Comparison of Rigid Divinylbenzene with Flexible 1,7-Octadiene Crosslinks in Acrylic Acid Resins—Effects on Kinetics of Swelling and Loading of Heavy Metal Ions from Water

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ABSTRACT: Acrylic acid–1,7-octadiene resin was synthesized in beaded form by a two-step process: suspension polymerization of ethylacrylate and 1,7-octadiene monomers, followed by hydrolysis using either 98% H_2SO_4 or 10 M NaOH. Acrylic acid–divinylbenzene resins were also synthesized by the same process for the purpose of comparing a rigid divinylbenzene with a flexible 1,7-octadiene crosslinkage in the acrylic acid resins. Swelling of the resins in distilled water shows that replacing divinylbenzenes with 1,7-octadiene makes the resin achieve greater swelling in a significantly shorter time. 1,7-Octadiene also allowed for an increase in crosslinkage to 20% compared to 4% in the case of divinylbenzene, without compromising the loading rates of toxic heavy metal ions like Pb^{2+}, Cu^{2+}, and Cr^{3+} from water samples. The acrylic acid–1,7-octadine resin was found useful for removal of the toxic heavy metal ions from wastewater samples. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41038.

INTRODUCTION

Water pollution due to toxic heavy metal ions and organic compounds is a serious problem worldwide. These pollutants are usually not biodegradable and tend to accumulate in the environment posing risks to human health.[1] Removal of these pollutants is required under new laws being enforced throughout the world. Several techniques are being developed for the removal of the pollutants, including adsorption, ion exchange, chemical precipitation, membrane filtration, and coagulation.[2] Among them, ion exchange techniques are the most common and effective due to high efficiency, high capacity, and re-usability of the resins after regeneration.[3] A variety of ion exchange resins have been investigated by various researchers for the removal of heavy metals from aqueous solutions.[4–7]

Synthesis of ethylacrylate–divinylbenzene (EA–DVB) copolymers in beaded form using a suspension copolymerization technique was reported before.[8] Hydrolysis converts ethylacrylate units into acrylic acid units in the copolymer. A comparative study of hydrolysis of the copolymer using alkali (NaOH) and acid (H_2SO_4) revealed that the acid hydrolysis can take place under milder conditions and imparts a higher ion-exchange capacity to the resin than alkali hydrolysis.[8,9] These resins were found useful for extraction of

pesticides[8] and heavy metals[9] from polluted water. However, the acid hydrolysis converted the copolymer into a bifunctional ion-exchange resin carrying —COOH and —SO_3H functional groups. It is desirable to synthesize a monofunctional resin carrying only —COOH groups that have higher selectivity toward heavy metal ions and are easier to regenerate than —SO_3H groups[10] Furthermore, replacing rigid divinylbenzene crosslinks in the copolymer with some flexible crosslinks (like an aliphatic chain) is also desirable to impart fast exchange of ions/reagents in the resin.

In this study, ethylacrylate–1,7-octadiene copolymer (EA–OD) beads were synthesized by suspension polymerization. The copolymer was then converted to a monofunctional resin carrying only —COOH groups by acid hydrolysis. Alkali hydrolysis was also carried out for comparison purposes. The use of 1,7-octadiene as the crosslinking agent not only eliminated —SO_3H groups during acid hydrolysis but can also potentially impart fast ion-exchange/adsorption kinetics to the resins. This is because of the fact that the aliphatic carbon chain in 1,7-octadiene is much more flexible than the rigid benzene ring of divinylbenzene. It was confirmed in this study. The new resin derived from acid hydrolysis of EA–OD copolymer beads was evaluated for the removal of trace levels of Cr, Pb, and Cu cations from wastewater samples.

EXPERIMENTAL

Chemicals and Apparatus

The chemicals used in this study were ethyl acrylate from Merck, 1,7-octadiene and benzoyl peroxide (97% purity, moistened with 25% H_2O) from Fluka, heptane from Fisher Scientific, and analytical grade 100 µg/mL stock standard solutions of Pb, Cu, and Cr from Merck. Double distilled deionized water was used for dilutions. pH adjustments were made with 0.1 M NaOH solution and monitored using a model 780 pH meter from Metrohm. An atomic absorption spectrometer Z-8000 (Hitachi, Japan) equipped with Zeeman background correction and hollow cathode lamps of Cu, Cr, and Pb as radiation sources was used for the estimation of Cu, Cr, and Pb.

Resin Synthesis

Synthesis and characterization procedures for EA–DVB copolymers have been reported earlier.[8,9] The same procedures were followed for the synthesis of EA-OD. The polymerization mixture was prepared by mixing ethyl acrylate and 1,7-octadiene in 8-to-2 molar ratio and diluted with *n*-heptane in a 6-to-4 volume ratio. Benzoylperoxide (1% by weight) was dissolved in the polymerization mixture. An aqueous phase was prepared by dissolving 1% by weight each of gum Arabic and gelatin in demineralized water. One part by volume of the polymerization mixture was poured into five parts of the aqueous phase in a jacketed reaction vessel at room temperature and stirred with a twin-blade turbine revolving at approximately 200 rpm. After 30 min, the temperature was gradually increased to 80°C in 30 min and maintained at 80°C for 20 h. Next, the copolymer beads were filtered out, washed with hot water, and then washed with acetone. The acetone washing was continued until the effluent showed no turbidity upon mixing with water. The washed copolymer beads were first air dried then oven-dried at 110°C for 24 h.
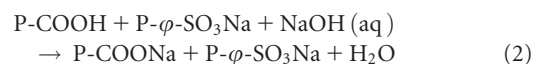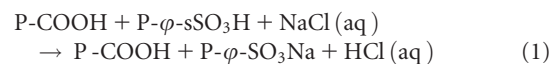
Conversion of the Copolymers to Cation-Exchange Resins

One part by weight of the dried copolymer was stirred with about 10 parts of either 10 M aqueous NaOH (alkaline hydrolysis) or 98% H_2SO_4 (acid hydrolysis) at 98°C for 2 h.[8,9] The treated copolymer was filtered, washed with demineralized water, followed by 2 M HCl, and finally with demineralized water till the effluent was neutral. In the case of acid hydrolysis, the washed resins were later refluxed with 1 M NaOH to convert any hydrides formed during sulfuric acid treatment to acid groups.[11]

Characterization of the Resins

The resin was dried in in an oven at 110°C for 24 h for density and FTIR spectroscopy. The density (d) was determined from their weight and volume using a measuring cylinder and a balance.[12] FTIR spectra of the dried copolymers and resins were recorded using a NICOLET 6700 FTIR spectrophotometer, in ATR mode using DTGS detector, 6 cm^{-1} resolution and 132 number of scans.

Strong and weak acid capacities, which are the same as the concentration of the —SO_3H and —COOH groups in the resins, were determined by the column method based on the amount of HCl produced and the amount of NaOH consumed, respectively, in the following reactions[13]:

$$P\text{-COOH} + P\text{-}\varphi\text{-sSO}_3H + NaCl\,(aq)$$
$$\rightarrow P\text{-COOH} + P\text{-}\varphi\text{-SO}_3Na + HCl\,(aq) \quad (1)$$

$$P\text{-COOH} + P\text{-}\varphi\text{-SO}_3Na + NaOH\,(aq)$$
$$\rightarrow P\text{-COONa} + P\text{-}\varphi\text{-SO}_3Na + H_2O \quad (2)$$

Swelling (S) of the dried resins in distilled water was determined on the basis of volume measurements using the following equation:

$$\%S = (V_t - V_o / V_o)100, \quad (3)$$

where V_o is the volume of the dried resin and V_t is the volume of the wet resin at time t. $T_{1/2}$ is the time calculated from the swelling curve of the resin at which the swelling is one half of the equilibrium value.

Diffusion of water into the polymeric matrix was calculated by the following equation[14]:

$$F = M_t / M_\infty = kt^n, \quad (4)$$

where M_t and M_∞ are the amount of solvent diffused into the polymer matrix at time t and at equilibrium, respectively. Based on this equation, a plot of $\ln(F)$ versus $\ln(t)$ yielded a straight line up to about a 60% increase in the resin volume due to water diffusion into the resin. The value of diffusional exponents was calculated from the slope of the graph.

Loading of Aqueous Pb^{2+}, Cu^{+2}, and Cr^{3+} Ions on the Resin

A batch-type equilibrium procedure was used for the study of the metal ion-exchange/retention capability of the resin. A 25 mg sample of the dried resin was stirred in a quartz flask with 25 mL of a mixture having a concentration in the range of 500–1500 µg/L of Pb^{2+}, Cu^{2+}, and Cr^{3+} metal ions and a pH in the range of 5–9 for a predetermined time at room temperature. The resin was filtered and the residual concentration of the metal ions in the solution was determined by atomic absorption spectroscopy (AAS). The percent (%) retention was calculated using the equation:

$$\% \text{ retention} = 100(C_i - C_f)/C_i, \quad (5)$$

where C_i and C_f are the initial and final concentrations, respectively, of the metal ions in the solution.

Loading of Pb^{2+}, Cu^{+2}, and Cr^{3+} Ions from Wastewater Samples on the Resin

Wastewater samples were collected from the Bara River of District Nowshera (Pakistan) in triplicate at three different locations (Akbarpura, Kurvi, and Banda Sheikh Ismail). Polyethylene bottles used for sampling were cleaned thoroughly with detergent and tap water followed by double deionized distilled water and rinsed with 1 mol/L HCl and finally with double distilled deionized water. Collected samples were filtered through 0.45 µm pore size membrane filters and acidified with 2% v/v HCl. The samples were analyzed by AAS before and after stirring with resin. The analytes were determined by applying a standard addition approach. One hundred milliliters of water was spiked with 500 ppb of each analyte (Cu, Pb, Cr). These samples were stirred with 0.25 g of the resin for about 35 min at pH 8. After stirring, the analytes in the solution were determined by AAS.
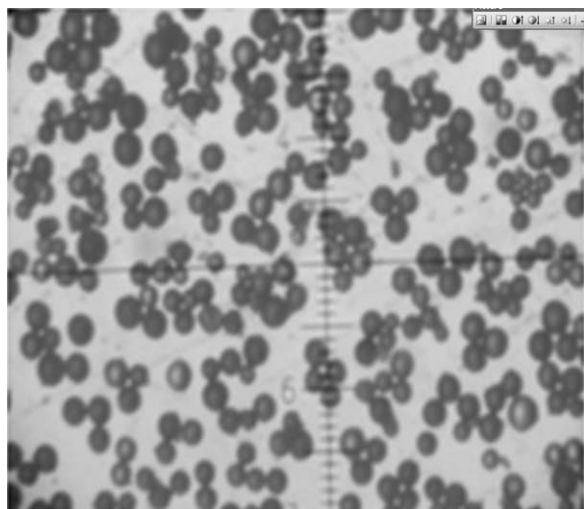
Figure 1. Image of resin derived by acid hydrolysis. One small division in the inserted scale is 30 μm.

RESULTS AND DISCUSSION

The EA–OD copolymer beads appeared semitransparent and elastic. They were strong enough to withstand osmotic shock when the medium was suddenly changed from strongly acidic (98% H_2SO_4) or strongly alkaline (10 M NaOH) to neutral (demineralized water) during washing after the hydrolysis reaction. The resin beads remained spherical with no cracks or any other damage when the resins were examined under an optical microscope, as shown in Figure 1. Although this is a gel-type resin, it is physically more stable and suitable for repeated uses because of its higher crosslinkage (20% in this case) than common gel-type resins having lower crosslinkage (usually <5%).

Reaction Scheme 1 illustrates the conversion of the monomers to copolymer and the conversion of the copolymer to the resin upon acid hydrolysis. The conversion of the copolymer to resin is also verified by FTIR spectra illustrated in Figure 2. In the FTIR spectra of the copolymer, the signal at 2800–3000 cm^{-1} assigned to C—H bond of the monomer and crosslinking agent is still present in the spectra of the resin. A strong peak in the spectra of the copolymer at 1650–1800 cm^{-1} with maximum at approximately 1730 cm^{-1}, which is assigned to C=O groups has shifted to 1530–1800 cm^{-1} with a maximum at

approximately 1680 cm^{-1} in case of the resin. The —COOEt groups of the copolymer have been transformed to —COOH groups in which the C=O absorption occurs at lower frequency. The presence of some carboxylate ions having asymmetric stretch near 1610–1550 cm^{-1} cannot be ruled out. Furthermore, some other C=O groups may also result under the sulfonation conditions detailed elsewhere.[13] Hydrogen bonding in the case of —COOH groups is also possible. These factors explain the broadening of the signal in the case of the resin. A broad absorption in the range of 2400–2800 cm^{-1} is a characteristic of O—H bond in the —COOH group. These observed changes in the spectra confirm the conversion of ester groups to acid groups during the hydrolysis. A broad absorption signal in the range of 3000–3600 cm^{-1} is due to moisture that is typically present in the resins.

Table I lists the basic characteristics of the resins derived from EA–OD and EA–DVB copolymers by acid hydrolysis and by alkali hydrolysis. It can be observed from Table I that acid hydrolysis imparts a higher concentration of —COOH groups to the resins than alkali hydrolysis under the same conditions. The calculated concentration of —COOH in poly(acrylic acid) is 13.89 meq/g. The maximum observed value for the resin synthesized in this study is approximately 83% of it, which is fairly close to the 80% acrylic acid monomer employed in the copolymerization reaction. The difference mentioned above can be explained by the following facts: "crosslinkage" in this study refers to the percentage of crosslinking monomer in the polymerization mixture which is usually a little higher than the percentage of crosslinking monomer actually incorporated in the copolymer.

The —SO$_3$H groups were observed in the case of acid hydrolysis of EA–DVB only. The acid hydrolysis reagent (98% H_2SO_4) is also a sulfonating agent for aromatic rings like those of divinylbenzene in this case. The sulfonation reaction introduces —SO$_3$H groups in the resins.[13] The absence of any aromatic ring in the case of EA–OD eliminated the formation of —SO$_3$H groups resulting in a monofunctional resin containing only —COOH groups.

The —COOH and —SO$_3$H groups make the resin hydrophilic which explains higher equilibrium swelling in water with the increase in the concentration of these groups in the resins.
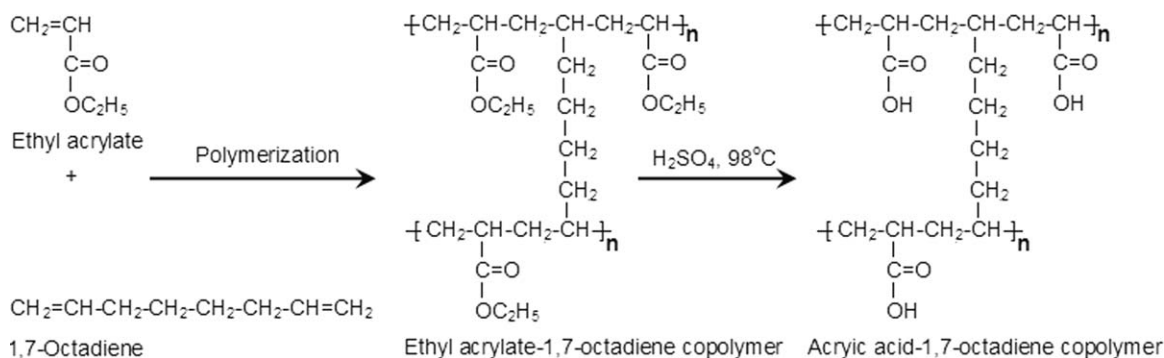
Scheme 1. Proposed mechanism of copolymer formation with 1,7-octadiene as a crosslinker and its subsequent acid hydrolysis to poly(acrylic acid-1,7-octadiene) resin.
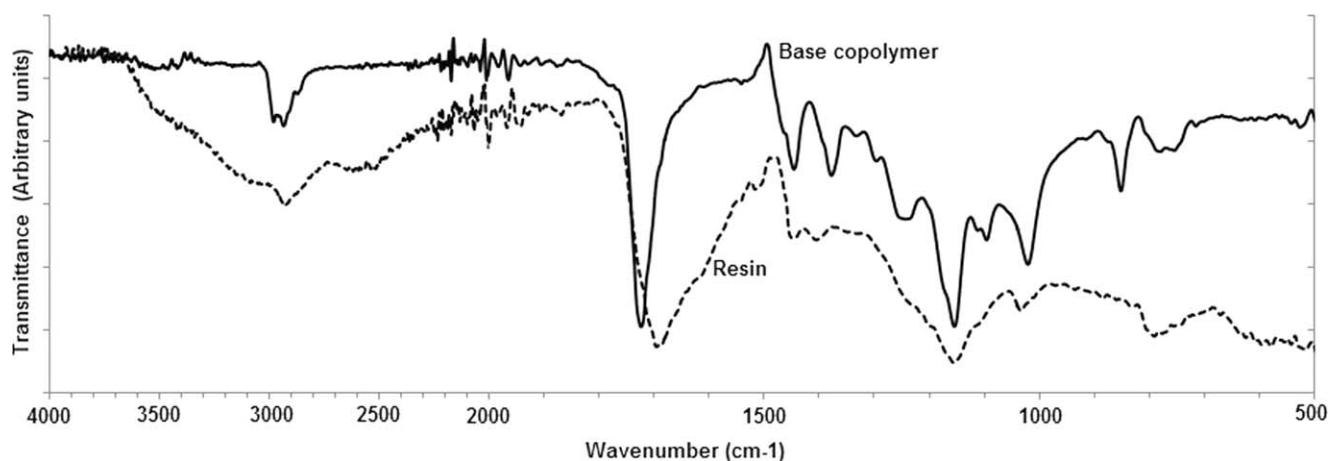
Figure 2. FTIR spectra of EA–OD copolymer and of the resin derived from it upon acid hydrolysis.

Resins derived from EA–OD swell significantly more than those derived from EA–DVB. This can be partly explained by the higher concentration of —COOH groups and partly by the flexible nature of 1,7-octadiene crosslinks in the former compared to rigid divinylbenzene crosslinks in the latter.

Figure 3 compares the kinetics of water absorption in the cases of four resins synthesized in this study. It can be observed from Figure 3 that acid hydrolysis of EA–OD results in the fastest swelling resin and acid hydrolysis of EA–DVB in the slowest swelling resin in this series. The resins derived by either acid or alkali hydrolysis of EA–OD have significantly faster swelling compared to those derived from EA–DVB. The same trend is reflected by the $T_{1/2}$ values listed in Table I.

The diffusion exponent (n) describes the type of diffusion mechanism—either Fickian or Anomalous/non-Fickian swelling. If the value of n is 0.45–0.50, the diffusion is Fickian and for the non-Fickian diffusion $0.50 < n < 1.0$. The value of the diffusion exponent (n) is greater than 0.50 in the case of all resins synthesized in this study. So, the diffusion is non-Fickian, where diffusion and relaxation are said to be isochronally effective.[15] It is explained as a consequence of slow relaxation of the polymer matrix.[16]

The results of the kinetics of water absorption are explained on the basis of the nature of the crosslinks in the resins. It can be observed from Figure 4 that rotation is possible on each of the four C—C bonds in the crosslink of EA–OD copolymer. It

Table I. Characteristics of the Resins Obtained by Hydrolysis of EA–OD and EA–DVB Copolymers

Base copolymer	EA-OD	EA-OD	EA-DVB	EA-DVB
Diluent	*n*-Heptane	*n*-Heptane	*n*-Heptane	*n*-Heptane
Dilutent/polymerization mixture	0.4	0.4	0.5	0.5
Crosslinkage (%)[a]	20	20	4	4
Appearance	Spherical	Spherical	Spherical	Spherical
Particle size (μm)	70-150	70-150	70-150	70-150
Hydrolysis agent	98% H_2SO_4	10M NaOH	10M NaOH	98% H_2SO_4
Color of resin	Dark brown	Off-white	Off-white	Dark brown
Density of resin (g/mL)	0.75	0.75	0.74	0.75
—COOH (meq/g)	11.56 ± 1.57	9.82 ± 0.27	7.55 ± 0.32	8.91 ± 0.24
—COOH (meq/mL)	3.05 ± 0.034	2.906 ± 0.153	1.91 ± 0.122	2.39 ± 0.028
—SO_3H (meq/g)	ND	ND	ND	0.51 ± 0.04
—SO_3H (meq/mL)	ND	ND	ND	0.13 ± 0.01
Equilibrium swelling in water (%)	254	209	142	182
Equilibrium water content (%)	85	80	66	65
$T_{1/2}$ (min)	1.16	1.80	2.90	6.13
Diffusional exponent[a] (n)	0.61	0.99	0.80	0.91

[a] Crosslinkage is the mole percent of 1,7-octadiene or divinylbenzenes in the monomers, ND means below detection limits, values after ± represent SD from the average values shown and the diffusional exponent is 'n' in eq. (4).
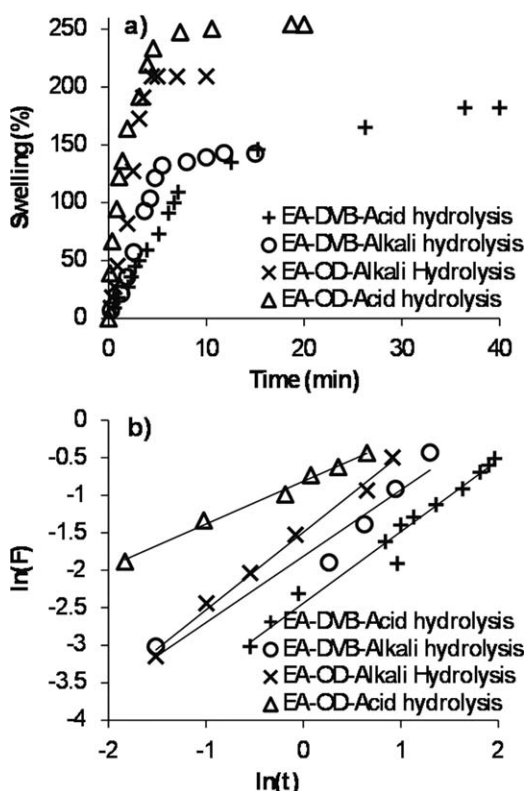
Figure 3. Swelling in distilled water versus time (a) and $\ln(F)$ versus $\ln(t)$ curves for the four resins synthesized in this study.

allows flexibility in the spaces between chains and crosslinks in the copolymer matrix that increases the diffusion of ions/reagents in and out of the copolymer matrix. The crosslinkage in the case of EA–DVB is relatively rigid which explains its decreased ability to swell and the relatively slow kinetics of swelling as observed in this study.

In the following, the kinetics of water absorption of the resins synthesized in this study are compared with some similar hydrogels reported as having fast swelling in water. Cryogels of crosslinked poly(isopropylacrylamide-co-acrylic acid) attained equilibrium swelling in about 1600 min,[17] which is a significantly longer time than the approximately 15 min in the case of hydrogels synthesized in this study. Similarly a novel porous hydrogel comprising poly(vinylalcohol) showed a high degree of swelling[18] but equilibrium required about five times longer than the hydrogels synthesized in this study.

Hydrogels are usually prepared in a rod shape. It usually takes a few hours to several days to reach swelling equilibrium.[19] The beads in this study have a larger surface area compared to the rod-shape hydrogels, which is one of the factors contributing to the faster swelling of the hydrogels. However, the water soluble monomer constituting the hydrogels cannot be synthesized in beaded form by oil-in-water suspension polymerization. Inverse suspension polymerization (water-in-oil suspension) has been attempted for this purpose, but often the copolymers thus obtained are not a good spherical shape.[20] In this study, the beaded hydrogel in a good spherical shape is synthesized in two steps: suspension polymerization of hydrophobic monomers to
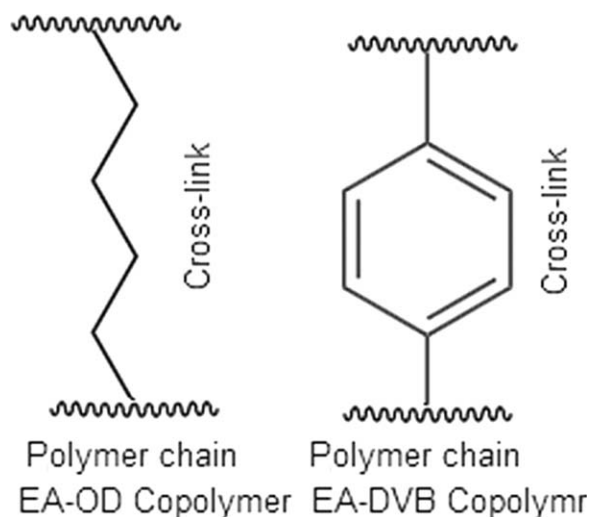

Figure 4. Flexible crosslink of the four carbon chain in the case of EA–OD copolymer and a rigid crosslink in the case of EA–DVB copolymer.

obtain a good spherical shape copolymer, and acid/alkali hydrolysis to convert the ester groups in the copolymer into the carboxylic acid groups of the hydrogels.

The resins synthesized can be used for removal/loading of heavy metal ions under neutral or alkaline conditions. Figure 5 and Table II show that the highest loading of the heavy metal ions can be achieved at pH 8. At pH < 8, a lower degree of ionization of —COOH groups and at pH > 8, precipitation of metal ions are responsible for the decrease in the % loading of the metal ions on the resin. Therefore, a pH of 8 was selected for the next study.

Figure 6 shows that the loading of the heavy metal ions on the resins increases with an increase in contact time. Almost complete loading can be achieved in 45 min contact time. Table III shows that almost complete loading can be achieved in 45 min from initial concentration varying from 500 to 1500 ppb. Another observation from Figure 6 is that the loading of the heavy metal ions is almost the same in the resin derived from
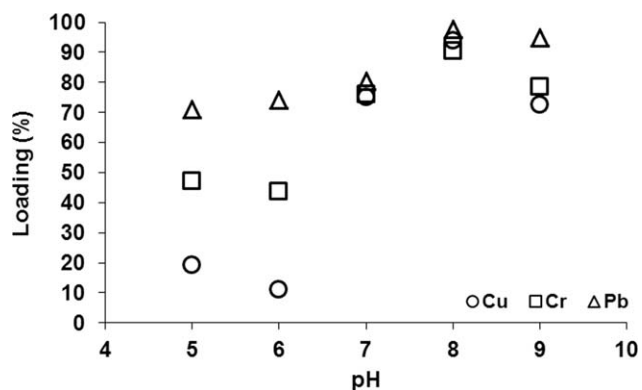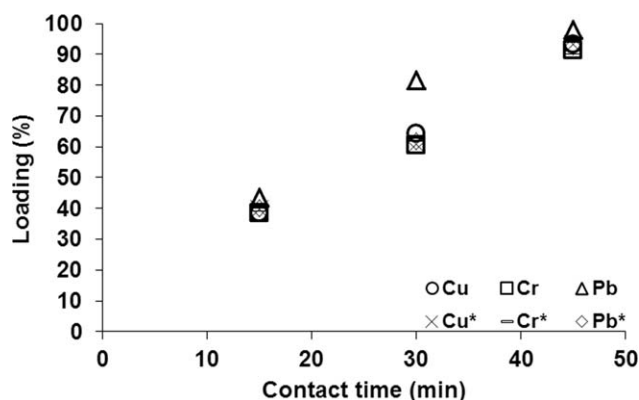

Figure 5. Loading of metal ions versus pH curves for resins obtained through acid hydrolysis of EA–OD copolymer. Contact time of the resin with the water samples was 60 min and initial concentration was 500 ppb in these experiments.

Table II. Residual Concentration of Heavy Metal Ions at Different pH Values from Water Samples Containing 500 ppb of the Metal Ions on Resin Obtained by Acid Hydrolysis of EA–OD in this Study

Analyte	pH 5	pH 6	pH 7	pH 8	pH 9
Cu	403.7 ± 14.4	444.4 ± 35.1	124.8 ± 0.6	30.1 ± 6.5	137.4 ± 12.8
Cr	264.4 ± 6.7	281.0 ± 19.2	119.5 ± 12.4	48.0 ± 5.7	106.8 ± 10.8
Pb	145.1 ± 7.4	126.3 ± 2.4	98.5 ± 3.9	10.1 ± 1.5	25.5 ± 5.5

Note: The values are in ppb ± SD.

Figure 6. Loading of metal ions versus contact time curves for resins obtained through acid hydrolysis of EA–OD copolymer (solid lines) and through acid hydrolysis of EA–DVB (dotted lines). pH was 8 and initial concentration was 500 ppb in these experiments.

EA–OD copolymer and in the resin derived from EA–DVB copolymer under the same experimental conditions. It should be kept in mind that EA–OD copolymer had a 20% crosslinkage while the EA–DVB copolymer had only 4% crosslinkage. Increase in crosslinkage usually makes the resins more stable and durable but at the cost of reduced ion-exchange kinetics. Results of this study show that the crosslinkage can be increased significantly without compromising the rate of loading of heavy metal ions on the resins, simply by replacing a rigid crosslink like that of divinylbenzenes with a flexible crosslink like that of 1,7-octadiene.

Finally, the resin obtained by acid hydrolysis of EA-OD was evaluated for removal of Cu, Pd, and Cr ions from a river water samples. The results are shown in Table IV. Concentrations of the heavy metals in the river water were comparable to those reported in literature.[21] It can be observed from Table IV that

Table III. Percent Loading of Heavy Metal Ions from Different initial Concentrations in Water Samples on Resin Obtained by Acid Hydrolysis of EA-OD in this Study

Initial concentration	500 ppb	1000 ppb	1500 ppb
Cu	94.0 (4.1)	88.8 (5.97%)	91.5 (5.92)
Cr	90.4 (3.1)	90.0 (3.29)	87.97 (4.72)
Pb	97.8 (5.9%)	95.8 (2.35)	97.7 (5.3%)

Note: Values are in %loading (RSD), contact time was 45 min and pH was 8 in these experiments.

85–96% of the metal contents were removed by the resin in this study. These results show that the acrylic acid-1,7-octadiene resin synthesized in this study has a potential for use in removal of toxic heavy metals from wastewater.

CONCLUSIONS

The following is concluded from this study:

1. Crosslinked monofunctional hydrogels/cation exchange resins carrying ─COOH as ion exchange groups can be synthesized in beaded form by a two-step process: suspension polymerization of ethylacrylate with a suitable crosslinking agent (1,7-octadiene in this study) followed by acid or alkaline hydrolysis.
2. Replacing rigid crosslinks in the copolymer (like that of divinylbenzenes) with flexible crosslinks (like that of 1,7-octadiene) makes the hydrogel/resin swelling significantly faster in water. Crosslinkage can be increased by this approach for the purpose of making the hydrogel/resin more stable and durable without compromising the rates of loading of toxic heavy metal ions from water samples.

Table IV. Loading of Heavy Metal Contents of Wastewater Samples from Bara River on Resin Obtained by Acid Hydrolysis of EA–OD in this Study

| Samples' location | Cu | | | | Pb | | | | Cr | | | |
	C_{SP}[a]	C_R	C_L	C_S	C_{SP}	C_R	C_L	C_S	C_{SP}	C_R	C_L	C_S
Akbar Pura	1310	69.5	740.5	810.0	960	19.2	440.8	460	670	26.8	143.2	170
Kurvi	1500	79	921	1000	1008	20.2	487.8	508	716	32.2	183.8	216
Banda	1640	88	1052	1140	1090	21.8	568.2	590	805	45.7	259.3	305

[a] The concentrations are in ppb. C_{SP} is the concentration in the sample after spiking with 500 ppb, C_R is the residual concentration in solution after loading, C_L is the concentration loaded on resin, and C_S is the concentration in the initial sample. RSDs were $\leq 6.0\%$ in all the cases.

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