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Pratish V. Dadhaniya[a]; Manish P. Patel[a]; Ranjan G. Patel[a]
[a] Department of Chemistry, Sardar Patel University, Gujarat, India

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Copper and Nickel Removal from Aqueous Solutions Using New Chelating Poly[Acrylamide/N-vinyl pyrrolidone/3-(2-hydroxyethyl carbamoyl)acrylic acid] Hydrogels

PRATISH V. DADHANIYA, MANISH P. PATEL, and RANJAN G. PATEL
Department of Chemistry, Sardar Patel University, Gujarat, India

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New poly[Acrylamide/N-vinyl pyrrolidone/3-(2-hydroxyethyl carbamoyl)acrylic acid], poly [AAm/NVP/HECA], chelating hydrogels with different composition of HECA monomer have been prepared via free radical solution polymerization using N,N-methylene bisacrylamide as a crosslinker. The hydrogels obtained were loaded with metal ions and characterized by FT-IR spectroscopy, Scanning Electron Microscope (SEM) and Thermogravimatric analysis (TGA). The removal of Cu^{2+} and Ni^{2+} from aqueous solutions by the hydrogel was examined by a batch equilibrium method. The influence of treatment time, pH, initial concentration of the metal ions and HECA content in the feed compositions on the amount of adsorbed metal ions was studied. Swelling of the hydrogel was also carried out in distilled water and metal ion solutions. The removal of the metal ions followed the following order: $Ni^{2+} > Cu^{2+}$. The amount of metal ions removed increased with increasing HECA content in the feed composition, treatment time, pH of the medium and initial concentration of metal ions. The desorption of metal ions were carried out using 1 N HCl and 0.5 N H_2SO_4. The poly[AAm/NVP/HECA] hydrogels could be used many times without significantly decreasing their adsorption capacity.

Keywords: metal removal; chelating hydrogel; adsorption; batch equilibrium; copper; nickel

1 Introduction

With increasing industrialization, one of the most important problems threatening our world has focused on environmental pollution. The fate of heavy metals in the environment has become an increasing concern. Process waste streams from mining operations, metal plating facilities, power generation facilities, electronic device manufacturing units, and tanneries often contain heavy metal ions like mercury, chromium, cadmium, lead, nickel, and copper at concentrations above local discharge limits.

The removal of toxic and polluting metal ions from industrial effluents, water supplies, as well as mine waters is an important challenge to avoid one of the major causes of water and soil pollution and it has received much attention in recent years (1–5). Traditional treatment techniques to remove the dissolved toxic metal ions from waste disposal by chemical treatment, ultra filtration or combination of chemical treatment and ultra filtration do not always provide a sufficient contaminant removal to meet pollution control limits.

Chelating resins containing various ligands have also been used for the removal of heavy metal ions from aqueous solutions (6–11). These are in general coordinating copolymers containing one or more electron donor atoms (Lewis base) such as N, S, O and P, which can form coordinate bonds with most of the toxic heavy metals (Lewis acid) (12). These polymers have many practical applications in water treatment, environmental protection, chemical analysis, etc.

Hydrogels are water-swollen networks i.e., crosslinked structures, of hydrophilic homo or co-polymers. They have acquired a great interest due to the facility of the incorporation of different chelating groups into the polymeric networks. Recently, it has been reported that chelating hydrogels having a specific functional group can be applied to the recovery of precious metal, removal of toxic or radioactive elements from various effluents and to metal preconcentration for environmental sample analysis (13–18). Such polymeric hydrogels are also promising materials in the field of hydrometallurgical application and water purification, due to their chemical, hydrolytic and thermal stability (19, 20).

In the present work a new monomer, 3-(2-hydroxyethyl carbamoyl) acrylic acid (HECA), has been used in the synthesis of co-polymeric [AAm/NVP/HECA] hydrogels and

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Address correspondence to: Ranjan G. Patel, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India. Tel.: +91 2692 226858, ext. 218; E-mail: patelranjanben@yahoo.com

investigated their swelling and metal adsorption characteristic properties by varying the HECA content in the feed composition. Variables, such as treatment time, pH, initial concentration of metal ions and the content of HECA in the feed compositions and their effect on the chelating ability of the prepared hydrogels, have been examined using batch equilibrium method.

2 Experimental

2.1 *Materials*

Acrylamide (AAm) and N-vinyl pyrrolidone (NVP) monomers, obtained from Aldrich Chemical, were used without further purification. Maleic anhydride (from Lancaster) was recrystalized by chloroform before use. Ethanolamine (from Merk) was distilled under reduced pressure before use. Potassium persulphate (KPS) and N,N-methylene bisacrylamide(MBAm) were obtained from Fluka and were used as received. Both the metal salts $NiCl_26H_2O$ and $CuCl_22H_2O$ were of analytical grade and were obtained from Merck. Double distilled water was used in all the experiments. Synthesis and characterization of HECA monomer has already been reported in our previous paper (21).

2.2 *Synthesis of Hydrogels*

Aqueous solutions of AAm, NVP and HECA monomers were prepared in 6 wt% of total wt of monomer in double distilled water with magnetic stirring in a 100 mL beaker. To the solution 0.15 mol% (of total mole) N,N-methylene bisacrylamide (MBAm) crosslinking agent and potassium persulphate as initiator were added. These mixtures were stirred to give homogeneous solutions. The solutions were then poured in a Petri dish and kept in an oven at 60°C for a period of 8 h, even though the gels were obtained within a 3 h period. The formed hydrogels were cut with the help of a cork borer into a cylindrical shape and were immersed and left in double distilled water for 24 h, while changing the water at 4 h intervals in order to remove the unreacted monomers and other water soluble reactants in the hydrogels. The swollen gels were spread on silicone paper and kept in an air forced oven at 60°C for 2 days. It was then transferred and kept in a vacuum oven at 70°C to a constant weight. The hydrogel sample code, composition detail and swelling characteristics of the hydrogels are presented in Table 1.

2.3 *Spectral, Thermal and Microscopic Analysis*

Characterization of the hydrogels, with and without chelated metal ions, was done using FT-IR, SEM and TGA analysis. FT-IR spectra were recorded on a Perkin-Elmer GX, FT-IR spectrophotometer, using KBr pellets in the range 4000-400 cm^{-1}. The thermal behavior of the hydrogels was investigated using a Perkin-Elmer PYRIS-1 thermogravimetric analyzer. The temperature range was from ambient to 600°C, at a heating rate of 10°C/min. Surface morphology of the hydrogels were observed using a Philips XL30 ESEM (Environmental Scanning Electron Microscope).

2.4 *Swelling Studies*

In order to determine the equilibrium percentage degree of hydration ($\%H_\infty$) of poly[AAm/NVP/HECA]hydrogels (H1-H5) in distilled water the gravimetric method was employed. Accurately weighed and dried hydrogel discs were immersed in distilled water and allowed to reach equilibrium. After attaining equilibrium, the swollen gels were taken out and the surface water was removed by filter paper, followed by weighing accurately using an electronic balance (Citizen CX 120 d = 0.1 mg). The swelling kinetics of hydrogel H5 in double distilled water and in 200 mg/L solutions of Cu^{2+} and Ni^{2+} were also determined at 30°C. The percentage degree of hydration was calculated using the following equation (22):

$$\%H = \frac{M - M_0}{M_0} \times 100 \tag{1}$$

Where M is the mass of the wet sample at time t and M_0 is the mass of the dry sample. The maximum percentage degree of hydration H_∞ was considered as the equilibrium percentage degree of hydration.

2.5 *Adsorption Experiments*

In order to explore the effect of influencing factors such as treatment time, pH, initial concentration of metal ions and the HECA content in the feed compositions, a series of

Table 1. Composition detail and swelling characteristic of studied hydrogels

Hydrogel code	AAm g	NVP g	HECA g	MBAm (total mol%)	KPS (total mol%)	% H_∞ (in distilled water)
H1	4.0	2.0	0.0	0.15	0.15	1918
H2	4.0	2.0	0.4	0.15	0.15	5094
H3	4.0	2.0	0.8	0.15	0.15	6019
H4	4.0	2.0	1.2	0.15	0.15	6225
H5	4.0	2.0	1.6	0.15	0.15	6665

batch experiments were conducted. The entire adsorption experiments were performed on hydrogel H5 as it has maximum percentage degree of hydration. The stock solutions were diluted to the required concentration. The adsorption experiments were performed by agitating specified (50 mg) amount of adsorbent (Hydrogel H5) 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 concentration of metal ions remaining in the solution were determined by a Shimadzu-18A UV-Visible spectrophotometer, using precalibrated curves. All measurements were carried out in duplicate. 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 equation (23):

$$Q = \frac{\langle C_0 - C_e \rangle V}{W} \tag{2}$$

Where Q(mg/g) is the amount adsorbed per unit mass of adsorbent at equilibrium, C_0 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).

3 Results and Discussion

In the present study, poly[AAm/NVP/HECA] hydrogels were prepared via free radical solution copolymerization, using KPS as initiator and MBAm as the crosslinker at 60°C. The polymerization process starts with the formation of free radicals by decomposition of KPS initiator. The free radical may interact with AAm, NVP, HECA and or with the crosslinker, thereby initiating polymerization, copolymerization and the crosslinking process simultaneously.

3.1 Spectral, Thermal and Microscopic Analysis

To examine the nature of the interaction between the metal ions and hydrogel, the FT-IR spectra of hydrogel H5 with and without chelated metal ions were investigated, with the various spectra shown in Figures 1–3.

The FT-IR spectrum of hydrogel H5 is presented in Figure 1. The FT-IR spectrum showed the presence of peaks corresponding to the functional groups of monomeric units present in the copolymer hydrogels. A strong peak appeared at 1598–1665 cm^{-1} corresponds to different C=O stretching present in the hydrogel. The -OH and $-NH_2$ groups are identified by peaks at 3346 and 3188 cm^{-1}, respectively. Other peaks represent C-C and C-H vibration of $-CH_2$ groups.

As a result of the interaction between metal ions and functional groups of the hydrogel, some bands disappeared and a certain shift took place in the IR spectra. In the IR spectra of Cu^{2+} and Ni^{2+} chelated hydrogels the absence of O-H band at 3346 cm^{-1} indicates the coordination of the -OH groups with both the metal ions. The N-H absorption peak at 3188 cm^{-1} is shifted to lower frequency in both the metal chelated IR spectra indicate the participation of the $-NH_2$ groups in chelation. The peaks in the region 400–800 cm^{-1} can be assigned to the M-O (Metal-Oxygen)

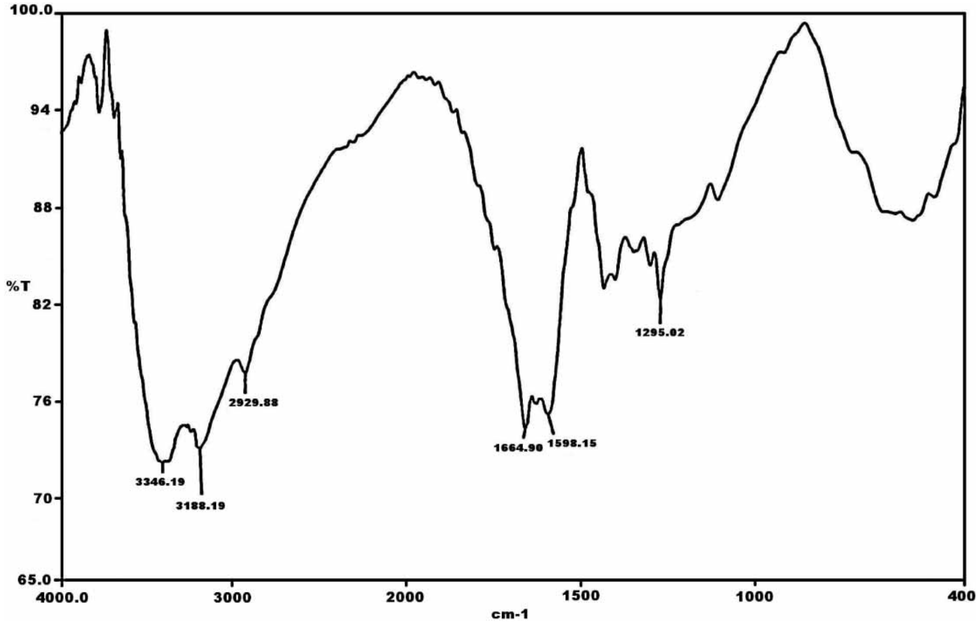

Fig. 1. FT-IR spectrum of poly[AAm/NVP/HECA] hydrogel H5.

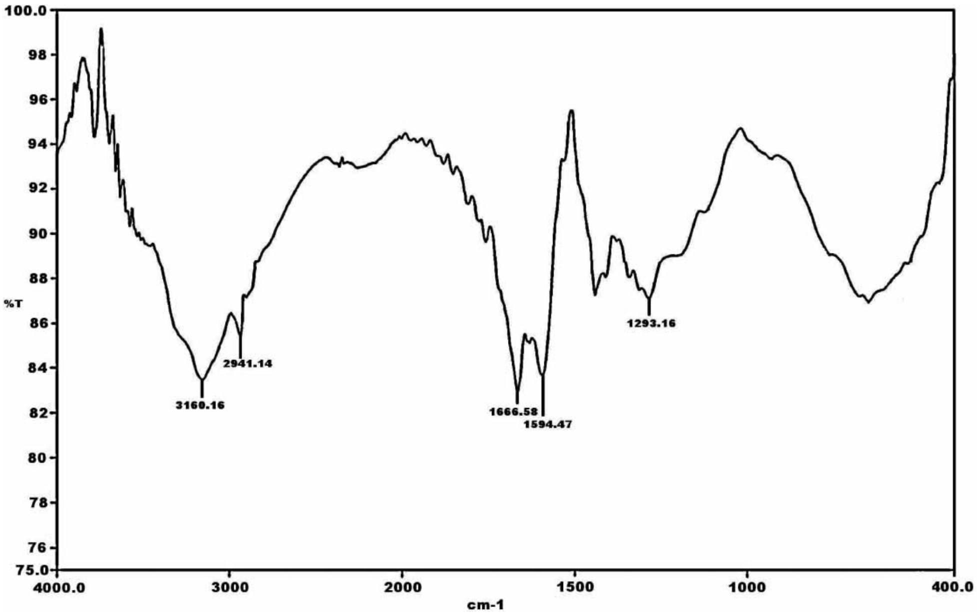

Fig. 2. FT-IR spectrum of Cu^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5.

stretching band. The absorption peak of C-H stretching at 2930 cm^{-1} is shifted to higher frequency at 2941 and 2945 cm^{-1} in both the metal chelated IR spectra. The reason behind it is not known to us.

To investigate the thermal stability of the polymer-metal complex, TGA thermograms were taken for hydrogels 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 (24).

The relative thermal stabilities of the different hydrogels were assessed by comparing the weight loss in the temperature range 35–600°C. The TGA data furnished in Table 2 and in Figures 4a–c show the nature of the thermograms of the hydrogel and the hydrogel with chelated metal ions. Hydrogel H5 shows two degradation steps, whereas Cu^{2+} and Ni^{2+} chelated hydrogels show three and four degradation steps, respectively.

The chelation of Cu^{2+} ions significantly increases the thermal stability of poly[AAm/NVP/HECA] hydrogel. The

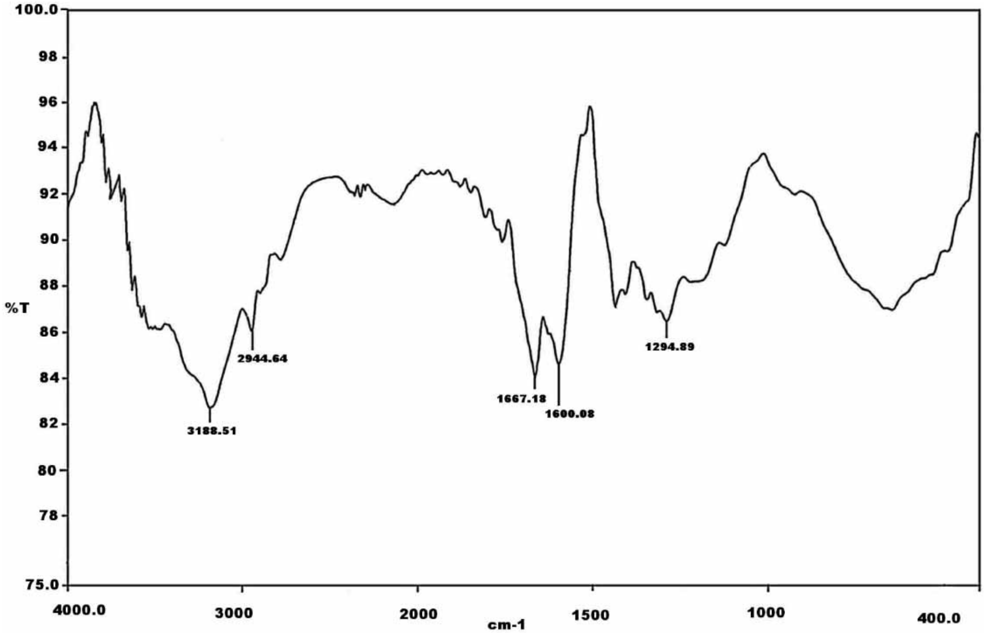

Fig. 3. FT-IR spectrum of Ni^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5.

Table 2. Phenomenological data on the thermal decomposition of hydrogel H5 and metal chelated hydrogel H5

		Metal chelated hydrogel H5	
Temperature (°C)	Hydrogel H5	Cu^{2+}	Ni^{2+}
100	4.94	9.655	13.49
150	6.59	11.70	18.11
200	7.57	17.52	19.47
250	13.24	25.07	25.28
300	22.98	30.35	30.44
350	48.58	39.45	37.89
400	77.19	46.87	42.80
450	81.72	48.96	45.89
500	82.63	50.40	56.83
550	83.28	52.34	68.43
600	84.11	54.55	79.15

% degradation at 200°C of poly[AAm/NVP/HECA] hydrogel is 7.5, whereas for Cu^{2+} and Ni^{2+} chelated hydrogels are 17.5 and 19.5, respectively.

The decrease in the thermal stability in the initial stage of decomposition may be due to the water coordination to the Cu^{2+} and Ni^{2+} ions, which were lost, resulting in the higher weight loss in the initial stage of decomposition (25).

The difference in the morphology of hydrogel H5 with and without chelated metal ions was observed by SEM analysis and the SEM photographs are presented in Figures 5a–c. The adsorbed metal ions on the surface of hydrogels are clearly seen in photograph 5b and 5c. The visual observation of the photographs also indicate that the adsorption of Ni^{2+} ions is more, compared to the Cu^{2+} ions on the surface of poly[AAm/NVP/HECA] hydrogel.

3.2 *Swelling Studies*

The hydrogels was immersed for two days in distilled water and in metal solutions until the hydrogel mass ceased to change.

Figure 6 shows the percentage degree of hydration in water and metal solutions with respect to time.

From Figure 6, it can be seen that the percentage degree of hydration increases with time until a certain point, when it becomes constant. Hydrogel shows maximum swelling in distilled water and minimum swelling in Ni^{2+} solution. In Cu^{2+} and Ni^{2+} aqueous solutions (200 mg/L) the % H_∞ values of hydrogel H5 is 4567 and 3123, respectively whereas in double distilled water it was 6665. Water diffusion into the hydrogel (swelling) and metal ion binding to functional groups, which decrease the ionic pressure inside the hydrogel (deswelling), are competitive (22), i.e., the metal having more binding capacity results in lower swelling. At the end of this evaluation, the hydrogel H5 in the aqueous solutions are swollen in the following order: Water $>$ Cu^{2+} $>$ Ni^{2+}.

3.3 *Rate of Metal Ion Chelation*

Time course metal ions chelation by hydrogel, which possess the maximum metal ion uptake, was investigated to follow the relative performance of such hydrogel and to determine the time at which equilibrium chelation takes place. The time course of Cu^{2+} and Ni^{2+} ions adsorption on the hydrogel H5 is presented in Figure 7.

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 (200 mg/L) and pH constant. Chelation takes place rapidly at first, then slows down and finally levels off after 20 h. The variation of contact time showed a maximum uptake of 44.52 mg/g for poly[AAm/NVP/HECA] hydrogel toward Ni^{2+} and 36.78 mg/g toward Cu^{2+}. As expected, this result parallels the result of the equilibrium degree of hydration.

3.4 *Effect of pH on Metal Adsorption*

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 (26). 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 overall charge of the ligands of the adsorbents (27). In order to optimize the pH for maximum removal efficiency, experiments were conducted with 50 mL of 200 mg/L of metal solution containing 50 mg of hydrogel H5 in the pH range 2 to 6 for Copper and 2 to 8 for Nickel at room temperature. This pH range is chosen because copper and nickel ions get precipitated above pH 6 and 8, respectively.

The adsorption behavior of Cu^{2+} and Ni^{2+} ions on the hydrogel H5 at various pH values are presented in Figure 8. As seen from the figure, for both the investigated metal ions, the adsorption increases with increasing pH values of the medium. This increment in metal adsorption could be attributed to the increase in the degree of swelling, which increases the diffusion of the metal ions into the hydrogel to reach chelating sites.

3.5 *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 Copper and Nickel ions. This study was carried out by equilibrating a fixed amount of hydrogel with a series of metal ion solutions of gradually increasing concentration. The sorption capacity is the maximum amount of metal ion removed from the solution when the chelating sites of the adsorbent are saturated.

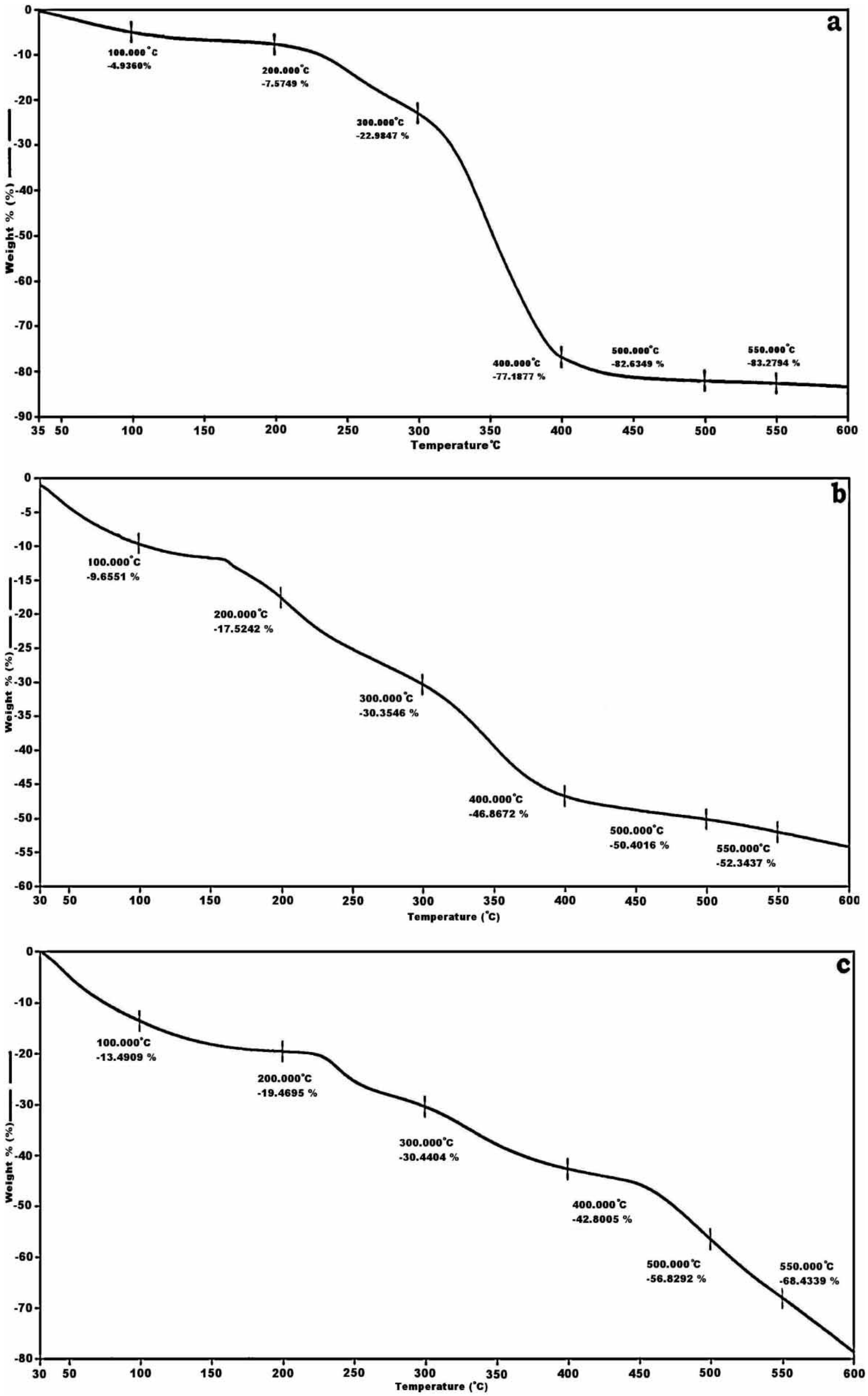

Fig. 4 (a) TGA thermograms of poly[AAm/NVP/HECA] hydrogel H5 (b) TGA thermogram of Cu^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5 (c) TGA thermogram of Ni^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5.

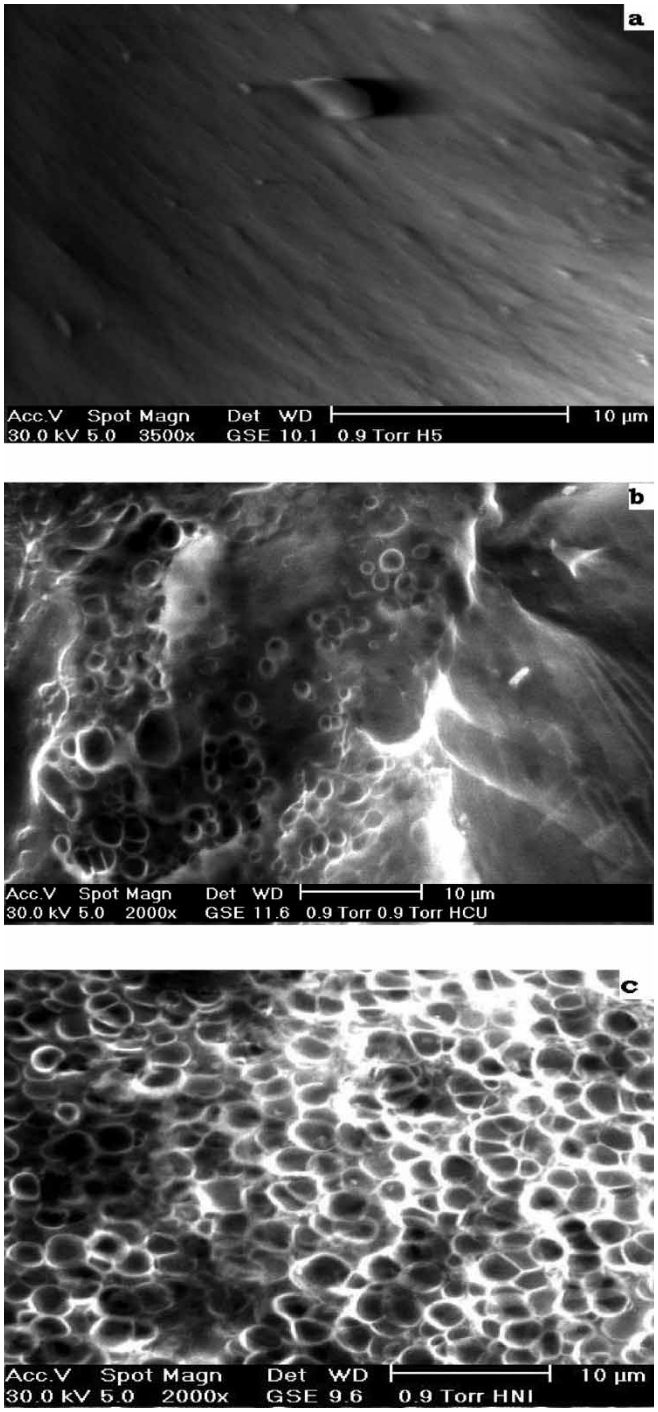

Fig. 5. (a) SEM photograph of poly[AAm/NVP/HECA] hydrogel H5. (b) SEM photograph of CU^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5. (c) SEM photograph of Ni^{2+} chelated poly[AAm/NVP/HECA] hydrogel H5.

Figure 9 show the uptake profile of hydrogel towards Cu^{2+} and Ni^{2+} ions with different initial feed solution concentration varying from 50 to 800 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 Cu^{2+} was observed at 250 mg/L where as for Ni^{2+} it was 400 mg/L.

3.6 Effect of HECA Content in Feed Composition on Adsorption

The variation of the adsorption of metal ions with the HECA content in the feed composition on the hydrogel was

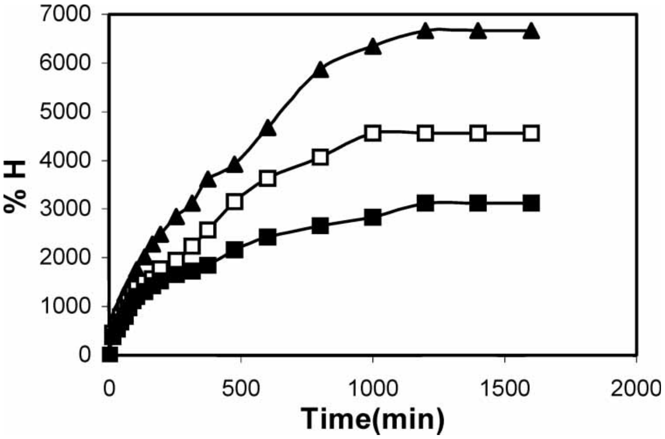

Fig. 6. The swelling curves of hydrogel H5 in (▲) distilled water and in 200 mg/L solutions of (□) Cu^{2+} and (■) Ni^{2+}.

investigated. The mass of adsorbed metal ions per gram of the hydrogel vs. the HECA content in the feed composition is plotted in Figure 10.

Uptake of Cu^{2+} and Ni^{2+} ions onto poly[AAm/NVP/HECA] hydrogels increases with an increase of the HECA content. Chelating groups on the hydrogels were increased by adding HECA to AAm and NVP monomers, therefore these hydrogels have many hydroxyl and carboxyl groups that can increase the interaction between the metal ions and the chelating groups of HECA in the hydrogels.

The relation between the nature of the copolymer and its metal chelation behavior is generally complicated by possible interactions. Oxygen atoms present as carbonyl and hydroxyl groups in the HECA monomer are responsible for the interaction of metal ions with the hydrogel. Since the oxygen atom is electron rich, the metal ions act as electron acceptors and are taken up by coordination to the donor oxygen.

3.7 *Re-use of the Chelated Hydrogels*

To be viable materials for use as a chelation system, the hydrogels must be chemically reusable. For possibility of re-use, the poly[AAm/NVP/HECA] hydrogel was investigated (Table 3). The hydrogel could easily be regenerated with 1 N HCl and 0.5 N H_2SO_4.

On re-use, the desorbed hydrogel chelated almost the same amount of metal ion even after four cycles. This points to the possibility of reusing the chelated hydrogel several times.

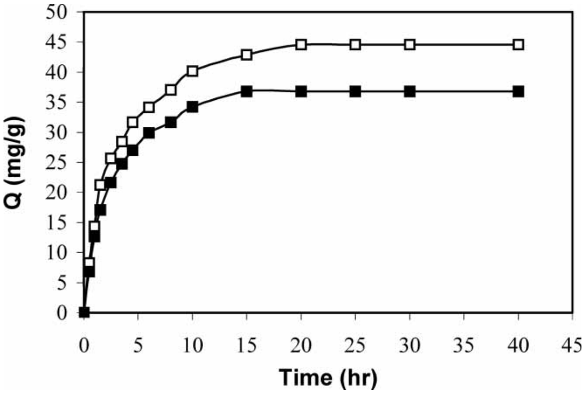

Fig. 7. The time course adsorption of (■) Cu^{2+} and (□) Ni^{2+} ions on the hydrogel H5 at the proper pH of each.

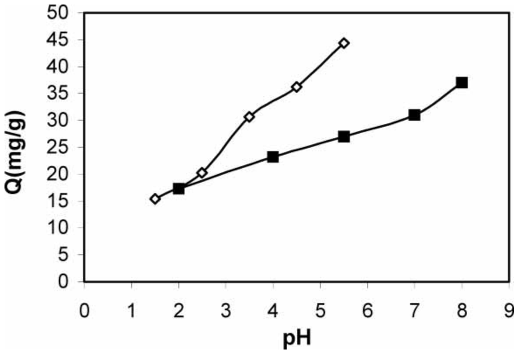

Fig. 8. The adsorption behavior of (□) Ni^{2+} and (■) Cu^{2+} ions on hydrogel H5 at various pH values.

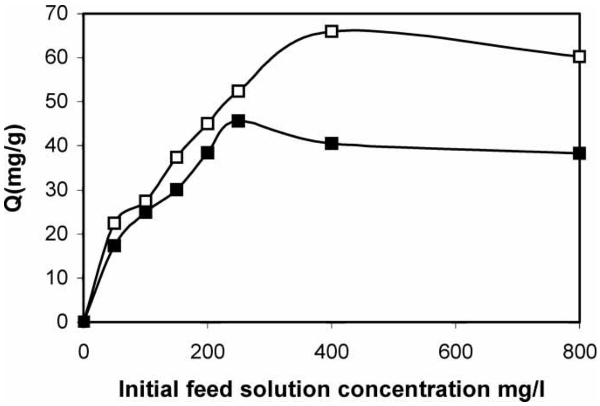

Fig. 9. The uptake profile of hydrogel H5 towards (■) Cu^{2+} and (□) Ni^{2+} ions with different initial feed solution concentrations.

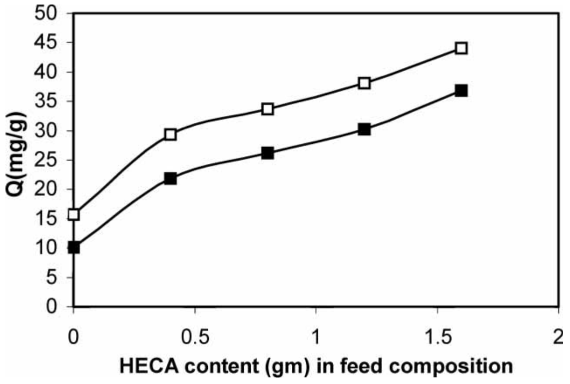

Fig. 10. The variation of the binding ratios of adsorbed metal ions onto poly[AAm/NVP/HECA] hydrogel with the HECA content in the feed composition: (■) Cu^{2+} and (□) Ni^{2+}.

Table 3. Recycling profile of poly[AAm/NVP/HECA] hydrogel H5 towards Cu^{2+} and Ni^{2+} 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)	
	Cu^{2+}	Ni^{2+}		Cu^{2+}	Ni^{2+}
1	37.11	44.52	1	37.52	44.11
2	36.35	44.0	2	36.86	43.06
3	36.0	43.28	3	36.12	42.50
4	35.34	42.62	4	36.0	41.23

This character of the possibility for re-using the hydrogel several times makes it economically suitable for use.

4 Conclusions

The foregoing study of the preparation, characterization and metal ion chelation of poly[AAm/NVP/HECA] hydrogel revealed the applicability of such a hydrogel to remove Cu^{2+} and Ni^{2+} metal ions from aqueous solutions. Swelling properties of poly[AAm/NVP/HECA] hydrogel in water and metal solutions were studied. Hydrogel swelling decreases in metal solutions as compared to that in distilled water. The maximum uptake obtained was 46 mg/g for Cu^{2+} and 66 mg/g for Ni^{2+} by optimizing the conditions. The adsorption of metal ions is heavily dependent on the concentration of metal ions, agitation time, pH of the metal solution and HECA content in feed composition. The thermal stability of metal chelated hydrogel is higher than the parent hydrogel. It was shown that poly[AAm/NVP/HECA] hydrogel could be used as metal adsorbents, applied to waste water and preconcentration of metal ions before analysis in environmental studies. These chelating hydrogels are also expected to be applicable to adsorption of other metal ions also.

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