cu(II)		Ni(II)	Cu(II)
1	559.44	54.90	1	559.44	54.28
2	549.93	48.85	2	539.92	48.90
3	539.92	40.13	3	539.92	35.93
4	529.88	35.93	4	519.91	33.74

(1800 mg/L) of Ni(II) and Cu(II) and the binding ratio was calculated at different time intervals until the equilibrium was reached. The time course of Ni(II) and Cu(II) ions adsorption on the P[AAm/DAPB/DAMB] hydrogel H1 is presented in Figure 12. The saturation time for metal uptake of the hydrogel was obtained by plotting the amount of metal uptake (mg/g) with time, keeping the initial metal concentration (1800mg/L). Chelation takes place rapidly at first, then slows down and finally levels off after 60 min. The variation of contact time showed a maximum uptake of P[AAm/DAMB/DAPB] hydrogel H1 at 1220.23 mg/g toward Ni(II) and 314.18 mg/g toward Cu(II).

Reuse of the chelated hydrogels

To be viable materials for use as a chelation system, the hydrogels must be chemically reusable. For possibility of reuse, the P[AAm/DAMB/DAPB] hydrogel was investigated (Table II). The hydrogel could easily be regenerated with 1 *N* HCl and 0.5 *N* H_2SO_4. On reuse, the desorbed hydrogel chelated almost the same amount of metal ion even after four cycles. At this point, to the possibility of reusing the chelated hydrogel several times. This character of the possibility for reusing the hydrogel several times makes it economically suitable for use.

CONCLUSIONS

The foregoing study of the preparation, characterization, and metal ion chelation revealed the applicability of such a P[AAm/DAMB/DAPB] hydrogel to remove Ni(II) and Cu(II) metal ions from aqueous solutions. The adsorption of metal ions is heavily dependent on the concentration of metal ions, contact time, pH of the metal solution and adsorbent doses of metal ions.

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