Acrylonitrile/Acrylamidoxime/2-Acrylamido-2-Methylpropane Sulfonic Acid-Based Hydrogels: Synthesis, Characterization and Their Application in the Removal of Heavy Metals

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ABSTRACT: Crosslinked acrylonitrile/acrylamidoxime/ 2-acrylamido-2-methylpropane sulfonic acid (AN/AAx/ AMPS)-based hydrogels were prepared by free radical crosslinking solution polymerization technique. The chemical structures of the hydrogels were characterized by FT-IR analysis. The morphology of the dry hydrogel sample was examined by scanning electron microscope (SEM). These hydrogels were used for the removal of Cd(II), Cu(II), and Fe(III) ions from their aqueous solutions. The influence of the uptake conditions such as pH, time and initial feed concentration on the metal ion binding capacity of hydrogel was also tested. The selectivity of the hydrogel towards the different metal ions tested was arranged in the order of Cd(II) > Fe(III) > Cu(II). It was observed that the specific interaction between metal ions and ionic comonomer in the hydrogel affected the metal binding capacity of the hydrogel. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 999–1011, 2011

Key words: hydrogel; 2-acrylamido-2-methylpropane sulfonic acid; acrylonitrile; wastewater; adsorption; heavy metal

INTRODUCTION

Many advances are being made to develop methods and materials to remove ionic species from sewage and industrial waste. Most common methods to remove metal ions from wastewater include filtration, chemical precipitation, ion exchange, and sorption. Both natural and synthetic polymers are recently being used for metal ion removal from aqueous systems. The hydrogels that carry binding ligands at the backbone or side chain or those that may be physically attached to generate an active support for metal ion uptake are finding increased use in metal ion removal from aqueous solutions.[1–5] Mono-functional crosslinked polymers with a single binding site per ligand include sulfonic and carboxylic acid ion exchange resins.[6] The metal ion complexation capacity of the polymer supported ligands is determined by certain characteristics of polymeric supports such as nature of monomers, the extent of crosslinking, and the structure of the spacer groups separating the ligands from polymeric chain.[4–7] Ease of handling, reusability and the possibility of semi continuous operations are other advantages which encourage the use of these materials and make them promising for water purification.[8–11]

The separation or adsorption of trace metal ions from an aqueous solution has been of considerable importance in different fields for solving wastewater problems, removing toxic metals from seawater, recovering raw materials, etc. The separation of metals can be achieved by using macromolecular compounds containing functional groups such as amino, carboxyl, phosphoric, imidazoline, thioamido, and amidoxime, etc., which have complexing ability towards metals ions.[12,13] Among them, amidoxime groups have high tendency to form strong complexes with a wide range of heavy metal ions. Much attention is paid to amidoxime chelating adsorbent in removing heavy toxic metals and/or selective-recovering of precious metals from different sources (for an example, the sorption of uranium from sea water.[12] 2-Acrylamido-2-methylpropane sulfonic acid (AMPS) has been used as a comonomer because of its thermal and hydrolytic stability. This monomer contains a spacer which allows the charged group to have a relatively high mobility when linked to a polymer backbone. In previous works,[14–17] AMPS was crosslinked with different monomers to prepare copolymer superabsorbent hydrogels. It has been determined that the polymers containing amidoxime

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groups have a tendency to form complexes with heavy metal ions, the complex with uranyl ions being one of the most widely investigated.[11] The standard procedure in the preparation of amidoximated resins is first to prepare acrylonitrile copolymers followed by conversion of nitrile groups into amidoxime. The aim of this study is to synthesize crosslinked polychelatogen hydrogels composed of acrylonitrile, acrylamidoxime and 2-acrylamido-2-methylpropane sulfonic acid. N,N-Methylenebisacrylamide (MBA) was used as a crosslinking agent. The influence of copolymer composition, crosslinking percentages and pH of aqueous solutions on the metal ions removal efficiencies was investigated.

EXPERIMENTAL

Materials

Acrylonitrile (AN, Fluka, Buchs, Switzerland) stabilized with 0.005% hydroquinone was purified and distilled to get fraction at 76–78°C before polymerization. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS, Merck, Darmstadt, Germany) was recrystallized twice from a mixture of methanol and 2-propanol or boiling methanol. The crosslinker N,N^- -methylenebisacrylamide (MBA, Merck, Darmstadt, Germany) was recrystallized twice in water. Potassium persulfate (KPS) was recrystallized from deionized water before use. Sodium bisulfite (SBS) analytical grade was used as received. 2, 2$^-$ -Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Dimethylformamide (DMF) was dried by stirring overnight with calcium hydride. Hydrochloric acid (Merck) was used as a desorption agent. Deionized water obtained from a Milli Q-water purification system (Millipore) used for the preparation of all solutions.

Buffer solution with ionic strength of 0.2M (citric acid/trisodium citrate) and 0.2M (sodium dihydrogen phosphate/disodium hydrogen phosphate) were used to prepare buffer solutions having pH ranged from 3 to 5 and 6–8, respectively. Totally, 0.2M HCl was used to prepare aqueous solutions of pH = 1. Sodium chloride was used to change the ionic strength of the buffer solution at pH = 7.

Hydroxylamine was prepared in alcoholic aqueous solution of neutralized hydroxylamine hydrochloride solutions (mol ratio 1 : 1)of $NH_2OH.HCl$: NaOH at temperature 50°C for 2 h. Hydroxylamine hydrochloride (40.1 g) was dissolved in 290 mL of methanol aqueous solution (methanol: water 5: 1). The hydroxylamine was neutralized with sodium hydroxide solution till pH = 10 and the NaCl salt was removed by filtration.

Atomic absorption spectrophotometer standard solutions of 1000 mg L^{-1} Cd (II), Cu(II), and Fe(III) were purchased from Merck, Darmstadt, Germany. Other dilute standard solutions were prepared from these stock solutions. All other chemicals were Prolabo products and were used as received.

Synthesis of hydrogels

Preparation of crosslinked homopolymers (PAMPS)

PAMPS hydrogel was prepared by free radical crosslinking solution polymerization of AMPS in deionized water at 60°C under a nitrogen atmosphere in cylindrical glass tubes. The concentration of AMPS monomer in deionized water was 50 wt %. Different mol percentages (0.0065–0.065 mol %) of MBA crosslinker (1–10 wt %) were added and 0.0004 mol % of KPS and SBS was used as initiator. The amount of the initiator and crosslinker was calculated with respect to the monomers. The procedure of preparation and purification was discussed in the previous work.[14]

Preparation of crosslinked polyacrylonitrile homoplymer (PAN)

Crosslinked acrylonitrile homoplymer was prepared by free radical crosslinking solution polymerization using different mol ratios of crosslinker (MBA) in the presence of DMF. AN concentration in DMF was 30 Wt%. AIBN used with 0.001 mol % as initiator. The reaction mixture was refluxed at 90°C with continuous stirring for 10 h. The heavy pale yellow precipitate was filtered off, washed several times with acetone, deionized water, and dried at 50°C. The crosslinked polyacrylonitrile with MBA was designated as PAN.

Synthesis of crosslinked AN/Amps

Crosslinked AMPS/AN copolymers were prepared via a crosslinking solution polymerization technique using DMF as a solvent. The monomers were dissolved in the presence of 0.065 mol % (10 wt %) of MBA as a crosslinker (mol % based on 100 mol % of the two monomers). AIBN was used as initiator (0.002 mol % based on mol percentages of two monomers). This procedure was repeated with different monomer feed ratio (mol % AMPS: mol % AN) viz. (90/10, 70/30, 50/50, 30/70, and 10/90).

Another series of AMPS (50 mol %)/AN (50 mol %) copolymers with different contents of MBA viz. (0.003, 0.0065, 0.013, 0.0195, and 0.0325 mol %) which equivalent to (0.5, 1, 2, 3, and 5 wt %) were prepared. The crosslinking polymerization reaction was carried out at room temperature (45°C) for 15 min and the reaction was kept under nitrogen gas, then the reaction temperature was raised up to 60°C for 5 h. The polymer rods were postcured at 105°C in an

air oven for 24 h to ensure complete polymerization. The rods were cut to thin discs that were used for determining the soluble fraction (SF%) and swelling parameters.

Synthesis of crosslinked acrylamidoxime resin

The hydroxylamine solution (30 g) was added to of AN/AMPS copolymers and heated at 70°C for 2 h with continuous stirring. Samples were analyzed from the reaction media at the predetermined time intervals. The produced polymers washed with distilled water and dried in vacuum oven at 35°C. The crosslinked acrylamidoxime/acrylonitrile/2-acrylamido2-methyl propane sulfonic acid with MBA was designated as AN/AAx/AMPS.

The conversion of nitrile groups to amidoxime was determined from FT-IR spectra. The percentage conversion of nitrile group was calculated using relation $C_n = [(A_0 - A_t) \times 100/A_0]$; where C_n is the percent of conversion and A_0 and A_t are the areas of CN band observed at 2200 cm^{-1} before and after the amidoximation time t, respectively.

Characterization

The dry hydrogels were ground and pressed with KBr and then were measured with FTIR spectroscopy (Mattson 1000, Unicam, England) from 400 to 4000 cm^{-1}.

Scanning electron micrographs were taken with a JEOL JSM 5400 scanning electron microscope (Japan). The specimens were prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of ~300 A°.

A Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer (FAAS) equipped with deuterium lamp for continuous background correction was employed. Merck atomic absorption standard solutions for the selected metals were used for calibration.

Surface area, pore size distribution and mean pore diameters were measured using a Micromeritics 2010C automatic analyzer equipped with high stability 1 Torr pressure transducer. Samples of polymers (80–100 mg, 0.30–0.60 mm), were outgassed at 60°C for 24 h on the degas port of the analyzer. Sorption isotherms were generated by dosing nitrogen onto the sorbent at 77 K. The density functional theory was used to calculate the specific surface area and pore size distribution values.

Sol fraction

The polymer rods were postcured at 100°C in an air oven for 24 h to ensure complete polymerization. These rods were cut to thin disks and dried in vac-

uum at 60°C to a constant weight. Cylindrical hydrogels were cut with a length of 10 mm. The dried xerogel discs were transferred into an extraction thimble and were subjected to Soxhlet extraction with deionized water at 100°C. After extraction for 24 h, the disks were dried under atmospheric pressure for several hours and then dried to a constant weight in a vacuum oven at 60°C. The sol fraction, SF, was expressed as the fractional loss in weight of xerogel, i.e., %SF $= [(W_0 - W)/W_0] \times 100$, where W_0 and W are the weights of the disk before and after extraction, respectively.

Swelling behavior of the hydrogels

The hydrogel samples were placed in vials filled with 25 mL of deionized water or different buffer solutions. The vials were placed in a temperature-controlled bath at 25°C. The hydrogel samples were periodically removed from the vials, wiped with filter paper to remove the superficial water or buffer solution, weighed and then placed in the same vials. The equilibrium water content, EWC, and swelling uptake of the hydrogels (q) were calculated from the following formula: EWC (%) $= [(m_t - m_0)/m_t] \times 100$ and q (g/g) $= m_t/m_0$; m_0, the initial mass of the hydrogel; m_t, the mass of the hydrogel at equilibrium time t.

Single-component heavy metal adsorption

The adsorption properties of hydrogels for metal ions Cd (II), Cu (II), and Fe (III) were examined in the batch experiments. Dry gel samples (0.1 g) were immersed in 1000 mg L^{-1} single ion solutions at pH 1.0–5.5 at room temperature and stirred magnetically at 200 rpm for 24 h. Buffer solution with ionic strength of 0.2M (citric acid/trisodium citrate) and 0.2M (sodium dihydrogen phosphate/disodium hydrogen phosphate) were used to prepare buffer solutions ranged from 3 to 5 and 6–8, respectively. 0.2M HCl was used to prepare solutions of pH 1. Sodium chloride was used to change the ionic strength of the buffer solution at pH 7. The pH values were precisely checked by a pH-meter (Digmed-DM21, accuracy ± 0.01).

The effect of the initial heavy metal ion concentration on the adsorption capacity was studied. The dry hydrogels were equilibrated for 24 h in different heavy metal ion aqueous solutions having different concentrations ranged from 5 to5000 mg L^{-1}. The aqueous solutions were prepared in buffer solution at pH 5.0 for Cd (II) and Cu (II) and at pH 2.5 for Fe(III). The concentrations of Cd (II), Cu (II), and Fe (III) ions were analyzed after separation of aqueous phase using a Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer via applying

a deuterium background correction. The instrument response was periodically checked with known heavy metal solution standards. Metal ion concentrations adsorbed per unit mass of the hydrogel (mg metal ion g^{-1} dry hydrogels) were calculated by using the following expression: The amount of metal ion adsorbed (mg/g) $Q = [(C_0 - C) \times V]/(m \times 1000)$; where C_0 and C are the concentrations of the metal ions in the aqueous phase before and after the adsorption period, respectively, (mg L^{-1}); V is the volume of the aqueous phase (mL) and m is the amount of dry hydrogel used (g).

Multicomponent heavy metal adsorption

Adsorption of heavy metal ions from synthetic wastewater was carried out in a batch system. The concentration of metal ions in synthetic wastewater is 1.00 mg L^{-1} for each of Ni(II), Zn(II), Co(II), Pb(II), Na(I), Cd(II), Cu(II), and Fe(III). To adjust salinity, 700 ppm of NaCl was added to the synthetic wastewater. A dry hydrogel sample was transferred into 10 mL of synthetic wastewater, stirred, and incubated at room temperature (pH 5.0). After adsorption, the concentration of the metal ions in the remaining solution was determined by FAAS as described above.

Recovery and reuse

Metal ions (0.1 g) loaded hydrogels were stirred with (10 mL, 2N) HCl solution at room temperature for 2 h to desorb the metal ions. The final metal ion concentration in the aqueous phase was determined by using a FAAS. The desorption ratio was calculated from the relation: desorption ratio = [(amount of metal ions desorbed into the elution medium/ amount of metal ions adsorbed onto the hydrogels)] $\times$ 100. Thereafter, the hydrogel was neutralized with dilute NaOH, washed with deionized water and again subjected to adsorption processes to determine the reusability of the hydrogels. Adsorption–desorption cycles were repeated five times by using the same hydrogels.

RESULTS AND DISCUSSION

AN and AMPS were used to prepare both crosslinked PAN or PAMPS homopolymers and AN/AMPS and AN/AAx/AMPS copolymers in the presence of MBA crosslinker by free radical crosslinking solution polymerization technique as described in the experimental section. Scheme 1 represented the synthesis of the (AN/AAx/AMPS) hydrogels. These gels are typically prepared via a free radical crosslinking polymerization mechanism, where monomer units are connected into long chains through their

double bonds as illustrated in Scheme 1 for AN and AMPS monomers and MBA crosslinker. The degree of crosslinking is controlled by the fraction of crosslinking agent present in the polymerization and the double bond conversion. The reactivity of MBA crosslinker toward AN and AMPS monomers can be determined from sol fraction measurements as described in the experimental section. Potential crosslinking is also lost due to intramolecular cyclization reactions, where both ends of the crosslinking agent reacted into the same growing polymer chain, forming a loop structure.

SF measurements

The present work aims to study the affinity of crosslinked PAN, PAMPS and AN/AMPS copolymers towards MBA crosslinker through measuring soluble fraction contents (SF %). In this respect, SF % was determined by measuring the soluble materials through Soxhlet extraction using water as solvent. It has been reported that water is a poor solvent for linear PAN, whereas DMF are good solvent for the same elastic chain. In this respect, the SF of the crosslinked PAN was measured through DMF Soxhlet extraction after 24 h. SF values of PAN, PAMPS, and AMPS/AN gels were determined and are listed in Table I. It was noted that the SF values decreased with increasing amounts of crosslinker concentrations. This can be attributed to the high reactivity of MBA crosslinker towards acrylate monomers.[18] On the other hand, it was found that the crosslinked PAN have lower SF values than PAMPS and AN/ AMPS copolymers. This can be attributed to the high reactivity of the PAN towards acrylate crosslinker, which is much higher than methacrylate crosslinkers.[19] The data listed in Table I arranged the reactivity of MBA towards AN or AMPS in the order PAN $\geq$ PAMPS $\geq$ AN/AMPS. On the other hand, SF values of the crosslinked AN/AMPS copolymers increased with increasing of AMPS mol % in the copolymerization reactions. Accordingly, it can be concluded that MBA is suitable to use as a crosslinker for AN/AMPS copolymers due to its capability to copolymerize well with AN and AMPS.

Chemical structure of crosslinked resins

The chemical structures of the hydrogels were characterized by FT-IR. Figure 1 represented the FT-IR spectrum of AN/AAx/AMPS hydrogel with 10 mol % AMPS content. FTIR spectra have been used to verify the modifications of certain functional groups in material because an individual chemical bond often shows a unique energy adsorption band.[20] As seen in Figure 1, the broad absorption band around 3100–3500 cm^{-1} is ascribed to the overlapping peaks
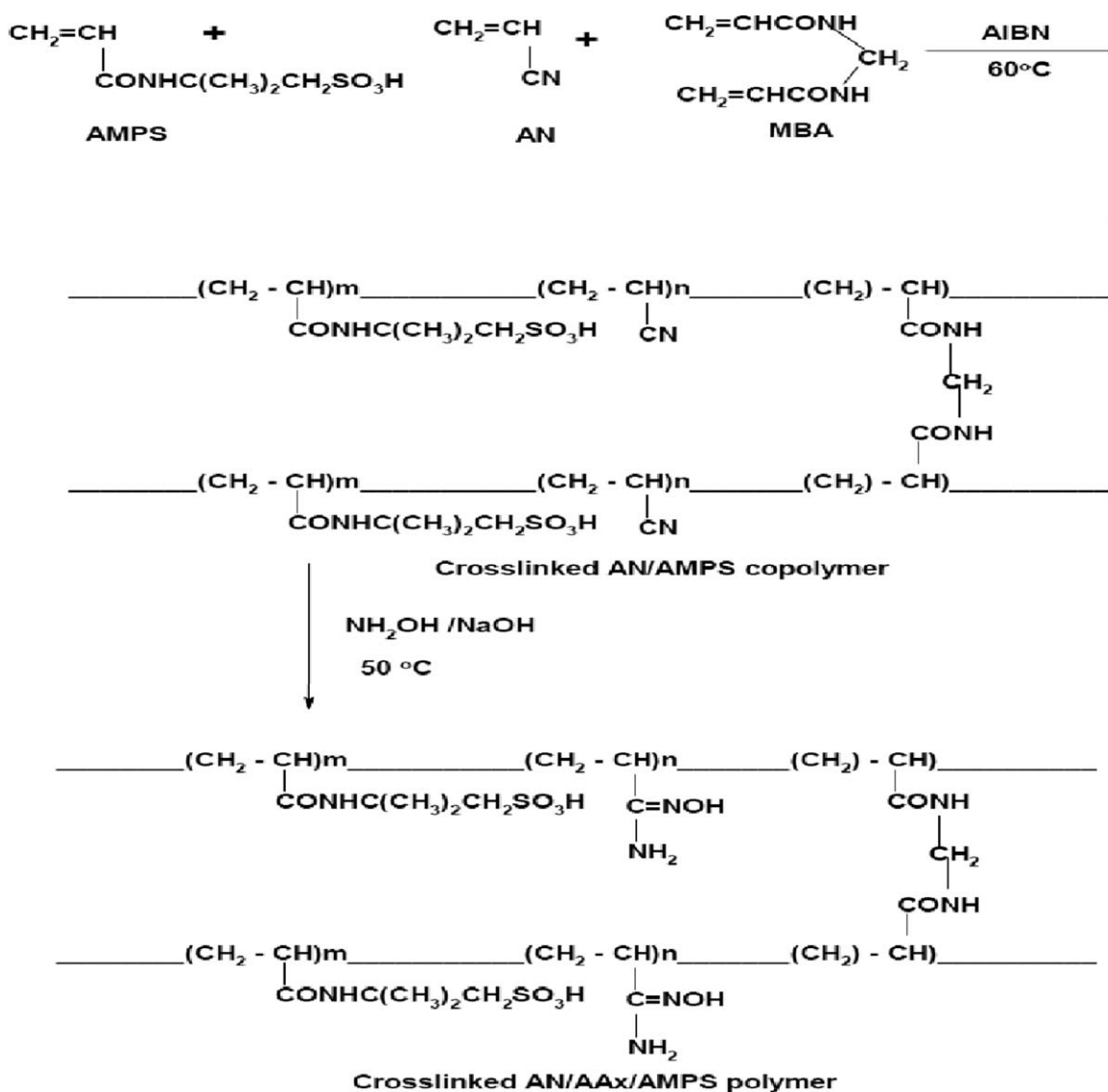
Scheme 1 Preparation of crosslinked AN/AAx/AMPS resins.

of NH and OH groups. The band appearing at 1721 cm^{-1} is associated with the C=O group of AMPS. The characteristic absorption bands of AMPS units can be seen at 950–1040 cm^{-1} due to the SO group. Sharp bands at 2230 cm^{-1} and 1340 cm^{-1} assigned to —CN and —CH— group of —AN were observed, respectively. The main absorption bands at 3200–3400, 1650, and 940 cm^{-1} were observed due to —OH, —C=N—, and >N—O— of amidoxime groups, respectively. The variation in absorption percentages at 2230 cm^{-1} indicated the conversion of nitrile groups as a result of the amidoximation.[21] The absorption band at 1550 cm^{-1} can be referred to the bending vibration of —NH$_2$ of amidoxime group as represented in Figure 1. These bands indicated that the modification reaction was successfully done.

The conversion of nitrile group to amidoxime in AN/AMPS copolymers can be determined from FTIR spectra as described in the experimental sec-

tion. The intensities of CN bands in hydrogel decrease proportionally with the amidoximation reaction time. The relative decrease in the area of characteristic CN bands in AN segments in hydrogels was plotted versus amidoximation time. The time required to obtain amidoxime was determined as 50 h. The percentage amidoximation conversion (C_n) was calculated and listed in Table II. Figure 2 shows the progress in percentage amidoximation with the amidoximation reaction time for all compositions of AN: AMPS copolymers. In general, the amidoximation increases with the increase in the reaction time. For the mol ratio of 90 : 10 (AN : AMPS), 69% amidoximation was found which is lesser than the values of 70 : 30 and 50 : 50 systems. The conversion reaction has been carried out in aqueous medium, the diffusion of NH$_2$OH into the structure becomes more difficult with the increase in the amount of AN in the polymeric systems due to

TABLE I
SF Content and Swelling Parameters of Crosslinked PAN, PAMPS, and AN/AMPS
in Aqueous Solution at 25°C

Copolymer compositions (AN/AMPS)	Crosslinker contents (mol %)	SF (%)	Swelling parameters	
			EWC (%)	q g water/g polymer
	0.0065	29.74	99.9	1449.1
	0.0130	19.25	99.9	1199.2
0/100	0.0260	15.07	99.9	840.6
	0.0650	10.52	99.8	598.4
	0.01300	8.10	99.7	362.7
10/90	0.0650	38.04	99.2	120.0
30/70	0.0650	36.15	99.0	97.9
50/50	0.0032	38.12	99.3	144.8
	0.0065	36.14	99.1	114.9
	0.0130	35.18	98.8	84.8
	0.0325	33.8	98.5	68.0
	0.0650	30.54	98.1	53.8
70/30	0.0650	24.41	97.8	45.1
90/10	0.0650	19.61	97.3	36.4
100/0	0.0065	16.64	94.5	18.3
	0.0130	14.75	93.5	15.4
	0.0260	10.97	92.0	12.5
	0.0650	6.84	87.9	8.3
	0.01300	4. 01	76.2	4.2

decrement of polymers hydrophilicity which decreased with increasing of AN contents. On the other hand, SF% data listed in Table I indicated the crosslinking degrees were increased with increasing AN contents. Accordingly, the interaction between polymer networks and NH_2OH decreased with increasing AN contents. Similar results were obtained with poly (acrylonitrile/N-vinyl 2-pyrrolidone) hydrogel systems.[22] On the other hand, C_n data of crosslinked AN (50 mol %)/AMPS (50 mol %) with different wt % of MBA crosslinker indicated that the conversion of nitrile group to amidoxime was decreased with increasing of MBA content. Accordingly, It can be concluded that, the conversion of nitrile groups to amidoxime groups has been decreased as the contents of AN and MBA increased in the structure of AN/AMPS copolymers.

SEM analysis

In this work, the morphology of PAN, PAMPS, AN/AMPS, and AN/AAx/AMPS crosslinked polymers was studied by scanning electron micrographs of the gold-coated samples. The photographs are represented in Figures 3 and 4 The photo of PAN [Fig. 3(a)] showed the partially spherical and gel form. While the SEM micrograph of PAMPS [Fig. 3(b)] shows globular structure. SEM micrograph of AN(10 mol %)/AMPS (90 mol %), Figure 3(c), shows that he surface texture of the hydrogel is smooth which means that the polymer is homogeneous. SEM image of AN/AAx/AMPS hydrogel with 10 mol % AMPS content [Fig. 3(d)] reveals very coarse irregularly

shaped pores and finely dispersed second phase particles. There are abundant pores distributed on the surface of AN/AAx/AMPS [Fig. 3(d)] which indicated that the porous structures of AN/AAx/AMPS polymer had not been damaged significantly during the reaction with NH_2OH. The pore structure of amidoxime polymer depends on the mol % of AN and MBA crosslinker contents as illustrated in SEM micrographs in figures [Fig. 4(a,b)]. There is, however, a very significant difference between the pore morphology of hydrogels with crosslinking degrees of AN/AAx/AMPS(50 mol %) crosslinked with
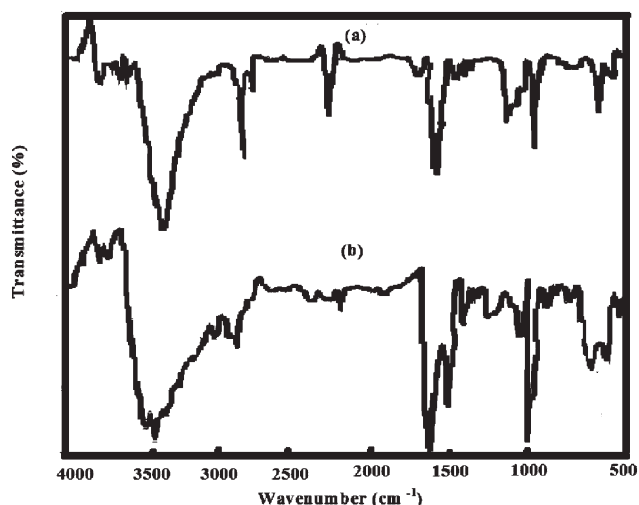

Figure 1 FTIR Spectra of (a) AN (50 mol %)/AMPS (50 mol %) and (b) AN (7.5 mol %)/AAx (42.5 mol %)/AMPS (50 mol %) crosslinked with MBA crosslinker.

Copolymer compositions (mol %)		Crosslinker contents (mol %)	Amidoxime percentage Cn* (%)	Amidoxime content (mol %)	Swelling parameters	
AN/AMPS	(AN/AAx/AMPS)				EWC (%)	q (g water/g gel)
10/90	7.5/2.5/90	0.0650	25	2.5	98.86	88.32
30/70	18/12/70	0.0650	40	12	98.45	64.82
50/50	5/45/50	0.0032	90	45	98.75	70.1
	7.5/42.5/50	0.0065	85	42.5	98.47	65.4
	12.5/37.5/50	0.0130	75	37.5	98.33	60.2
	15/35/50	0.0325	70	35.0	98.22	56.4
	17.5/32.5/50	0.0650	65	32.5	98.14	53.86
70/30	17.5/52.5/30	0.0650	75	52.5	97.71	43.68
90/10	14.4/75.6/10	0.0650	84	75.6	97.11	34.62

Calculated from FT-IR.

0.032 and 0.065 mol % MBA crosslinker. In the hydrogel with crosslinking degree of MBA 0.032 mol % [Fig. 5(a)] the pore structure has a sponge-like shape with spherical open and interconnected cells. On the other hand, in the hydrogel with crosslinking degree of 0.065% [Fig. 5(b)] the pore structure is composed of channel-like pores whose main axes are lined with the vertical axis of the mold, forming a regular and oriented tubular microstructure. The generation of these two different morphologies was confirmed at different MBA contents with crosslinking degrees of 0.013 mol % (spherical cells) and 0.045 mol % (tubular cells). On the other hand, as the mol % of AN increased, the average pore radius, and the pore volume were increased and hence the polymer exhibits a higher porosity as represented in Figures 3(d) and 4(b).

Pore structure analysis

It was observed from SEM images (Figs. 3–5) that pore size of AN/AAx/AMPS copolymers became la-

ger than the unmodified AN/AMPS copolymers, which indirectly suggested that the cyano group had transformed into amidoxime (AO) group. There were abundant pores distributed on the surface of AN/AMPS and AN/AAx/AMPS copolymer indicating that the porous structures of AN/AMPS copolymer surfaces had not been damaged significantly during the reaction with NH$_2$OH HCl. From SEM images, it was obvious that the internal of AN/AMPS and AN/AAx/AMPS copolymers were all

Figure 3 SEM micrographs of crosslinked (a) PAN, (b) PAMPS, (c) AN(10 mol %)/AMPS (90 mol %), and (d) AN(14.4 mol %)/AAx (75.6 mol %)/AMPS (10 mol %).
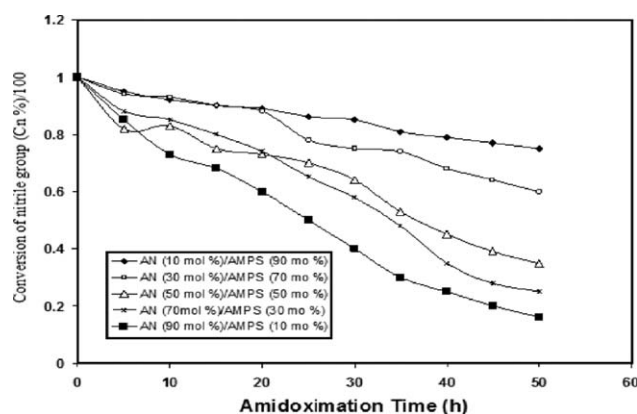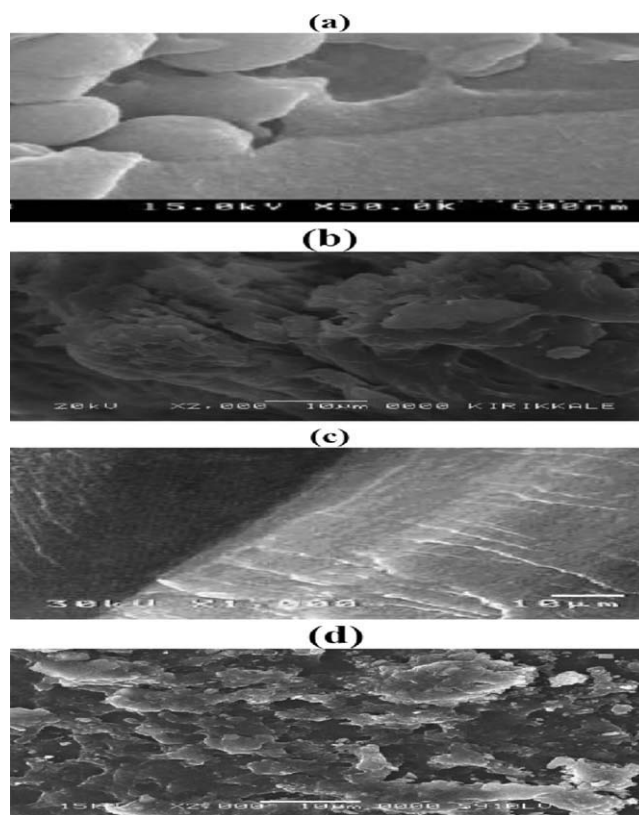
Figure 2 The change of the relative intensity of nitrile band of crosslinked AN/AMPAS copolymers with reaction time.
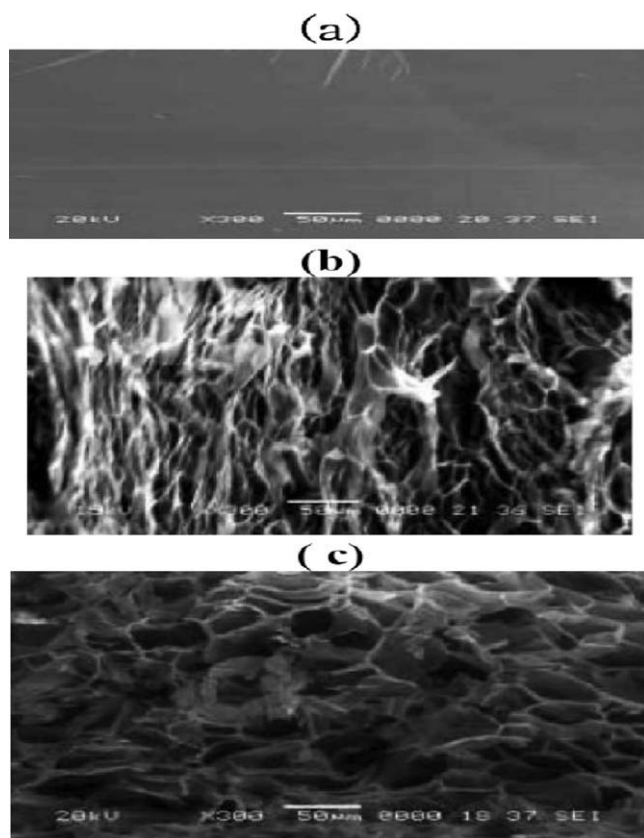
Figure 4 SEM micrographs of crosslinked (a) AN (7.5 mol %)/AAx (2.5 mol %)/AMPS (90 mol %), (b) AN (18 mol %)/AAx (12 mol %)/AMPS (70 mol %) and (c) AN (14.4 mol %)/AAx (75.6 mol %)/AMPS (10 mol %).

Figure 5 SEM micrographs of AN/AAx/AMPS (50 mol %) crosslinked with (a) 0.0325 and (b) 0.0650 mol % of MBA crosslinker.

loose. Both the surface pores and loose internal structure would provide convenient diffusion channel of metal ions into the interior of the copolymer beads when it was used in adsorption of metal ions in aqueous solution.

The nitrogen adsorption–desorption isotherm was used to determine the pore size structure of modified and unmodified crosslinked AN/AMPS copolymers. In this respect, AN/AMPS crosslinked with 0.065 mol % of MBA, having equal 50 mol % of AN and AMPS, was selected to study the nitrogen adsorption–desorption isotherm. Results for the porous AN/AMPS and AN/AAx/AMPS are illustrated in Figure (6). All the isotherms were Type IV according to the IUPAC classification.[23] Characteristic features of this type isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high P/P_o. As the mechanism of micropore filling, almost no nitrogen adsorbed by the copolymers at lower P/P_o, indicating that there was few microspores in the copolymers. Figure (7) showed BJH desorption pore size distributions of AN/AMPS crosslinked with 0.065 mol % of MBA having equal 50 mol % of AN and AMPS. As shown
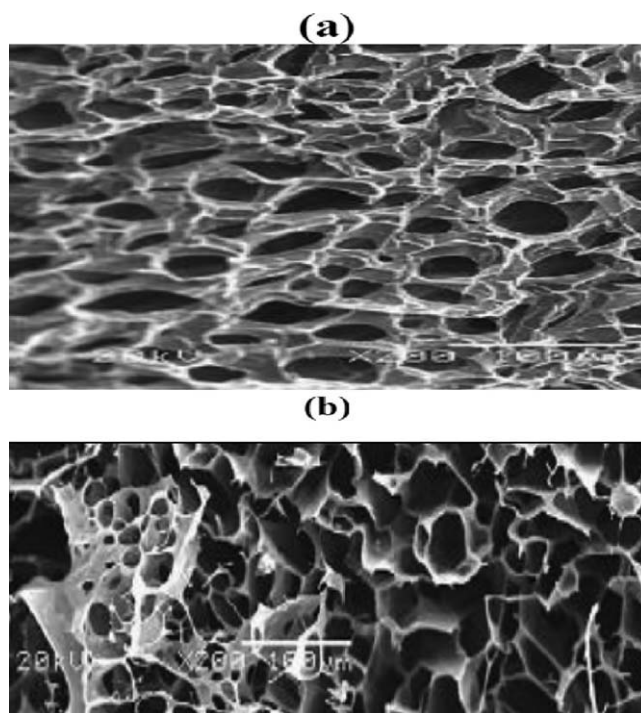
in Figure (7), the pores between 50 and 200 nm were dominant for all the copolymers, that is, both mesopores and macropores were presented in the
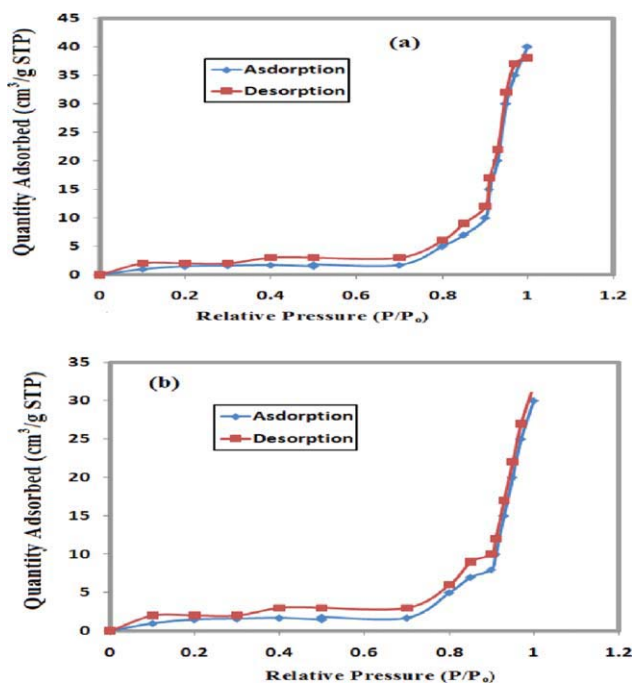

Figure 6 Nitrogen adsorption-desorption isotherms of (a) AN/AMPS and (b) AN/AAx/AMPS crosslinked with 0.065 mol % of MBA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
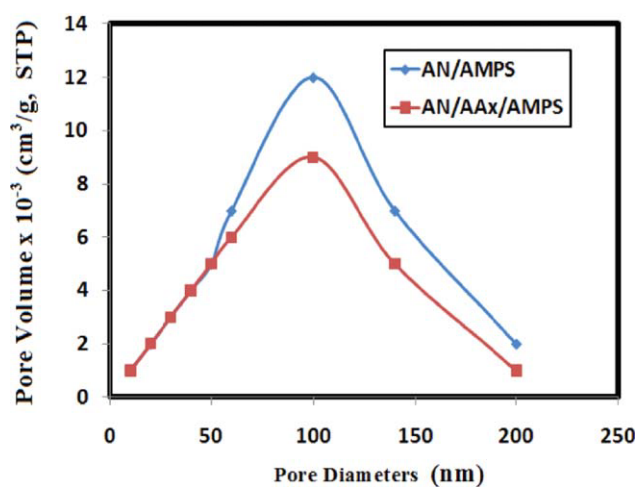
Figure 7 BJH desorption pore size distributions of AN/AMPS and AN/AAx/AMPSA crosslinked with 0.065 mol % of MBA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymers, which was in accordance with the results of SEM analysis. After the reaction of AN/AMPS with NH_2OH HCl, the pores between 50 and 160 nm decreased and the amount of those between 160 and 200 nm increased slightly. The porous structure parameters of the copolymers from the basis of the nitrogen adsorption data are BET surface area of 489 m^2/g and a BJH desorption volume of 55 cm^3/g were obtained for AN/AMPS, which decreased to 231 m^2/g and 41 cm^3/g, respectively, after modified with NH_2OH HCl. This could be attributed to the formation of an organic layer in the pores, which blocked the adsorption of nitrogen molecules. In addition, the pore size slight increased was probably because sodium hydroxide, which was utilized to remove HCl to make NH_2OH free (experimental section), partially destroyed the framework of AN/AMPS copolymers and made its pore diameter increase. Consequently, the pore size allows easy access of any hydrated metal ions into the interior surface of the resin. Similar explanation for chelating resin silica-gel supported diethylenetriamine was reported in literature.[24]

Swelling parameters of AN/Amps copolymers

In this section the influence of copolymer composition and crosslinker concentrations on the swelling behaviors of AN/AMPS copolymer in deionized water were considered. All AN/AMPS and AN/AAx/AMPS xerogel discs were swollen in water at room temperature and all gels swelled uniformly, and have smooth edges and definite shape. The swelling parameters, such as EWC and q for crosslinked AN/AMPS and AN/AAx/AMPS with MBA crosslinker in deionized water at room temperature

(25°C), were determined and listed in Tables I and II. These parameters were also determined for AN/AMPS copolymers (having 50% mol ratio of AMPS) crosslinked with different mol percentages of MBA crosslinker (Tables I and II). It was noticed that the q values were increased with formation of amidoxime copolymers. This behavior can be attributed to increment in hydrophilicity of the AN/AMPS networks. The relation between swelling time and q values of crosslinked PAMPS was represented in Figure 8(a). The relations between swelling time and q for crosslinked AN/AMPS with different weight ratios of MBA and were plotted in Figure 8(b). The relation between swelling capacity (q) and swelling time for AN/AMPS (50/50 mol %) and AN/AAx/AMPS hydrogels was plotted in Figure 9(a,b). Table I indicated that the q of AN/AAx/AMPS hydrogels in water increased with increasing AMPS content. This is due to the osmotic pressure exerted by counterions of AMPS units. The data of swelling show that the overall swelling attains its maximum at different times ranging between 3 and 8 h based on the copolymer composition and on the percentage of MBA crosslinking agent. It was also observed that the swelling time was decreased at high crosslinker content. These behaviors can be attributed to the formation of less elastic network structures due to high crosslinker content.[15] Tables I and II show the variation of the swelling degree with amidoximation degrees.

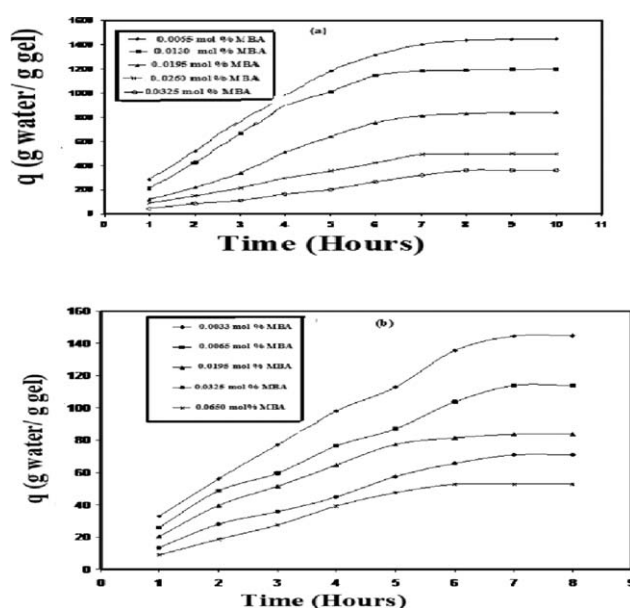Crosslinked AN/AMPS copolymers contain different ionic contents such as SO_3H, COOH, and weak

Figure 8 Swelling uptake versus time for crosslinked (a) PAMPS, (b) AMPS/AN (50 mol %/50 mol %) with different mol % of MBA crosslinker in aqueous solution at 25°C.
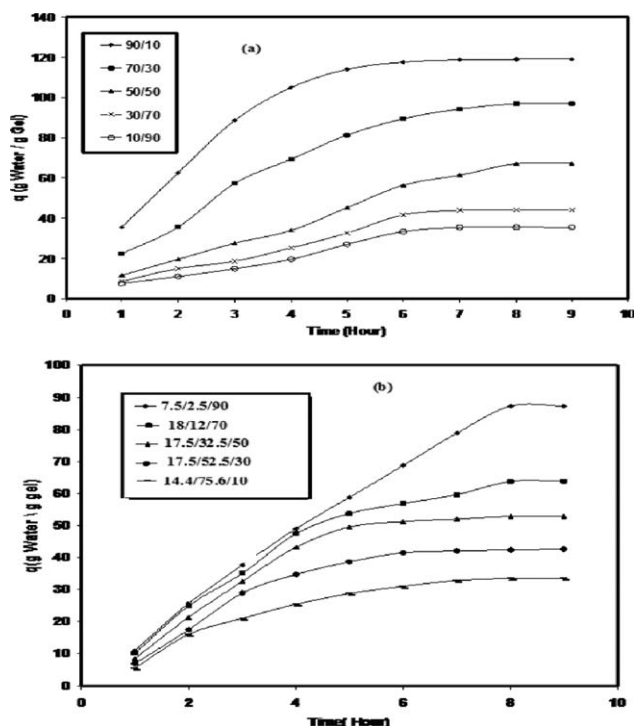
Figure 9 Swelling uptake versus time for crosslinked (a) AMPS/AN and (b) AMPS/AAx/AN copolymers with 0.0650 mol % MBA in aqueous solution at 25°C.

due to the presence of strong hydrogen bonds between SO_3H and amide groups. Increasing the pH of the external solution increased the ion dissociations of SO_3H and, consequently, the charges on the polymeric chains were increased which increases the gel expansions. The swelling capacities of the gel were gradually increased. On the other hand, swelling capacity of PAMPS hydrogel was reduced at elevated pH (above 11). By addition of sodium hydroxide, excess Na^+ prevents ionic repulsive interactions which cause shielding or screening effect. As a result, it behaves in this solution like an uncharged hydrogel.[25] Huglin purposed chelation mechanism is occurred between $SO3^-$ and Na^+ at pH 12 which leads to swelling reduction.[26]

Application of AN/Amps copolymers for heavy metal adsorption

Metal ion uptake on hydrogels can be affected by hydrophilic-hydrophobic balance, the nature of monomer and the extent of crosslinking of macromolecular supports. In this work, AN/AAx/AMPS resins were selected due to their hydrophilicity and porous morphology to uptake the metal ions from
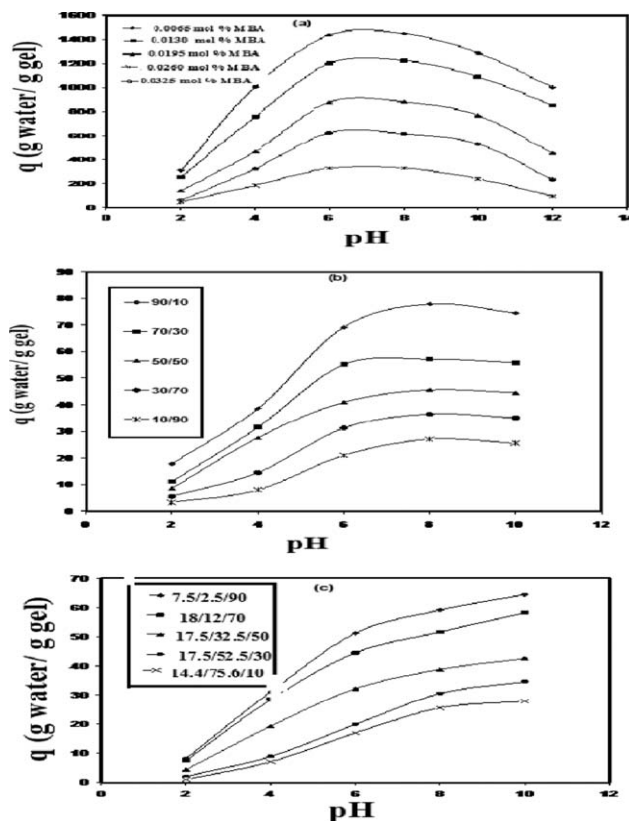
base amide and it is expected that the ionic content will change their swelling equilibrium at different pH media. In this respect, the swelling capacities of the prepared copolymers were measured at 25°C in different buffer pH solutions. Figure 10 represented pH dependence of the equilibrium mass swelling percentage of AN/AAx/AMPS hydrogels at 25°C in buffer solutions from pH 2 to 12. It was noted that, the swelling capacity was increased with increasing the pH of aqueous solution up to 8, and then sharply decreased. Figure 10 shows that under acidic conditions, anionic SO_3H groups are protonated and the network shrinks significantly. It is well known that, the acid dissociation constant of SO_3H acid of AMPS is pKa = 2.[17] However, swelling was significantly decreased at pH lower than 3 and higher than 11. In highly acidic conditions, lots of hydrogen cations shield the repulsive pendant anions located on the polymer chains. Since the anion–anion repulsion is the main force for swelling of the ionic hydrogels, the "shielding effect" of the excess cations reduces the swelling capacity. At pH > 3.5, the dissociation of the SO_3H acids favors and the swelling ratio of the hydrogel were increased. It was also observed that, as the AMPS content decreased, the pH dependency in swelling becomes more pronounced. This result can be explained on the basis that the presence of both amidoxime and SO_3H group at lower pH solution have low tendency to dissociate

Figure 10 Swelling uptake of crosslinked (a) PAMPS (b) AMPS/AN, and (c) AMPS/AAx/AN crosslinked with MBA in different pH aqueous solution (ionic strength 0.2M) at 25°C.
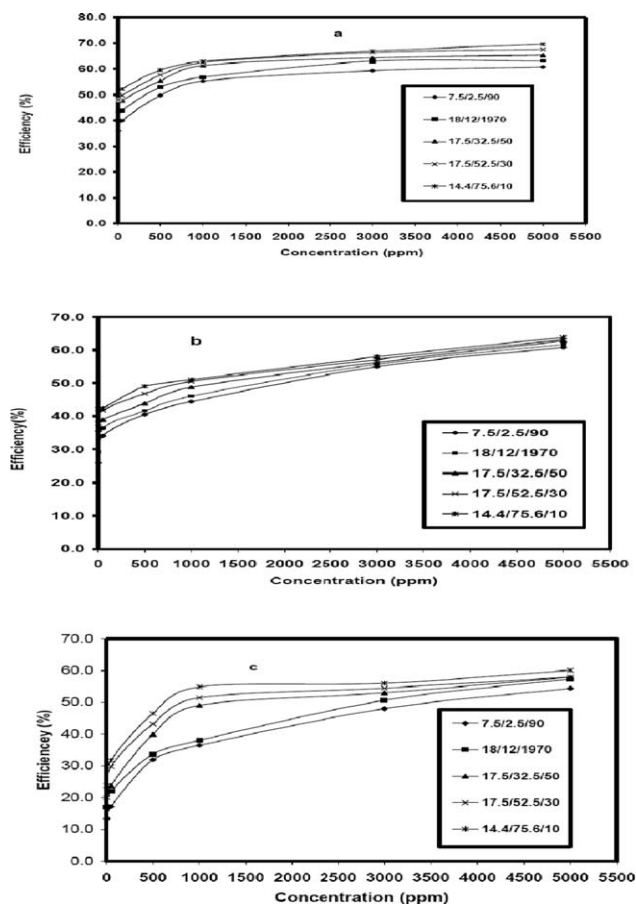
Figure 11 Metal ion uptakes of crosslinked AN/AAx/ AMPS at different concentrations of (a) Cd(II) of pH 5, (b) Cu (II) of pH 5, and (c) Fe(III) of pH 2.5 at 25°C.

their aqueous solutions. It is well known that the pH is a critical parameter that can affect the hydrogel performance which influenced its swelling and ion uptake capability In this study, metal ion uptake was examined at different metal ion concentrations (from 5 to 5000 mg L^{-1}). The relation between metal ion uptake (efficiency %)for Cd(II), Cu(II), and Fe(III) ions and their concentration was represented in Figure 11. The data indicated that, the rapid interaction of metal ions with the adsorbent is very favorable for the feasible processes. As seen from Figure 11, the maximum binding of all the metal ions occurred within the first 3 h and remained uniform throughout the 24 h. The adsorption capacity of Cd (II) ion is higher than that determined for both Cu (II) and Fe (III) ions. It appears that the synthesized hydrogel exhibits the strongest affinity for Cd (II). The affinity order of metal ions at initial concentration of 1000 mg L^{-1} is Cd (II) > Fe (III) > Cu(II), which is mainly dependent on polarity, electronic configuration, ionic radius, etc., and also importantly on the nature of interaction with the functional groups of the hydrogel. This can be attributed to complex formation capacity of the polymers towards heavy metal.[27,28]

The ─CONH and ─SO$_3$H groups of AMPS comonomer in the hydrogel structure and ─OH and ─NH$_2$ groups in AAx are primarily responsible for the specific binding of metal due to the coordination between metal ions and (─OH, ─NH2, ─SO3H) groups. The resins complexation capacity decreased as the crosslinking degree increased, i.e., as the macro-porosity decreased. The low porosity of the resins hindered the access of the copper ions to amidoxime groups located in the bulk of the beads.[19] Resins with high complexation capacity were obtained when an adequate porous structure with a high concentration of active accessible groups were produced. The data indicated that AN/AAx/AMPS (AMPS 10 mol %), with the highest proportion of acrylonitrile, was the best result of complexation capacity among other polymers. However, the surface morphologies of AN/AAx/AMPS (AMPS 10 mol %) hydrogel after metal uptake was tough as represented in Figure 12. The metal salts appeared as small white spots adsorbed on the hydrogel. These spots indicated metal uptake by the hydrogel via complexation with ─SO$_3$H, ─NH, and ─OH functional groups. On the other hand, data show that the cation exchange capacity increased with an increase in the amount of AAx to reach a maximum point. Moreover, increasing of AMPS content decreased the cation exchange capacity of the synthesized amidoxime resins. The selectivity of a chelating resin for metal ions is mainly attributed to the nature of the ligand immobilized on the polymer matrix. However since the ligand groups are chemically bound to the rigid polymer matrix, their free motions are greatly restricted. The observed extraction of metal ions is attributed to the complex
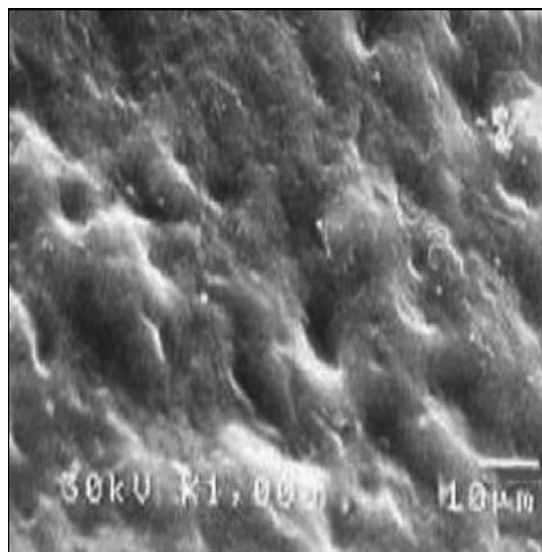

Figure 12 SEM micrograph of Cd (II) adsorbed AN/ AAx/AMPS (10 AMPS mol %) hydrogel.

formation with the introduced ligand. In addition, the flexibility of the linear ligand is likely to contribute to the rapid adsorption. On the other hand at higher pHs, sulfonic acid groups of hydrogel are ionized, therefore, formation of specific interaction with metal ions is more pronounced. The results indicated that the maximum adsorption values of the metal ions were obtained at pH 5.0 for Cd (II) and Cu (II), and 2.5 for Fe (III). Adsorption experiment for Fe (III) ions could not be performed at pH > 3 due to the insolubility of the metal hydroxide. An increase in pH decreases the competition of H+ ions for the resin sites and the complex formation of the metal ion is favored. At lower pH values the sulfonic acid is protonated and metal ions must compete with the proton.[29] The improved binding capacity towards all the metal ions at high pH proves that the binding is occurring mostly at the nitrogen centers which are being blocked by protonation at low pH values.

Initial metal ion concentration effect

Adsorption capability of the hydrogel towards Cd (II), Co (II), and Fe (III) ions with different initial ion solution concentrations varying from 5 to 5000 mg L^{-1} was illustrated in Figure 11. All measurements were performed at optimum pH. Data indicated that, the metal uptake increased rapidly with increasing initial metal ion concentration. Cd (II), Co (II) metal uptakes reach a maximum at 3000 mg L^{-1}, it levels off. From these plateau values, one can easily estimate the maximum load capacities as 250 and 200 mg g^{-1} dry hydrogel for Cd (II) and Cu (II), respectively. On the other hand the metal uptakes of Fe (III) ions were increased with increasing metal ion concentrations and reach only 200 mg L^{-1} at 5000 mg L^{-1}. These results showed that the removal of such metals from wastewater by using AN-AAx-AMPS hydrogels may find potential application in industry.

Multicomponent heavy metal chelation

The initial rate of chelated metal ions and the maximum uptake value are very dependent on the type of metal ion, its coordination and stability constant, and the steric effect of these copolymer complexes. However, the ionic size of the investigated metal ions has a great influence not only on the maximum uptake but also on the initial rate. This can be reasonably explained by a consideration of the diffusion of these metals through the porous ionic hydrogels, which is mainly dependent on their polarity, electronic configuration, ionic radii, and so forth and also is dependent on the nature of the interaction with the functional groups of the hydrogels. It is

essential to investigate the competitive binding affinity of different metal ions towards hydrogel which present in the wastewater. Different factors, such as hydrogel structure, metal combination, metal ion concentration, uptake time and experimental conditions affect the interaction between the metal ion and the reactive sites at hydrogel.[30] In this case crosslinked AN/AAx/AMPS copolymers were selected to investigate the competitive binding affinity of ions in the wastewater. The results show that, the binding capacities of all ions were increased under the competitive conditions. The binding capacities were 0.95 mg/g for Cd (II), 0.87 mg/g for Cu (II), and 0.83 mg/g for Fe(III). In this case, the hydrogel also adsorbed other metal ions Zn(II), Mn (II), Co(II), Pb(II), and Na(I), the binding capacities were 1.00, 0.77, 0.73, 0.72 and 0.18 mg g^{-1}, respectively. Therefore, the ionic size is a very important factor because of permeability and diffusivity problems through porous hydrogels of certain diameters and pore sizes. The complexing ability of the metal ion is highly dependent on its ionic radius, valence, and hydration energy.[31]

Recovery and reuse

It is clear that metal ion uptake drops significantly at low pHs. Therefore, it is assumed that the metal ions can be recovered by decreasing the pH. Therefore it is assumed that the metal ions can be recovered by decreasing the pH. The AN/AAx/AMPS hydrogels were completely saturated with the metal at the optimum pH and time. Then, all adsorbed metal ions were desorbed by using 2 mol L^{-1} HCl aqueous solutions. The final metal ion concentration in the aqueous phase was determined by using atomic absorption spectrometer. After washing with excess water, the hydrogel is available for reuse. The applicability of extracting of heavy metal ions from the metal loaded hydrogel was tested. It was found that, the desorption of Cu(II), Co (II), and Cd(II) from the metal-loaded in a 2 mol L^{-1} HCl solution. The metal ions were desorbed by 40 and 58%, respectively, within 2 min. The amount of recovered metals was over 90% after 1 h. These results strongly suggest that the crosslinked AN/AAx/AMPS copolymers have a great potential as a filter for recycling metals from different sources. The recovered efficiencies of Cd (II), Cu(II), and Fe(III) were found to be 96, 93, and 94%, respectively. To determine reusability of the AN/AAx/AMPS hydrogel, adsorption-desorption cycles were repeated five times by using the same hydrogel. The data indicated that the prepared hydrogels reused five times without loss of adsorption capacity. This data indicated that the AN/AAx/AMPS hydrogels were not decomposed with 2 mol L^{-1} HCl aqueous solutions.

CONCLUSIONS

The investigation herein points out many outcomes in the use of hydrogel materials for environmental applications:

1. The conversion of AN/AMPS to oxime in the hydrogel increased with increase in the reaction time.
2. It has been found that the adsorption capacity of hydrogels increases with increasing amidoxime content in the gel structure.
3. It was seen that the adsorption capacity of the hydrogel was increased approximately three times by incorporation of amidoxime comonomer into the structure.
4. The adsorption studies also showed that pH and initial metal ion concentration are the basic parameters affecting the maximum metal uptake capacity of the hydrogels.
5. The desorption capacity of the metals from the AN/AMPS oxime Hydrogel in a 2 mol L^{-1} HCl solution increased with desorption time. Most of the absorbed metals (more than 90%) were recovered within 1 h, indicating the potential use of the AN/AAx/AMPS hydrogel for recycling metals from wastewater.

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