

Removal of Toxic Metals Using Superabsorbent Polyelectrolytic Hydrogels

P. K. Roy,¹ V. Swami,² D. Kumar,² C. Rajagopal¹

¹Explosive Safety Division, Centre for Fire, Explosive and Environment Safety, Brig. S. K. Majumdar Marg, Delhi 110054, India

²Department of Applied Chemistry and Polymer Technology, DCE, Delhi 110042, India

Received 15 December 2010; accepted 13 February 2011

DOI 10.1002/app.34384

Published online 17 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Because of the presence of carboxylic acid moieties, poly(acrylic acid) possesses a unique ability to form stable complexes with divalent metal ions. However, its practical use for the removal of heavy metals from aqueous solutions is restricted because of its inherent water solubility. To address this issue, crosslinking of this polymer has been attempted to synthesize hydrogel, which is stable in aqueous medium over a wide range of pH values. The hydrogels, prepared by redox polymerization of acrylic acid in the presence of polyethylene glycol diacrylate as the crosslinker, were characterized by Fourier transform infrared spectrometry, elemental analysis, thermal analysis, and swelling studies. This chelating hydrogel-bearing O, O donor groups exhibited high-metal sorption capacity of 41.1,

58.2, 43.1, and 81.2 mg/g for Cr⁶⁺, Ni²⁺, Cu²⁺, and Pb²⁺, respectively, under optimum conditions. The effect of parameters including pH, concentration, and interference of common ions on metal uptake was also investigated. Langmuir and Freundlich adsorption isotherms have been used to validate the metal uptake data. High recovery (>97%) was achievable for all metal ions with 1N HCl as eluting agent, and the regeneration tests revealed that the sorbent could be used repeatedly for at least 10 cycles without any loss in chelating efficiency. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2415–2423, 2011

Key words: chelating hydrogel; crosslinked polyacrylate; preconcentration; sorption capacity

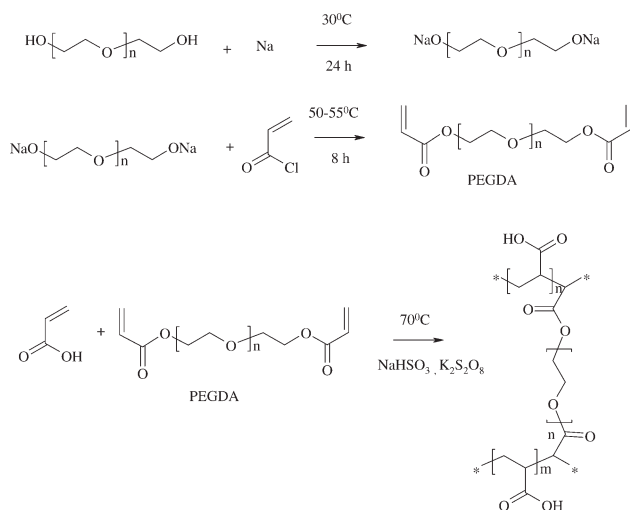
INTRODUCTION

Mineral processing and metal finishing industries generate large amount of waste effluents containing harmful metals like chromium, zinc, cadmium, copper, and nickel in soluble form, which cannot be separated by conventional filtration techniques. The necessity to reduce the concentration of heavy metals to permissible limits in wastewater stream and the need for low-cost metal recovery processes in both hydrometallurgical and environmental applications has led to an increased interest in polymer-based sorbents.

In this regard, chelating polymers have gained importance in environmental applications owing to their high degree of selectivity, high-loading capacity, versatility, along with enhanced durability.^{1,2} Conventional procedures to treat contaminated effluents include precipitation with chemical agents, adsorption onto activated carbon,^{3,4} ion-exchange, and membrane filtration processes.^{5,6} Precipitation results in the formation of large amounts of hazardous sludge, while ion-exchange process is applicable only for sol-

utions with low-dissolved solids.² Chelating polymers or polychelators have been used for remediation in homogenous reactions in the form of water-soluble polymers coupled with ultrafiltration or in heterogeneous reactions of solid polymer beads or semipermeable membranes.^{7,8} In such polymers, chelating functionalities are present in the polymeric side chains or are embedded in the backbone. The choice of the type of ligand, ligand density, structure, and solubility of the polymer, as well as pH, governs the metal ion affinity, retention efficiency, and selectivity.⁹ Recently, a lot of attention has been paid to the use of hydrogels containing chelating functional groups toward the removal of toxic metal ions.¹⁰ Sorption process, being a surface phenomenon, is limited by the number of surface adsorbing groups. In the case of hydrogels, metal ions can enter the polymeric network easily and, hence, are expected to exhibit a higher sorption capacity. Detailed literature survey revealed that hydrogels based on grafted cellulose,^{11,12} macroporous poly[acrylamide/*N*-vinylpyrrolidone/3-(2-hydroxyethylcarbamoyl)acrylic acid],¹³ poly(acrylic acid-*co*-acrylamide),^{14,15} and poly(acrylic acid) (PAA)-poly(ethyleneglycol) blend^{14,15} exhibit high-sorption capacity. In the present study, we aimed at investigating the sorption behavior of crosslinked PAA as a low-cost polymeric sorbent for the effective removal of heavy metal ions. The

Correspondence to: P. K. Roy (pk_roy2000@yahoo.com).



Scheme 1 Reaction sequence for the preparation of XPAA.

uncrosslinked linear polymer-containing carboxylic acid groups suffer from the disadvantage of being soluble in aqueous medium, thereby restricting its use as a sorbent. Acrylic acid can be crosslinked by several crosslinkers. However, PEGDA was chosen as the crosslinker for the present study as a recent comparison of crosslinkers revealed that the polymers crosslinked by PEGDA exhibited excellent repeated absorbancy over a large number of drying-swelling cycles.¹⁶ The crosslinked hydrogel is found to be stable in acidic as well as basic medium, thereby greatly enhancing its applicability for wastewater remediation.

EXPERIMENTAL

Materials

Acrylic acid (Merck) was distilled under reduced pressure before use. Potassium persulphate was purified by recrystallization from 66% ethanol/water solution (w/w). Poly(ethylene glycol) 200, acryloyl chloride, sodium metabisulphite “AR” grade (Merck) and sodium (Qualigens) were used without further purification. Standard 1000 $\mu\text{g/mL}$ aqueous stock solutions of chromium (VI), nickel (II), copper (II), lead (II), and calcium (II) were prepared by dissolving requisite amounts of potassium dichromate, nickel nitrate, copper nitrate, lead nitrate, and calcium chloride separately in 0.1M of the corresponding acid. These were diluted accordingly to prepare solutions of requisite concentration. Milli Q ultrapure water was used throughout the course of this work.

Preparation of glycol-based macromer

Poly(ethylene glycol)-200 was reacted with excess sodium under nitrogen atmosphere to prepare its

sodium salt (Na-PEG). The reaction was allowed to proceed for 24 h at 30°C, after which it was transferred to a separating funnel, and the lower fraction, excluding the solid sodium pieces was collected, weighed, solubilized in dichloromethane, and purged with nitrogen to remove dissolved oxygen.¹⁷ Stoichiometric quantity of acryloyl chloride was added to the solution, and the reaction was allowed to proceed at 50–55°C for 8 h. The solvent was removed under vacuum in a rotary evaporator, and the diacrylate (PEGDA) was collected.

Preparation of crosslinked PAA (XPAA)

For the preparation of XPAA, an oxygen-free aqueous solution of acrylic acid (3 mol/L) was polymerized in the presence of poly(ethylene glycol) diacrylate (PEGDA) (1.1–5.0 mol %) as the crosslinking agent in glass tubes of 5 mm diameter. An equimolar redox mixture of potassium persulphate (0.1 mol %) and sodium metabisulphite (0.1 mol %) was used as an initiator for the polymerization. The reaction mixture was maintained at 70°C for 30 min, after which the stable gels were formed, which were dried and subjected to Soxhlet extraction with acetone. For comparison purposes, the polymerization of acrylic acid was also carried out in the absence of crosslinking agent to prepare linear poly (acrylic acid) (PAA). The reaction scheme depicting the entire process has been presented in Scheme 1, and the various formulations prepared have been listed in Table I. The table also reports the crosslinking ratio (χ), which has been defined as the ratio of the moles of crosslinking agent to moles of PAA repeating unit.¹⁸

Structural characterization

Fourier transform infrared spectrometry (FTIR) was carried out on a Perkin–Elmer Spectrum 2000 FTIR with an attenuated total reflectance crystal accessory (Golden Gate). All spectra were calculated by means of 16 individual scans at 2 cm^{-1} resolution in the 4000–600 cm^{-1} interval with corrections for atmospheric water and carbon dioxide. The carbon and hydrogen content was determined by elemental analyzer (Elementar, Vario EL). Carboxyl content in the

TABLE I
Sample Designations of Various Formulations Prepared

Sample designation	Moles (PEGDA)	Crosslinking ratio (χ)/(10 ⁻²) ^a
PAA	–	0
XPAA-5	8.0×10^{-4}	1.1
XPAA-10	1.6×10^{-3}	2.3
XPAA-15	2.4×10^{-3}	3.4
XPAA-20	3.2×10^{-3}	4.6

^a Moles of AAc: 6.0×10^{-2} .

polymer was determined chemically. For this purpose, a known amount (~ 0.5 g) of the dry polymer was swelled in excess water. Thereafter, the solution was titrated against previously standardized NaOH, in the presence of phenolphthalein as indicator. The accessible carboxyl-content was then calculated using the following equation:

$$\text{Carboxyl content} = \frac{(V_1 - V_2) \times N_1}{W \times 1000}$$

where V_1 and V_2 are the volume (mL) of NaOH consumed by polymer and blank, respectively, N_1 is the normality of NaOH, and W is the mass (g) of the polymer used.¹⁹

Thermal characterization

The thermal behavior of the polymer was investigated using Perkin–Elmer Diamond SDTA under N_2 atmosphere (200 mL/min) in the temperature range of 50–600°C. A heating rate of 10°C/min and sample mass of 10 ± 0.5 mg was used for this purpose. The deswelling behavior of the swollen hydrogel was studied isothermally using the SDTA, for which 10 ± 0.5 mg of the equilibrated swollen hydrogel was placed in ceramic crucibles at three different temperatures (30, 40, and 50°C) under flowing nitrogen atmosphere (200 mL/min). The mass loss profile was monitored till no further decrease in mass was observable.

Swelling ratio

Because all the chelation experiments were performed in aqueous medium, the swelling behavior of all the formulation was studied over the entire pH range. For this purpose, weighed amounts of dried hydrogels were dipped in distilled water of pH varying between 2 and 10, which was adjusted by adding requisite amounts of acid or alkali. The pH measurements were made with Labindia pH analyzer equipped with glass electrode (Toshniwal, India) and calibrated with Titrisol buffers. At suitable time intervals, the swollen gels were lifted, patted dry, and weighed. The swelling studies were performed till the equilibrium swelling was achieved. The swelling ratio (SR) was calculated as per the following equation²⁰:

$$\text{SR}\% = \left(\frac{W_s - W_d}{W_d} \right) \times 100\%$$

where W_s is the weight of the swollen polymer and W_d is the initial weight of the dry polymer. The kinetics of water uptake was also investigated for all the prepared formulations at a pH of 5.

Analytical characterization

The total concentration of metal ions such as Ni^{2+} , Cu^{2+} , Pb^{2+} , Cr^{6+} and Ca^{2+} in water, both before and after chelation, was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin–Elmer Optima 2100) operated using WINLAB 32 software.

Analytical procedure

Batch equilibration technique was used to determine the sorption capacity of the sorbent and optimum sorption conditions like pH. The chelating hydrogel was equilibrated with a known volume of metal ion solution. Post-equilibration, the hydrogel was filtered and the metal concentration in the filtrate was quantified. The amount of metal ions sorbed on the hydrogel was determined by the equation:

$$N_f = \frac{(X - Y)}{Z}$$

where X is the initial amount of metal ion (mg), Y the amount of metal ions in the supernatant (mg), N_f the amount of metal ion adsorbed (mg/g), and Z the amount of chelating hydrogel (g).

Optimum pH of metal ion uptake

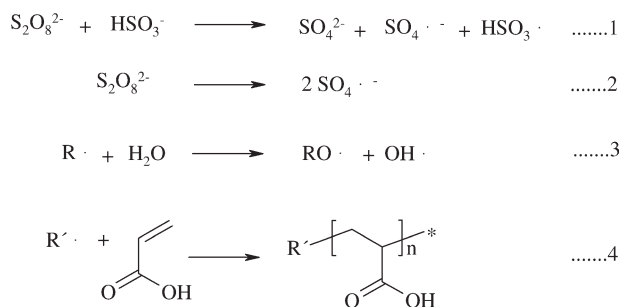
Optimum pH of metal ion uptake was determined by batch equilibration technique. Excess metal ion solution (50 mL and 100 $\mu\text{g}/\text{mL}$) was shaken with 50 mg of dried hydrogel for 2 h. The pH of the solution was adjusted before equilibration with buffer solution. The hydrogel was filtered off, and the amount of metal ion remaining in the filtrate was determined. The sorption experiments were carried out in triplicate to determine the precision of the method.

Adsorption isotherms

The adsorption isotherm studies were carried out by shaking 50 mg of hydrogel in the presence of different concentration of metal ion solution of Ni^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{6+} at 30°C for 24 h. The solution was then filtered, and the concentration of the metal in the filtrate was determined.

Total sorption capacity

Total sorption capacity of the hydrogel was determined by shaking an excess of metal ion solution (100 mL and 100 $\mu\text{g}/\text{mL}$) with 50 mg hydrogel for 24 h at optimum pH at 30°C in a mechanical shaker to ensure complete equilibration. The hydrogel was



Scheme 2 Reaction mechanism of persulphate-bisulphite redox initiation.

filtered off, and the concentration of metal ion in the filtrate was determined.

Recovery and hydrogel stability

For establishing the stability of the hydrogel, 50 mg of the hydrogel was stirred with 100 mL of 50 $\mu\text{g}/\text{mL}$ solution of 24 h at 30°C. Post-equilibrium, the sorbed metal was eluted with 20 mL of 1N HCl for 4 h to ensure complete regeneration. The regenerated hydrogel was again placed in 100 mL of 50 $\mu\text{g}/\text{mL}$ solution and eluted with 1N HCl as described previously. This adsorption-desorption cycle was repeated for 10 times, and the metal content in the filtrate and eluent was determined to establish the stability of the hydrogel.

Effect of interfering ions

The effect of a representative interfering ion (Ca^{2+}) on the sorption behavior of Pb^{2+} was investigated at its optimum pH. For this purpose, 50 mg of the dried hydrogel was shaken with different metal ion solution in which the concentration of Pb^{2+} was maintained at 100 $\mu\text{g}/\text{mL}$, and the concentration of Ca^{2+} was increased from 10 $\mu\text{g}/\text{mL}$ to as high as 200 $\mu\text{g}/\text{mL}$. The pH of the solution was maintained at the optimum pH of 5.

RESULTS AND DISCUSSION

Crosslinked polyacrylic acid was prepared by redox-initiated polymerization of acrylic acid in the presence of polyethylene glycol diacrylate as the crosslinker. The synthesized polymer was characterized and evaluated as a sorbent for the removal of toxic metal ions (Ni^{2+} , Cu^{2+} , Pb^{2+} , and Cr^{6+}) from aqueous solutions.

Reaction mechanism

The mechanism of redox initiation due to the combined action of persulphate and metabisulphite has been well reported in the literature²¹ and is pre-

sented in Scheme 2. Reaction (1) is expected to be the most predominant radical producing reaction; however, at higher temperatures, thermal decomposition of persulfate ion may lead to the generation of sulfate radical ions as shown in eq. (2). Reaction (3) [where R represents any of the radicals produced in reaction (1)] is again a likely contributor of radicals due to the presence of a large quantity of water present in the system. Each of these radical/radical ion species (R') can subsequently lead to the initiation of the polymerization reaction as per reaction (1) and form the end group in the resulting macromolecule.

Structural characterization

The carbon, hydrogen, and oxygen contents in the polymer as obtained by elemental analysis are presented in Table II. It can be seen that the results compare well with the theoretical values, the slight difference being attributed to hydration of the polymer because of its hygroscopic nature. The carboxyl content of all the formulations as determined by titration with alkali was found to be 1.35–1.45 meq/g (~ 54.5 –58 mg of NaOH/g), which is far lower than the expected value of 1.38×10^{-2} eq/g (~ 555.5 mg of NaOH/g) assuming complete neutralization. This can be attributed to the fact that interaction with base results in neutralization of only a fraction of the carboxylic acid groups due to extensive hydrogen bonding between carboxyl groups of neighboring polymer chains.²² The FTIR spectra of PEG, PEGDA, and XPAA-10 are presented in Figure 1. PEG exhibited characteristic peaks at 3463 cm^{-1} ($-\text{OH}$ stretch), 2917 cm^{-1} (alkyl $-\text{CH}$ stretch), and 1099 cm^{-1} for the ether ($-\text{C}-\text{O}-\text{C}$) group (Fig. 1). Whereas, in the spectrum of the synthesized PEGDA, no absorption was observed in the range of 3200–3600 cm^{-1} (characteristic of $-\text{OH}$ stretch), which indicated the conversion of the hydroxyl groups to ester. Another characteristic peak was observed at 1199 cm^{-1} resulting from the ester linkage and at 1721 cm^{-1} due to $\text{C}=\text{O}$ stretching. The FTIR spectra of XPAA-10 exhibited characteristic peaks at 1704 cm^{-1} ($\text{C}=\text{O}$ stretching band) and a broad absorption in the hydroxyl region ~ 3400 cm^{-1} due to the presence of COOH groups.

TABLE II
Result of Elemental Analysis of Formulations

Sample name	Experimental (%)			Calculated (%)		
	C	H	O	C	H	O
PAA	49.51	5.61	44.88	50.01	5.55	44.44
XPAA5	49.91	5.48	44.61	50.01	5.55	44.44
XPAA10	49.89	5.58	44.83	50.01	5.55	44.44
XPAA20	49.93	5.58	44.49	50.01	5.55	44.44

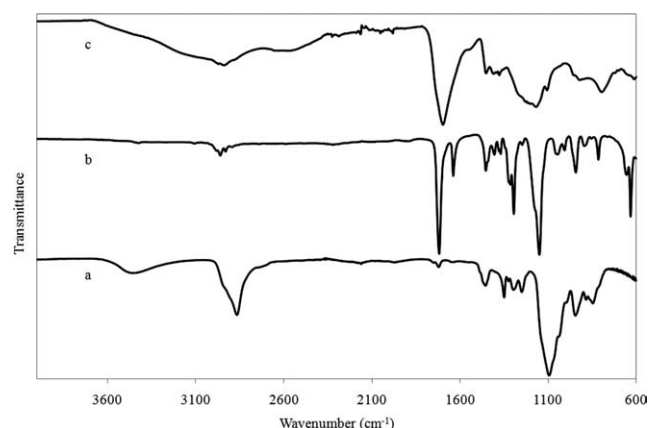


Figure 1 FTIR spectra (a) PEG 200, (b) PEGDA, and (c) XPAA-10.

Thermal characterization

The thermal behavior of the samples was investigated, and the thermogravimetric traces of the formulations prepared are presented in Figure 2. Double-step decomposition was observed in all samples, the first loss being the loss of water molecules from adjacent carboxylic moieties to form anhydride and the second step being the loss of CO_2 , which coincides with the decomposition of the main chain.²³ The thermal stability was evaluated by comparing the T_i (initial temperature of degradation), T_{\max} (temperature of maximum rate of weight loss), T_f (final temperature of degradation), and char yield at 600°C , which are presented in Table III. The results reveal that crosslinking does not lead to any significant change in the thermal degradation behavior. However, crosslinking resulted in an increase in the char content, which was found to be directly proportional to the degree of crosslinking.

Swelling studies

Linear PAA is completely soluble in common solvents such as water, methanol, and DMSO. This in-

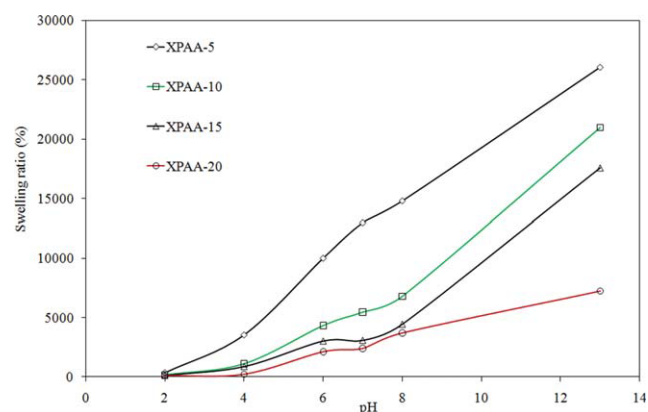


Figure 2 Effect of pH on the swelling behavior of the hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Characteristic Decomposition Temperatures of Formulations

Sample	T_i ($^\circ\text{C}$)	T_{\max} ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	% Weight loss	% Char yield at 600°C
PAA	256	292	338	39	9.8
	355	400	501	48	
XPAA-10	251	284	317	38	12.1
	317	418	559	48	
XPAA-15	251	283	318	39	14.3
	318	417	549	45	
XPAA-20	256	276	305	35	16.6
	310	420	550	47	

herent solubility of PAA in water limits its ability to be used for metal removal from aqueous solutions. As expected, crosslinking of PAA with PEGDA results in its insolubility in all solvents; however, the extent of swelling depends on the medium and pH. The increase in the SR of the formulations in water as a function of pH is presented in Figure 3. As can be seen, the SR increases with the increase in pH and varies inversely with the crosslinking ratio. The $\text{p}K_a$ value of poly(acrylic acid) has been reported 4.28; therefore, at lower pH, PAA chains exist in the collapsed state, thus reducing the SR. As the pH increases, the polymeric network gets charged due to deprotonation of carboxylic protons, which set up repulsive forces between the adjacent groups. This results in an expansion of the polymer chain conformation, thereby leading to the observed rapid increase in SR.

The kinetics of water uptake for the hydrogels has been studied at a pH of 4. The increase in mass due to sorption of water as a function of time has been presented in Figure 4. It can be seen that rapid swelling takes place initially which levels off subsequently. Highly crosslinked samples (crosslinking ratio $> 2.3 \times 10^{-2}$) reached equilibrium within 5 h

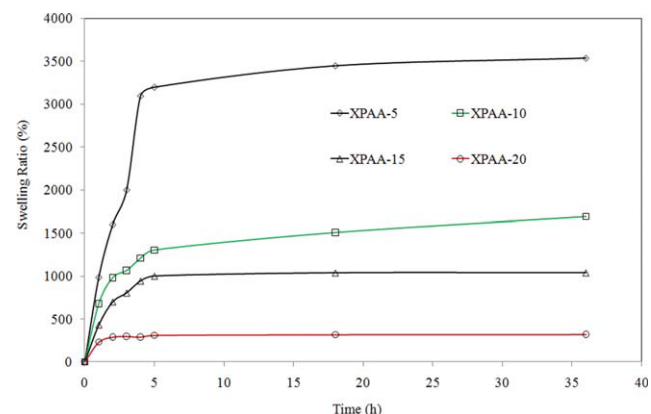


Figure 3 Kinetics of water uptake for different formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

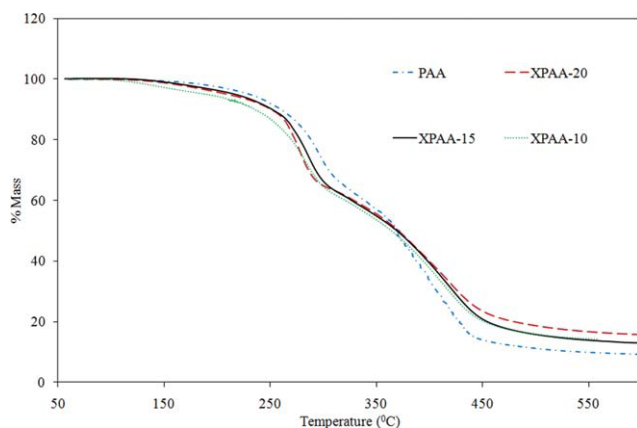


Figure 4 TG traces of formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of immersion, while samples with lower degree of crosslinking (crosslinking ratio $< 2.3 \times 10^{-2}$) require much longer time periods, that is, 18–19 h to reach $>95\%$ swelling. However, when the swelling investigations are performed at higher pH, the water absorption occurred instantaneously, and the samples reached equilibrium within 5 min of immersion. The deswelling behavior of the gels was investigated under isothermal conditions under flowing nitrogen atmosphere, and the results are presented in Figure 5. It can be seen that the release of water from the gel is strongly dependent on the temperature and at high temperatures (50°C), the gel becomes completely dry within 50 min of exposure to flowing nitrogen gas.

Sorption of metal ions as a function of pH

To investigate the effect of crosslinking ratio on the sorption of metal ions, 50 mg of the dried sample was dipped in 50 mL of aqueous solution containing

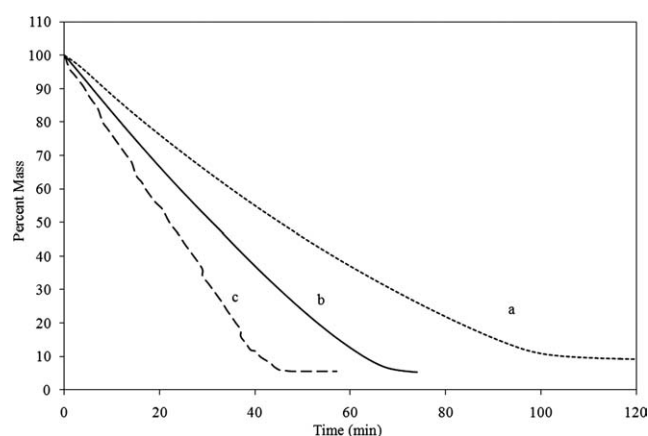


Figure 5 Isothermal TG traces indicating deswelling of hydrogel (a) 30°C , (b) 40°C , and (c) 50°C .

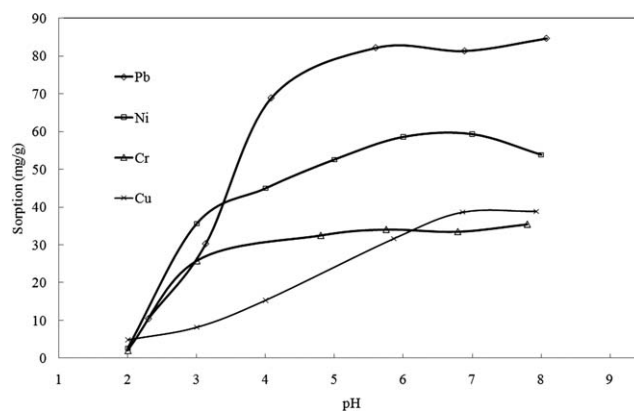


Figure 6 Effect of pH on metal sorption.

$100 \mu\text{g/mL}$ of a representative toxic metal ion (Pb^{2+}) at a pH of 5. The studies revealed that with the increase in crosslinking ratio, the sorption of metal decreases from 83.2 mg/g (XPAA-5) to 81.2 mg/g , 75.5 mg/g and 70.2 mg/g for XPAA-10, XPAA-15, and XPAA-20, respectively.

Being a surface phenomenon, all sorption processes are limited by the number of chelating sites available on the surface. Because of the increased hindrance offered by the network resulting from increased level of crosslinking, the number of surface sites decreases and so does the sorption capacity. However, when we compare the number of such sites with other sorbents, which are not hydrogels, this capacity is much higher. In hydrogels, owing to their hydrophilic nature, metal ions can enter the polymeric network easily and, hence, exhibit a higher extent of chelation. The only disadvantage of using hydrogel for the removal of metal ions is their inferior mechanical strength, which can be improved by crosslinking. Although XPAA-5 exhibited highest sorption capacity, its mechanical strength was extremely low, which disintegrated during handling. All further sorption investigations were performed on XPAA-10, as it was mechanically stable and maintained its integrity over the entire pH range.

Figure 6 shows the effect of pH on percentage sorption of different metal ions on XPAA-10. A decrease in the pH of the solution was observed during the sorption process, which could be attributed to the release of protons from the sorbent during equilibration. A significant increase in the sorption was observed as the pH of the solution was raised from 2 to 4 for all the metals under investigation. This can be related to the ionization and conformational behavior of the poly(acrylic acid). For the metal ions under investigation, we restricted our region of interest to $\text{pH} < 8$, because all the metal ions formed insoluble metal hydroxides at higher pH, particularly $\text{pH} > 8$. In general, the extent of

TABLE IV
Sorption Capacity of the Chelating Hydrogels at Optimum pH

Metal	Optimum pH	Loading capacity of XPAA10 (mg/g)	Loading capacity of XPAA10 (mmol/g)
Copper	5–6	43.1	0.67
Nickel	5–6	58.2	0.98
Lead	5–6	81.2	0.39
Chromium	5–6	41.1	0.78

sorption of metal ions increases with increase in pH, reaching a limiting value in each instance.

Total sorption capacity

Sorption capacity is an important factor for determining the amount of sorbent required for complete removal of a specific metal ion from the solution. To determine the total sorption capacity of the hydrogel, a known amount of the hydrogel was immersed in the metal solution at optimum pH at a temperature of 30°C. The mixture was stirred for 24 h followed by filtration, and the metal ion concentration in the filtrate was determined by ICP-OES. From the carboxyl content determination, the hydrogel is expected to have a sorption capacity of the order of 0.7 meq/g on the basis of monovalent–divalent exchange process. The experimental loading capacity of the hydrogel was found to be in the same range (Table IV). XPAA was observed to exhibit the highest sorption capacity for Pb²⁺, followed by Ni²⁺, Cu²⁺ and Fe²⁺. The exceptional chelating ability, especially for Pb²⁺, can be explained on the basis of the high-stability constant of the lead complex with carboxylic acids in the entire transition metal series.²⁴ However, this sorption capacity is much lesser compared to the theoretical value (6.8 meq/g), expected based on the number of carboxylic acid groups actually present in the polymer chain, which can again be attributed to the hindrance offered by

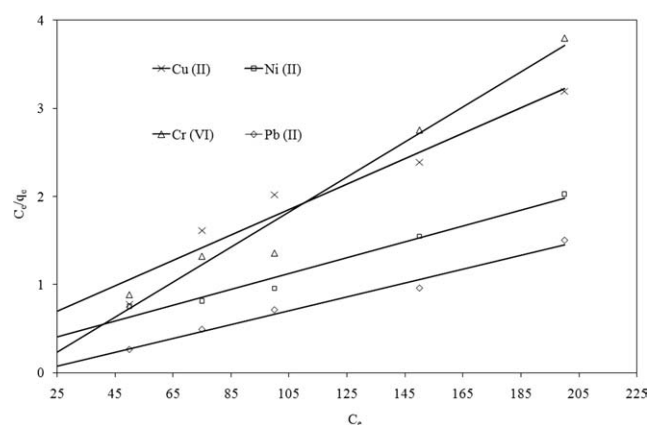


Figure 7 Langmuir isotherms for adsorption of metals.

TABLE V
Langmuir Coefficients for Metals

Metal	Langmuir equation	K	b	R ²
Cu	$C_e/q_e = 0.33 + 0.01 C_e$	0.043	68.96	0.94
Ni	$C_e/q_e = 0.18 + 0.009 C_e$	0.049	111.11	0.97
Pb	$C_e/q_e = 0.25 + 0.01 C_e$	0.040	99.00	0.97
Cr	$C_e/q_e = 0.47 + 0.02 C_e$	0.041	50.00	0.97

the network to the metal complexation process and also to the hydrogen bonding between the different carboxylic groups. In comparison with other hydrogels, which have been studied for their metal uptake capacity, the crosslinked PAA prepared in the present study exhibits a sorption capacity similar to that reported by other copolymers/blends. In this context, macroporous poly [acrylamide/*N*-vinylpyrrolidone/3-(2-hydroxyethylcarbamoyl) acrylic acid]¹³ has been reported to adsorb 46 mg/g of Cu²⁺ and 66 mg/g of Ni²⁺ under optimal conditions. In another study, PAA–PEG interpenetrating network has been reported to exhibit a sorption capacity of 102.34, 49.38 and 33.41 mg/g for Ni²⁺, Cr³⁺ and Cd²⁺ respectively.^{14,15}

Adsorption isotherm

The adsorption data for Cr⁶⁺, Ni²⁺, Cu²⁺, and Pb²⁺ metal ions were analyzed by a regression analysis to fit the Freundlich and Langmuir isotherm model. These data were plotted as the amount of metal ion sorbed on the hydrogel at equilibrium as a function of the metal concentration of the solution at equilibrium. The coefficients of these two models were computed using linear least square curve fitting.

Langmuir model was used to explain the observed sorption behavior. The equilibrium data were analyzed using the following linearized equation:

$$\frac{C_e}{q_e} = \frac{1}{kb} + \frac{C_e}{b}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and k and b are the Langmuir constants related to adsorption capacity and the energy of adsorption, respectively. The linear plot (Fig. 7) for the four metal ions reveals that the adsorption obeys the Langmuir model. The Langmuir constants were evaluated and have been reported in Table V.

The adsorption behavior was also fitted into the Freundlich model:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount of metal adsorbed (mg/g). A

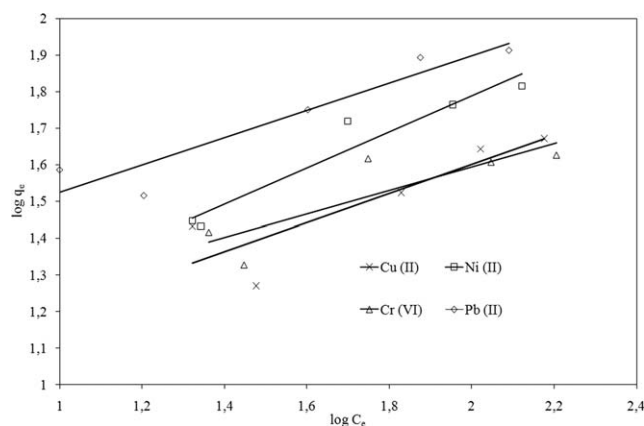


Figure 8 Freundlich isotherm for adsorption of metals.

linear plot (Fig. 8) of $\log q_e$ versus $\log C_e$ shows the applicability of the Freundlich model. The Freundlich constants k_f and n were calculated and are reported in Table VI. It can be seen that for all the metals under investigation, the value of coefficient n is greater than 1, which confirms positive sorption of metal.²⁵ Correlation indices (R^2) were determined to compare the two models, and our investigation revealed that the adsorption data fitted well into both the models.

Ion-exchange process

This study was undertaken to understand the multi-valent metal ion removal process by ion exchange with monovalent protons/sodium ions present in the hydrogel network. For this purpose, XPAA-10 sample was equilibrated in distilled water and then allowed to contract in solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ of varying molar concentrations at a pH of 5. The SR was monitored, and the results are presented in Figure 9. The investigation revealed that significant decrease in the SR of the hydrogel occurred as the ionic strength of the solution was increased. This can be attributed to the additional interaction between the negatively charged polymeric network with the positively charged cations, which do not allow the network to swell further thereby leading to the observed decrease in the SR.¹⁴ The greatest extent of deswelling was observed in the case of Pb^{2+} , followed by

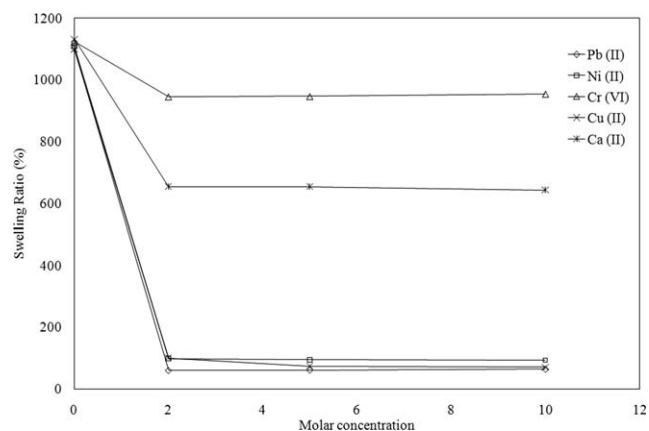


Figure 9 Effect of increasing ionic strength on the swelling ratio of hydrogel.

Cu^{2+} , Ni^{2+} , Ca^{2+} and $\text{Cr}_2\text{O}_7^{2-}$, which indicate the binding affinity of the polymer toward the metal ion species.

Transition metal ions like Pb^{2+} , Cu^{2+} , and Ni^{2+} have a stronger complex forming tendency with polyanions when compared with the alkaline earth metal ions like Ca^{2+} . The lower deswelling in the case of Cr^{6+} is due to the presence of a large fraction of the metal ion being present in the anionic form, as $\text{Cr}_2\text{O}_7^{2-}$. Because of the repulsion between the negative charge of the polymer and the oxoanion species, the contraction is limited.

Regeneration and hydrogel stability tests

To test the hydrogel stability, the hydrogel was subjected to several loading and elution cycles. Interestingly, the sorbent was found to be stable and could be used repeatedly for at least 10 cycles as shown in Figure 10. The metal sorbed on the hydrogel could be easily eluted with 1N HCl. The resin being a weakly acidic ion exchanger is expected to exhibit a high-regeneration ability. For all the metal ions under investigation, more than 97% recovery could be obtained at $\text{pH} < 2$. The acid basically increases the hydrogen ion concentration, which, in turn, protonates the carboxylic acid groups. This leads to a reduction in the ionic attraction between the anionic groups of carboxylate and the metal ions, thereby leading to the regeneration of the hydrogel.

Effect of interfering ions

The effect of a representative interfering ion (Ca^{2+}) on the sorption behavior of Pb^{2+} was investigated by batch equilibration technique. It was observed that even when the concentration of interfering alkali metal ion (Ca^{2+}) was increased from 10 to 200 $\mu\text{g}/\text{mL}$ in the presence of 100 $\mu\text{g}/\text{mL}$ Pb^{2+} , the sorption capacity for Pb^{2+} remained unaltered at 81–82

TABLE VI
Freundlich Coefficients for Metals

Metal	Freundlich equation	K	n	R^2
Cu	$\log q_e = 0.80 + 0.39 \log C_e$	6.42	2.51	0.75
Ni	$\log q_e = 0.80 + 0.49 \log C_e$	6.35	2.02	0.93
Pb	$\log q_e = 0.57 + 0.52 \log C_e$	14.12	2.68	0.89
Cr	$\log q_e = 0.950 + 0.32 \log C_e$	8.912	3.10	0.73

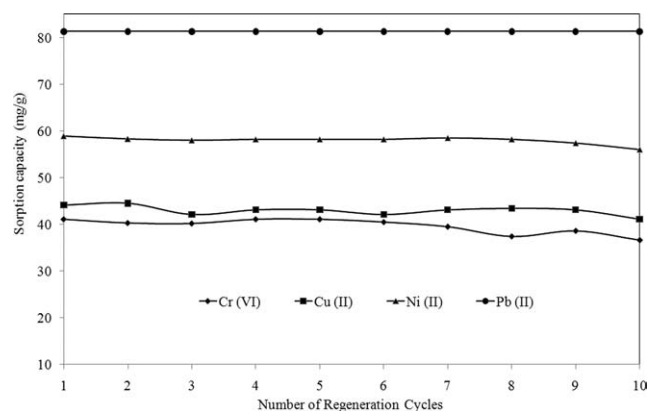


Figure 10 Effect of regeneration cycle on the sorption capacity of the chelating hydrogel.

mg/g. It can be concluded that due to the stronger interaction of hydrogel with Pb^{2+} ions, its complexation with Pb^{2+} is preferred even in the presence of Ca^{2+} . Because industrial effluents contain large amount of such interfering ions, this study confirms that the hydrogel can be used for the removal of Pb^{2+} for practical purposes.

CONCLUSIONS

This work describes the synthesis, characterization, and analytical evaluation of superabsorbent cross-linked PAA as a sorbent for the uptake of metal ions like Pb^{2+} , Ni^{2+} , Cu^{2+} , and Cr^{6+} from aqueous solutions. The synthesized hydrogel exhibits high-metal uptake, and the sorbed metal can be readily eluted by 1N HCl. A high recovery (>97%) was obtained for all the metal ions with 1N HCl as eluting agent. The metal uptake data was found to fit well into both Langmuir and Freundlich adsorption models. The crosslinked polymer was found to be stable over the entire pH range when compared with its linear analog, which is soluble in aqueous solutions. The hydrogel was stable and could be reused for at least 10 times without any loss in its metal chelation efficiency.

The authors are thankful to the Director, Centre for Fire, Explosive and Environment Safety for taking keen interest and for providing the laboratory facilities.

References

- Garg, B. S.; Sharma, R. K.; Bhojak, N.; Mittal, S. *Microchem J* 1999, 61, 94.
- Sauer, N. N.; Ehler, D. S.; Duran, B. L. *J Environ Eng ASCE* 2004, 130, 585.
- Goel, J.; Kadirvelu, K.; Rajagopal, C. *Adsorp Sci Technol* 2004, 22, 257.
- Ahn, C. K.; Park, D.; Woo, S. H.; Park, J. M. *J Hazard Mater* 2009, 164, 1130.
- Fu, F. L.; Chen, R. M.; Xiong, Y. *Sep Purif Technol* 2006, 52, 388.
- Lebrun, L.; Vallee, F.; Alexandre, B.; Nguyen, Q. T. *Desalination* 2007, 207, 9.
- Choo, K. H.; Han, S. C.; Choi, S. J.; Jung, J. H.; Chang, D.; Ahn, J. H.; Benjamin, M. M. *J Ind Eng Chem* 2007, 13, 163.
- Roy, P. K.; Rawat, A. S.; Choudhary, V.; Rai, P. K. *J Appl Polym Sci* 2004, 94, 1771.
- Roy, P. K.; Rawat, A. S.; Rai, P. K. *Talanta* 2003, 59, 239.
- Sharaf, M. A.; Arida, H. A.; Sayed, S. A.; Younis, A. A.; Farag, A. B. *J Appl Polym Sci* 2009, 113, 1335.
- Chauhan, G. S.; Guleria, L. K.; Mahajan, S. *Desalination* 2001, 141, 325.
- Chauhan, G. S.; Lal, H. *Desalination* 2003, 159, 131.
- Dadhaniya, P. V.; Patel, M. P.; Patel, R. G. *J Macromol Sci Part A: Pure Appl Chem* 2007, 44, 769.
- Bajpai, S. K.; Johnson, S. *React Funct Polym* 2005, 62, 271.
- Tang, Q. W.; Sun, X. M.; Li, Q. H.; Wu, J. H.; Lin, J. M. *Sci Technol Adv Mater* 2009, 10, 1.
- Xie, J. J.; Liu, X. R.; Liang, J. F.; Luo, Y. S. *J Appl Polym Sci* 2009, 112, 602.
- Pytlewski, L.; Krevitz, K. U. S. Pat. 4,349,380 (1982).
- Hernandez, R.; Lopez, D.; Mijangos, C. *J Appl Polym Sci* 2006, 102, 5789.
- Collins, E.; Bares, J.; Billmeyer, F. *Experiments in Polymer Science*, Vol.305; Wiley-Interscience: New York, 1973; p 365.
- Gupta, A.; Kumar, R.; Upadhyay, N. K.; Surekha, P.; Roy, P. K. *J Appl Polym Sci* 2009, 111, 1400.
- Ebdon, J. R.; Huckerby, T. N.; Hunter, T. C. *Polymer* 1994, 35, 250.
- Furukawa, M.; Farinato, R. S.; Kokufuta, E. *Colloid Polym Sci* 2008, 286, 1425.
- Burugapalli, K.; Bhatia, D.; Koul, V.; Choudhary, V. *J Appl Polym Sci* 2001, 82, 217.
- Bunting, J.-W.; Thong, K. M. *Can J Chem* 1970, 48, 1654.
- McKay, G.; Blair, H. S.; Gardner, J. R. *J Appl Polym Sci* 1982, 27, 3043.