

Study on the Synthesis of a Macroporous Ethylacrylate-Divinylbenzene Copolymer, Its Conversion into a Bi-Functional Cation Exchange Resin and, Applications for Extraction of Toxic Heavy Metals from Wastewater

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ABSTRACT: Macroporous ethylacrylate-divinylbenzene copolymers were synthesized by suspension polymerization using diethyl phthalate and *n*-heptane as diluent. A hydrolysis study revealed that conversion of esters into carboxylic acid groups was dependent on three factors: (1) crosslinkage: increases with a decrease in crosslinkage, (2) reagent: sulfuric acid > aqueous NaOH > NaOH in a 1 : 1 water to ethylene glycol, and (3) pore volume (PV): highest when PV was $\sim 0.7 \text{ mL g}^{-1}$. Sulfuric acid hydrolyzed ester to $-\text{COOH}$ and introduced $-\text{SO}_3\text{H}$ on phenyl rings, thus producing a bi-functional resin. The functional groups were verified by IR spectroscopy and quantified by acid–base titration. The bi-functional resin's capacity for toxic heavy metals in water samples was 12.51, 10.43, 9.43, 13.21, and 11.12 mg g^{-1} for Cu, Cd, Ni, Pb, and Zn, respectively and the recoveries exceeded >95% in range of pH 2–8, showing that it is suitable for water purification. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2234–2243, 2013

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INTRODUCTION

Water pollution due to heavy metals is a serious problem worldwide because of their toxicity and widespread use. Heavy metals are common pollutants in industrial, municipal, and agricultural wastewaters. The most common heavy metals in the wastewaters are lead, copper, nickel, cadmium, zinc, mercury, arsenic, and chromium. These metals are not biodegradable and tend to accumulate in the environment posing significant risks to the public health.¹ Removal of these pollutants is mandated under new laws being enforced throughout the world.

A number of techniques, such as adsorption, ion exchange, chemical precipitation, membrane filtration, and coagulation are being employed to remove the heavy metals from wastewater.² Ion exchange techniques are the most common and effective for the removal of the metals from wastewater due to their high treatment capacity, high removal efficiency, and fast kinetics.³ Different types of ion exchange resins have been investigated by various researchers for the removal of heavy metals

from aqueous solutions.^{4–7} Ion exchange resins are insoluble in water and re-usable which makes them environmentally compatible and economical.

We have reported the synthesis of gel type (non-porous) copolymer beads of ethylacrylate-divinylbenzene using a suspension copolymerization technique⁸ and developed a method for converting the copolymer into a bi-functional ion-exchange resin carrying $-\text{COOH}$ and $-\text{SO}_3\text{H}$ functional groups. The resin appears suitable for extraction of toxic metals from water based on the ion-exchange and coordination complex formation capability of these functional groups. The pH dependent ionization of the functional groups/coordination complexes in such resins allow regeneration and re-use under suitable conditions. Pores, specifically macroporous porosity (pores of a permanent nature that do not disappear during drying), are desirable in the resin as they provide fast access of ions/reagents to the interior of the copolymer.⁹ The macroporous pores are developed due to phase separation between the copolymer and the diluent during the copolymer synthesis.^{10–14}

In this study, the synthesis has been extended to porous ethylacrylate-divinylbenzene copolymer beads. This was achieved by varying diluents and crosslinkage. Conversion of the copolymers into cation exchange resin was studied using different reagents. This study revealed copolymer with lower crosslinkage (10%) and optimum pore volume (PV) of 0.7 mL g^{-1} was converted into bi-functional resin with highest concentration of functional groups. The resin was tested for extraction of several toxic metals commonly found in wastewater and ground water. Excellent performance of the resin observed in this study for extraction of these metal ions shows that it has potential applications in wastewater treatment and in other related applications, such as concentrating metal ions from water samples.

EXPERIMENTAL

Reagents/Chemical

The reagents used for resin synthesis were: ethyl acrylate 99% from E. Merck, Germany, DVB (60% divinylbenzenes and the rest mostly ethylvinylbenzenes), gum Arabic, and gelatin from Panreac, Spain, benzoylperoxide (97% purity, moistened with 25% H_2O) from Fluka, Germany, *n*-heptane from Riedel-de-Haën, Germany, diethyl phthalate from BDH, Germany, acetone and sulfuric acid from E. Merck, Germany.

Specpure multi-element plasma standard solutions from Alfa Aesar, Massachusetts, were used as metal stock solutions of Cu, Cd, Ni, Pb, and Zn. Working solutions of the desired concentration were prepared by appropriate dilution of these stock solutions. All other chemicals/reagents used were of analytical grade from E. Merck, Germany.

Procedures for the synthesis of the copolymer, conversion of the copolymer to ion-exchange resins, and characterization of the copolymers and the resins were same as reported earlier for similar copolymers.^{8,9,15}

Synthesis of the Copolymers

The polymerization mixture was prepared by mixing monomers (ethyl acrylate and divinylbenzenes) and the diluents (diethyl phthalate or *n*-heptane) in a 1 : 1 ratio by volume and adding benzoylperoxide 1% (wt/vol). The aqueous phase was prepared by dissolving 1% by weight each of gum Arabic and gelatin in demineralized water. One part polymerization mixture was poured into five parts by volume of the aqueous phase in a jacketed reaction vessel and stirred with a twin-blade turbine at about 200 rpm at room temperature for half an hour. The temperature was raised to 80°C in 30 min and maintained at 80°C for 20 h. The copolymer beads were filtered and washed with hot water. Unreacted monomers and diluents were extracted with acetone.

Characterization of the Copolymers

The copolymer beads were dried in an oven at 110°C for 24 h, cooled to room temperature in a desiccator, and their density was determined on the basis of dry weight and volume of the beads. PV, surface area (SA), and pore size distribution in the dried copolymers were determined by the mercury penetration method using a Mercury Porosimeter "Autopore II 29220" from Micromeritics, Georgia. The attenuated total reflectance (ATR) spectra were recorded using a NICOLET 6700 ATR spectropho-

tometer. The dried polymer beads were allowed to swell in different organic solvents for 24 h. Excess solvent was removed by centrifugation and the solvent-swollen volume of the copolymer was measured. The swelling coefficient (SC) was calculated using the formula: $\text{SC} = (V_{\text{wet}} - V_{\text{dry}})100/V_{\text{dry}}$, where V_{wet} and V_{dry} are wet and dry volumes of the copolymer. The SCs in acetone (SC_a), benzene (SC_b), acetonitrile (SC_n), and methanol (SC_m) were measured.

Conversion of the Copolymers to Weak Acid Cation-Exchange Resins

One part by weight of the dried copolymer beads was stirred in 10 parts by volume of aqueous sodium hydroxide (NaOH) of 1M, 5M, 10M, or 10M NaOH solution in a 1 : 1 mixture of water and ethylene glycol at 98°C for 2 h. The resin beads were filtered and washed with demineralized water followed by 2M hydrochloric acid and finally by demineralized water till the effluent was free of acid.

Conversion of the Copolymers to Bi-Functional Cation-Exchange Resins

The dried copolymer beads were stirred in 98% sulfuric acid (H_2SO_4) in 1 : 7 (wt/vol) ratio at 98°C for 2 h. The mixture was then poured slowly along the inner side wall of a beaker while stirring into ice cold demineralized water in a volume about 20 times that of the resin slurry. The resin beads were filtered and washed with demineralized water till the effluent was free of acid. The beads were later refluxed with 1M NaOH to convert any hydrides formed during sulfuric acid treatment to acid groups.¹⁶ Again, the resin was washed with demineralized water followed with 2M hydrochloric acid and finally with excess demineralized water.

Characterization of the Resins

The SCs of the resins in H-form in water (SC_w) were calculated using the formula: $\text{SC}_w = (V_{\text{wetH}} - V_{\text{dryH}})100/V_{\text{dryH}}$, where V_{wetH} and V_{dryH} represent volumes of the resin in the wet and the dry state, respectively. The SC for the change from H-form to Na-form of the resin ($\text{SC}_{\text{H-Na}}$) was calculated by using the formula: $\text{SC}_{\text{H-Na}} = (V_{\text{wetNa}} - V_{\text{wetH}})100/V_{\text{wetH}}$, where V_{wetNa} and V_{wetH} represent wet volumes of the resin in Na-form and H-form, respectively.

The resin slurry was packed in a column and treated with an excess of 2M HCl to convert it to H-form, followed by washing with demineralized water till the effluent was neutral. About 2M NaCl, equal to about four resin bed volumes (RBV), was passed through the resin followed by demineralized water of about three RBV and, as a result, effluent of about seven RBV was collected. After that, about two RBV of 0.2M NaOH was passed through the same resin followed by about three RBV of demineralized water and the combined effluent of about five RBV was collected. The millimoles of hydrochloric acid in the first combined effluent, which were determined by acid–base titration, are equal to the millimoles of $-\text{SO}_3\text{H}$ groups in the resin. The millimoles of sodium hydroxide retained in the resin, which were determined by acid–base titration of the second combined effluent, are equal to the millimoles of $-\text{COOH}$ groups in the resin.

Table I. Comparison of Different Eluents (HNO₃ and HCl) for % Recoveries of Metals^a

Eluent	Eluent Concentration (mol L ⁻¹)	Cd	Cu	Ni	Pb	Zn
HCl	0.1	73	75	73	70	79
HNO ₃	0.1	68	70	69	67	73
HCl	0.5	85	84	88	83	86
HNO ₃	0.5	82	80	83	78	81
HCl	1.0	90	92	93	91	94
HNO ₃	1.0	85	85	87	87	89
HCl	2.0	101	100	101	99.9	101
HNO ₃	2.0	96	94	95	92	96

^aExperimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, 1 μg mL⁻¹, eluent = 5 mL, loading/elution rate = 7 mL min⁻¹, pH = 6.5.

Determination of Ion Exchange Capacity of the Resin for Various Heavy Metal Ions

An iCAP 6500 inductively coupled plasma-optical emission spectrometer (ICP-OES) from Thermo Fisher Scientific, UK was used for measurement of the metals. It is equipped with ITEVA (version 8) operating software for full control of all instrument functions and data handling, and a high performance solid state CID camera system having a RACID 86 detector containing a 512 × 512 array of charge injection devices (CID). A high precision peristaltic pump having 12 rollers and 4 channels with adjustable speed (0–125 rpm) is employed for sample introduction into the plasma. The pH measurements were made on a Metrohm 780 pH meter from Metrohm, Herisau, Switzerland. A solid phase extraction system from Supelco consisting of a 12 port manifold with a 210 W vacuum pump from Buchi Labor-technik V 700 was used for the extraction of metals.

Twenty-five milliliters of a 100 μg mL⁻¹ aqueous solution of each metal was stirred with 1.0 g of resin in H-form and left for 24 h to ensure complete equilibrium. The solution was decanted and the concentration of metals in the supernatant liquid was measured by ICP-OES and compared with the original concentration. The decrease in the concentration of elements was used to evaluate the capacity using the following equation: Capacity = (X – Y)/Z, where Z is the amount of resin, X is the initial amount of metal ion, Y the amount of metal ions in the supernatant.

Extraction and Recoveries of Metals from Water

A column procedure was used for the optimization of parameters and for the extraction of metals from water samples. For this purpose, the extraction system was set up by packing 1 g of air-dried resin into an empty 6-mL polypropylene solid phase extraction (SPE) tube with Teflon frits fixed at both ends of the tube. The tube was placed in a vacuum manifold assembly. The ion exchange column was filled with deionized water and left for 6 h before use to let it achieve equilibrium swelling. The column was conditioned by passing 10 mL of 2 mol L⁻¹ HCl through it, followed by washing with 10 mL of de-ionized water.

The extraction efficiency of the resin for selected metals was studied in a pH range of 2–10. A series of solutions, each hav-

ing 25 mL volume and concentration of 1 μg mL⁻¹ of each of the selected metals, were loaded on the resin at the rate of 7 mL min⁻¹. The pH of each solution was adjusted to the desired value (the pH was 6.5 if it is not mentioned otherwise). Solutions were passed through an ion exchange column packed with 0.2 g of resin, pre-adjusted to the same pH value. The metals sorbed on the resin were eluted with 5 mL of 2.0 mol L⁻¹ HCl at flow rate of 7 mL min⁻¹ (unless mentioned otherwise) and their concentration was determined by ICP-OES. Percentage recoveries were calculated to evaluate the extraction efficiency of the resin at different pH values. The obtained data reflected in Figure 5 shows that the percentage recoveries of almost all metals from pH 2 to 10 were >99% except for Pb. It was observed that at pH >8, Pb started to precipitate out of the solution. The removal of Pb due to precipitation accounts for the decrease in recovery observed in this study.

Hydrochloric acid and nitric acid were also investigated for desorption of metal ions retained on the resin. Better recoveries were obtained using hydrochloric acid. Concentration and volume of hydrochloric acid was also optimized, 5 mL of 2.0 mol L⁻¹ HCl was found to be adequate for desorption of all metals from the resin as shown in Tables I and II.

The flow rate for sample loading on the column and eluent flow rates for desorption of metals were examined separately keeping one constant and changing the other. The flow rates were studied in the range 1–10 mL min⁻¹ under the optimum conditions (pH, eluent, etc.). It was found that no significant

Table II. % Recoveries with Different Volumes of HCl as Eluent^a

Eluent volume (ml)	Cd	Cu	Ni	Pb	Zn
1	81	84	83	80	85
2	93	91	90	94	92
5	101	100	101	99.9	101
8	102	100	100	100	101

^aExperimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, 1 μg/mL, eluent = 2 mol L⁻¹ HCl, loading/elution rate = 7 mL min⁻¹, pH = 6.5.

Table III. Experimental Conditions and Characteristics of Ethyl Acrylate-Divinylbenzene Copolymers

Expt. no.	Diluent ^a	X (%)	d_b (g mL ⁻¹)	Pore volume (mL g ⁻¹)	Surface area (m ² g ⁻¹)	Swelling coefficients			
						SC _a %	SC _b %	SC _n %	SC _m %
1	DET	10	0.60	-	-	152	200	140	91
2	DET	20	0.56	0.0827	42	110	133	110	100
3	DET	30	0.46	0.4410	138	124	143	122	111
4	Hep	10	0.39	0.7259	92	262	256	246	200
5	Hep	20	0.27	1.2558	184	165	170	170	166
6	Hep.	30	0.25	1.3344	214	125	135	134	123

^aDET is diethyl phthalate, 'Hep' is *n*-heptane, 'X' is % crosslinkage calculated by using formula: $X = 0.6M_{DVB}/(M_{DVB} + M_{EA})$, where M_{DVB} is the moles of DVB (60% pure) and M_{EA} is the moles of ethyl acrylate in the polymerization mixture, ' d_b ' is density of the copolymer, 'SC_a', 'SC_b', 'SC_n', and 'SC_m' are swelling coefficients of the copolymers in acetone, benzene, acetonitrile and methanol, respectively.

change in percent recoveries of all selected metals was found at a range between 1 and 7 mL min⁻¹, but beyond that, a gradual decrease in percent recoveries was observed. The optimum flow rate was found to be 7 mL min⁻¹ for both sample loading and elution.

Industrial wastewater and ground-water samples were collected and filtered through a 0.45- μ m membrane filter and their pH values were noted. A portion of each sample was passed through a pre-conditioned column under optimized conditions. Extracted metals were eluted from the column with 1.0 mol L⁻¹ HCl and their concentrations were measured by ICP-OES. For percentage recoveries, water samples were spiked with a known concentration of selected metals and passed through the column under the same conditions, concentrations were measured with ICP-OES and recoveries were calculated.

RESULTS AND DISCUSSION

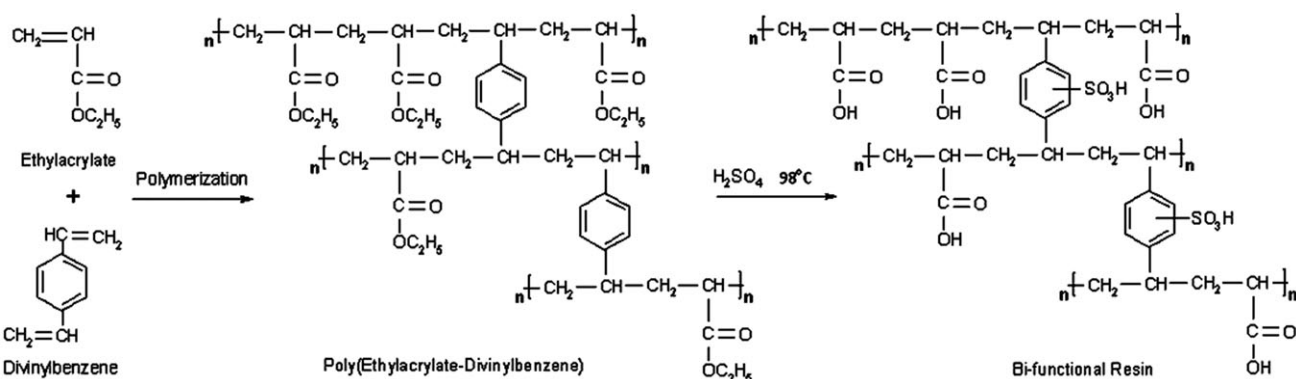
Three copolymers having 10%, 20%, and 30% crosslinkage were synthesized using diethyl phthalate as diluent. Similarly, three copolymers were synthesized using *n*-heptane as diluent. Characteristics of the six copolymers are shown in Table III. The reaction mechanism for the synthesis of the copolymers and their conversion into resin carrying -COOH and -SO₃H functional groups is illustrated in Scheme 1. Rounded beads without any apparent cracks or abnormalities were obtained in all the experiments as illustrated in Figure 1. The range of bead

diameters was 270–450 μ m with more than 70% particles falling in the 350–450 μ m range.

In our earlier study, a gel-type copolymer was synthesized by employing diethyl phthalate as diluent with 4% crosslinkage.⁸ The copolymer remained gel-type at 10% crosslinkage in Experiment 1 of this study, which is reflected by no PV in the dry state. However, some PV in the dry state was observed when the crosslinkage was increased to 20% (Experiment 2) and it increased even more with a further increase in crosslinkage or by employing *n*-heptane as diluent, showing that the copolymers of Experiments 2–6 were the macroreticular type. The porosity characteristics of the macroreticular type copolymers are discussed in the following sections.

The densities of the copolymers decreased and PV and SAs increased with an increase in crosslinkage and with the change of diluent from diethyl phthalate to *n*-heptane. Statistical analysis following the procedure described earlier^{17,18} and visual observation from Figure 2 shows that the PV can be calculated from the density of the copolymer using the formula: $PV = -4.0937d_b + 2.3481$, and the SA by using the formula: $SA = -182.36\ln(d_b) - 48.127$.

Pore size distributions in the copolymers from Experiments 2–6 are shown in Figure 3. Cumulative pore size distributions show a gradual shift toward larger pores with an increase in PV in



Scheme 1. Mechanism of copolymerization and functionalization of the copolymer.

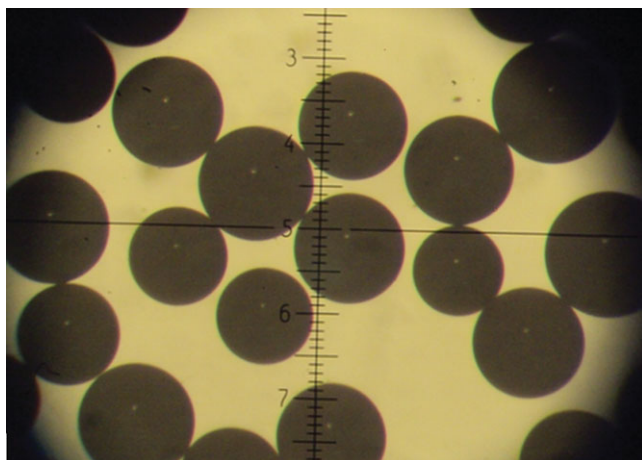


Figure 1. Photograph of a representative sample of copolymer beads obtained from experiment number 4 in Table III. One small division in the inserted scale is $30\ \mu\text{m}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

going from Experiment 2 to 6. PV density distributions, which are defined as the linear derivatives of the cumulative PV curves with respect to their pore diameters, show that the pores of all

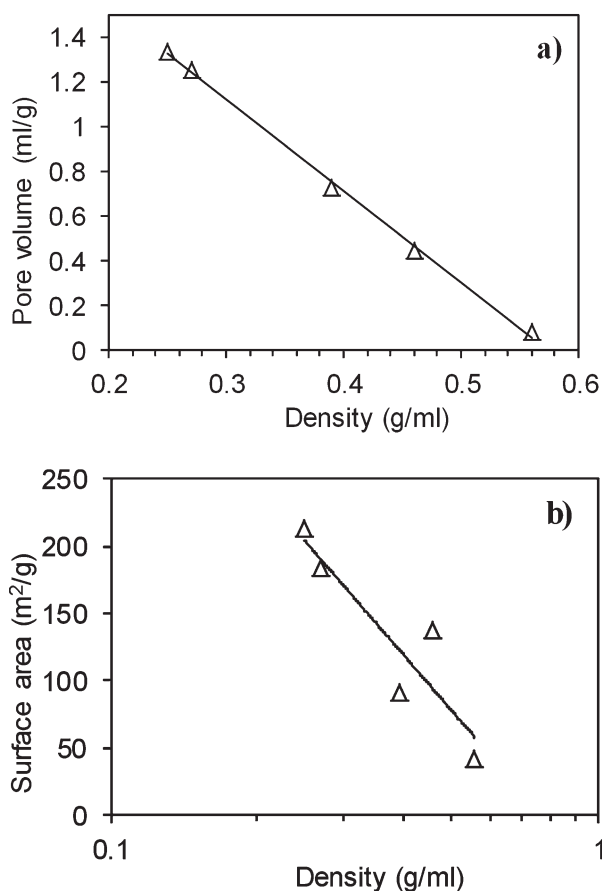


Figure 2. Density versus PV (a), and density versus SA (b), curves for ethyl acrylate-divinylbenzene copolymers synthesized in this study: Δ represents experimental points and continuous lines represent the best fit equations.

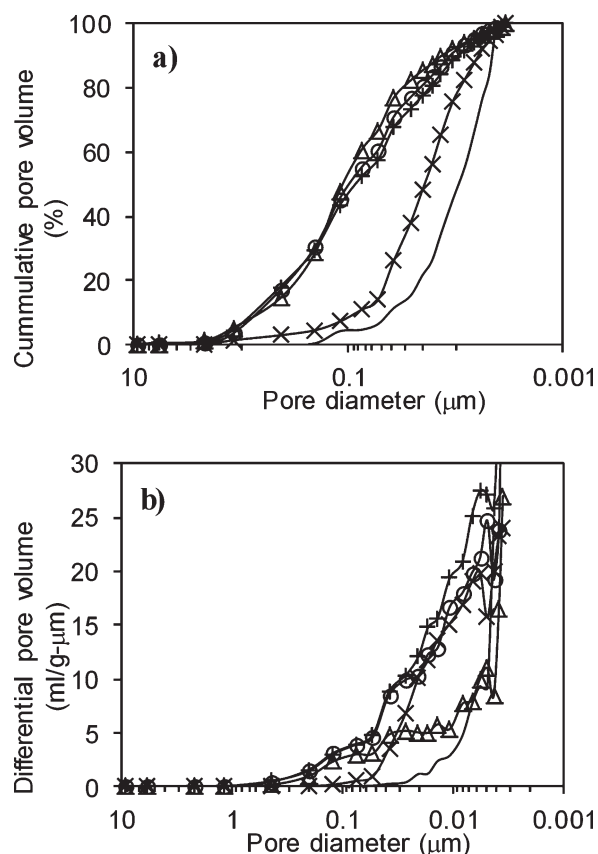


Figure 3. Pore size distributions of the copolymers synthesized in this study: (a) cumulative pore size distributions, and (b) PV density distributions: $-$ experiment 2, $- \times -$ experiment 3, $- \Delta -$ experiment 4, $- \circ -$ experiment 5 and $- + -$ experiment 6.

sizes increase with an increase in PV in going from Experiment 2–6 with the exception of Experiment 4. Earlier studies on related porous copolymers conclude that pores of all sizes increase with an increase in PV when crosslinkage is $>15\%$.^{15,18} The exception to this general trend in this study, i.e., the copolymer from Experiment 4, had lower crosslinkage (10%) and it shows a significantly lower contribution from pores having diameters $<0.03\ \mu\text{m}$ toward the overall porosity. Apparently a significant portion of pores having a diameter $<0.03\ \mu\text{m}$ collapsed during drying, due to low mechanical strength when the crosslinkage was low (10% in this case).

With *n*-heptane as diluent, SCs of the copolymers in different organic solvents decreased with an increase in crosslinkage as shown in Table III. The copolymers absorb the solvents and swell due to a strong affinity between the copolymer and the solvent. However, the swelling stops at a certain point, due to the stretch force at the crosslinkage points within the copolymer. It explains the lower swelling at a higher crosslinkage. With diethyl phthalate as the diluent, this trend, with respect to crosslinkage, was not regular. There is a decrease in swelling with an increase in crosslinkage from 10% to 20%. Further, the SCs are significantly lower compared to the case of the same crosslinkage with *n*-heptane as the diluent. This is because there is well developed macroreticular porosity in the case of the *n*-heptane diluent. The

Table IV. Characteristics of Bi-Functional Cation-Exchange Resins Obtained After Treating the Copolymers with Sulfuric Acid

Expt. no.	d_r^a (g mL ⁻¹)	SC _w (%)	SC _{H-Na} (%)	-COOH		-SO ₃ H	
				meq mL ⁻¹	meq g ⁻¹	meq mL ⁻¹	meq g ⁻¹
1	0.81	127	25	1.26	6.80	0.39	1.35
2	0.80	106	2.6	1.18	5.18	0.42	1.86
3	0.65	101	ND	1.00	2.03	0.48	1.96
4	0.58	170	3.8	1.36	9.70	0.42	1.29
5	0.43	161	3.4	0.69	4.83	0.83	1.95
6	0.36	158	ND	0.41	1.68	1.04	2.15

^a d_r is density of resin, 'SC_w' is swelling coefficient of resin in water, and 'SC_{H-Na}' is swelling coefficient for change from H-form to Na-form of resin and ND is not detected.

macroporous pores provide fast access of solvents/reagents to the interior of the copolymer beads which explains higher SCs.

The SCs in the case of Experiment 3 are higher compared to Experiment 2 although the crosslinkage is increased from 20% to 30%. This is because the copolymer from Experiment 3 has well developed macroporous porosity, as reflected by a PV of 0.44 mL g⁻¹ compared to the negligible macroporous porosity in the case of Experiment 2, as reflected by about five times lower PV of 0.083 mL g⁻¹. It shows that the macroporous porosity overrides the effect of crosslinkage in this case. The SCs in the case of Experiment 3 are almost the same as in the case of Experiment 6. This is because both copolymers have the same degree of crosslinkage and both have well developed macroporous porosity. These results show that there are two major factors affecting the swelling of the copolymers by solvents: (i) degree of crosslinkage, i.e., the higher the crosslinkage, the lower the swelling, and (ii) type of porosity, i.e., macroporous copolymers swell significantly more than gel-type copolymers having the same degree of crosslinkage. These two factors explain the highest SCs in the case of Experiment 4 where the

crosslinkage was the lowest (10%) and macroporous porosity was well-developed as reflected by the PV of ~ 0.7 mL g⁻¹.

Alkaline hydrolysis converts ester groups (-COOC₂H₅) in the copolymers to carboxylic acid groups (-COOH).¹⁹ The -COOH groups were quantified on the basis of the consumption of NaOH in the following reaction: P-COOH + NaOH(aq) → P-COONa + H₂O, where P represents the polymer backbone. In Experiment 4, alkaline hydrolysis using 1M, 5M, and 10M NaOH yielded 1.19 meq g⁻¹, 2.01 meq g⁻¹, and 3.18 meq g⁻¹ of -COOH groups, respectively. Alkaline hydrolysis using a 10M NaOH solution in a 1 : 1 mixture of water and ethylene glycol²⁰ yielded 1.74 meq g⁻¹ -COOH in Experiment 4 and 0.12 meq g⁻¹ in Experiment 5. The concentration of -COOH groups was below our analysis limits in the case of all other copolymers.

Earlier literature on chemical reactions in porous copolymers show that the best yield is obtained at a certain optimum PV in the copolymers.^{9,21} This is because access of the reagents to the interior of the copolymers is dependent on the macroporous

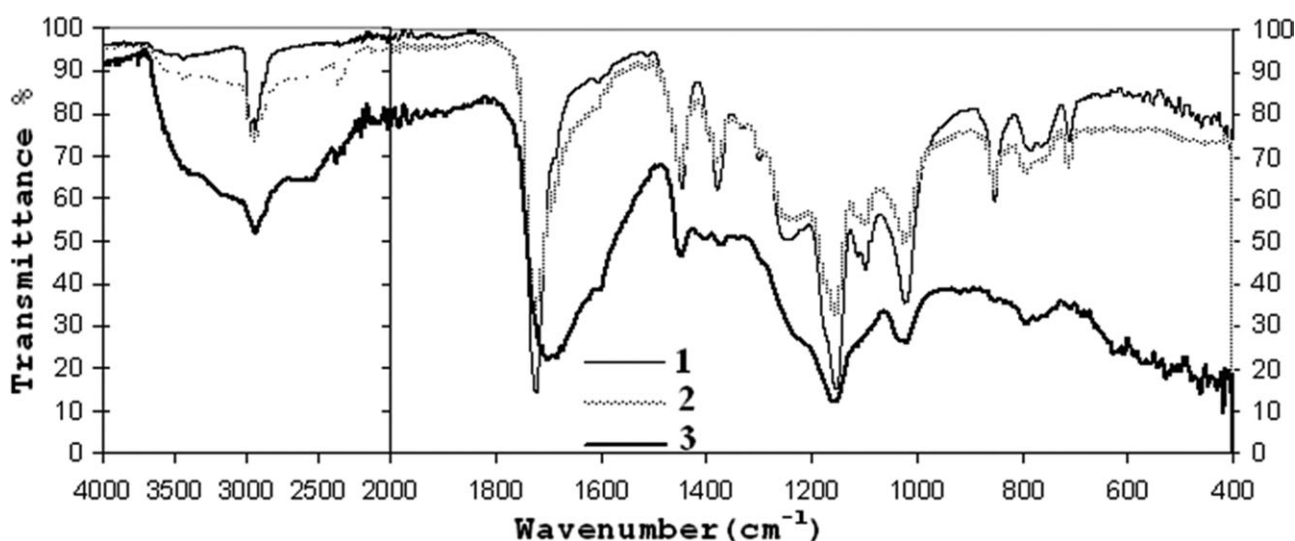


Figure 4. Comparison of ATR spectra of ethyl acrylate-divinylbenzene copolymer of experiment no. 4 and cation-exchange resins (in H-form) derived from it: ethyl acrylate-divinylbenzene copolymer (1), Weak acid cation-exchange resin derived by hydrolysis with 10M NaOH solution (2) and bifunctional cation-exchange resin derived by treatment with concentrated sulfuric acid (3).

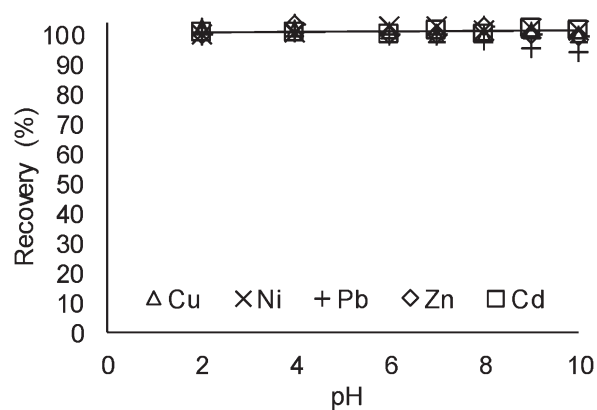


Figure 5. Percentage recoveries of metals at different pH ranges. Experimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, $1 \mu\text{g mL}^{-1}$, eluent = 5 mL of 2 mol L^{-1} HCl, loading/elution rate = 7 mL min^{-1} .

porosity, most probably on the diameters of the available pores which is related with the PV.¹⁸ The present results show that the optimum PV for hydrolysis with NaOH is close to 0.7 mL g^{-1} that was in the case of Experiment 4. Further, lower cross-

linkage in Experiment 4 (10%) may allow faster diffusion of reagents into the copolymer matrix. These factors, i.e., optimum macroreticular porosity for faster access of reagents into the interior of the copolymer beads and lower crosslinkage for faster diffusion of the reagents in the copolymer phase, explain the highest yield of the chemical reaction in the case of Experiment 4.

Concentrated sulfuric acid is another reagent that has the potential to hydrolyze ester groups in macroporous copolymers.^{8,22,23} All the copolymers synthesized in this study were treated with concentrated sulfuric acid under same experimental conditions as in the case of alkaline hydrolysis, i.e., at 98°C for 2 h. The characteristics of the resins obtained by treatment of the copolymers with sulfuric acid are listed in Table IV. Conversion of ester groups in copolymers to $-\text{COOH}$ groups in resins was significantly higher in the case of hydrolysis with sulfuric acid than in the case of alkaline hydrolysis. For example, the concentration of $-\text{COOH}$ groups in the resins obtained from Experiment 4 was 9.70 meq g^{-1} with sulfuric acid which is significantly higher than the highest value of 3.18 meq g^{-1} achieved with 10M NaOH. The highest conversion yield with sulfuric acid treatment was observed in the case of Experiment 4 as it was in the case of NaOH reagent.

Table V. Comparison of Capacities of Various Adsorbents^a

Material used	Analyte	Capacity (mg g^{-1})	Reference
Phosphonate ester/phosphonic acid grafted styrene-divinylbenzene copolymer microbeads (polymer A, B)	Cu	2.75	28
		7.17	
	Ni	Not retained	
Amberlite XAD-7/Xylenol orange	Cd	2.0	29
	Ni	2.6	
	Zn	1.8	
Amberlite XAD-2 (AXD-2-DHP)/2,3-dihydroxypyridine	Cd	7.39	30
	Ni	12.92	
	Zn	11.48	
Fluorinated β -diketone/SDVB	Cd	10.20	31
	Ni	6.45	
	Zn	9.80	
Multiwalled nano tubes	Cd	7.42	32
	Ni	6.89	
Silica gel salicyldoxime (acid red)	Cd	11.7	33
	Ni	11.3	
	Cu	12.1	
Bifunctional-cation exchange resin	Cd	12.51	This study
	Cu	10.42	
	Ni	9.43	
	Pb	13.21	
	Zn	11.12	

^aExperimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, $1 \mu\text{g mL}^{-1}$, eluent = 5 mL of 2 mol L^{-1} HCl, loading/elution rate = 7 mL min^{-1} , pH = 6.5.

Table VI. Concentration ($\mu\text{g L}^{-1}$) of Heavy Metals Obtained in Different Water Samples and Percentage Recoveries in Spiked Samples*

Water source	Elements	Raw water	Spiked conc.	Spiked water sample	% Recovery ^d
Well water	Cu	0.82	0.5	1.30	98.48
	Cd	0.21	0.2	0.49	97.56
	Ni	0.32	0.3	0.60	96.77
	Pb	0.54	0.5	1.03	99.03
	Zn	5.51	5.0	11.00	104.66
Rawal Lake ^a	Cd	1.11	1.00	2.12	100.47
	Cu	22.43	22.00	44.43	99.50
	Ni	0.84	1.00	1.85	100.54
	Pb	19.42	20.00	38.05	96.52
	Zn	30.51	30	60.60	100.14
River Swan ^b	Cd	2.12	2.00	4.00	97.08
	Cu	72.53	70.00	141.00	98.22
	Ni	6.34	5.00	10.90	96.11
	Pb	16.44	15.00	32.00	101.78
	Zn	13.20	10.00	24.00	103.44
Industrial waste water ^c	Cd	17.41	16.00	32.00	96.06
	Cu	72.52	70.00	140.00	98.23
	Ni	20.12	20.00	39.00	97.20
	Pb	17.53	16.00	35.00	104.38
	Zn	100.12	100.00	201.11	100.49

*'a' is Rawal Lake—a lake supplying drinking water to Islamabad city, 'b' is River Swan—a local river containing industrial waste & poultry waste, 'c' is industrial waste water—from a stream contaminated with industrial waste from a beverage factory, 'd' corresponding sorption data (capacities) of the resin is shown in Table V.

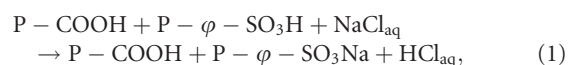
*The experimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, eluent = 5 mL of 2 mol L⁻¹ HCl, loading/elution rate = 7 mL min⁻¹, pH = 2–8 (Note: the % recovery remains constant in this pH range as shown in Figure 5).

Sulfuric acid treatment not only hydrolyzes ester groups, it also incorporates sulfonic acid groups ($-\text{SO}_3\text{H}$) in benzene rings of divinylbenzenes and ethylvinylbenzenes.^{21,24–26} The functional groups in the resins were verified by IR spectroscopy. IR spectra of the copolymer and resins from Experiment 4 are compared in Figure 4. There are two additional peaks in the case of resin obtained with NaOH treatment compared with the base copolymer: (i) a broad absorption extending from 2500 cm^{-1} to 2900 cm^{-1} assigned to O–H bond in $-\text{COOH}$ groups, and (ii) a broad absorption extending from about 3100 cm^{-1} to 3600 cm^{-1} assigned to moisture absorbed in the copolymer sample. This result confirms the hydrolysis of some ester groups into $-\text{COOH}$. These two broad peaks, become intense in the case of resin obtained after sulfuric acid treatment, which indicates that the resin carries a significantly higher concentration of $-\text{COOH}$ groups compared with the resin obtained with NaOH treatment of the copolymer. Another major change in the spectra is that a sharp peak due to C=O groups in the base copolymer at 1720 cm^{-1} and covering a range from 1650 cm^{-1} to 1800 cm^{-1} , shifts to 1700 cm^{-1} and becomes broad, covering the range from about 1500 cm^{-1} to 1800 cm^{-1} . The downwards shift and the broadening of the signal due to C=O groups indicates strong hydrogen bonding in the case of resin obtained with sulfuric acid treatment compared to weak or no hydrogen bonding in the rest of the copolymers. The absorption in the region of 1050 cm^{-1} to 1300 cm^{-1} also becomes broad and intense in the resin obtained after

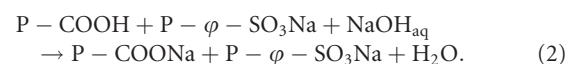
treatment with sulfuric acid. This is due to $-\text{SO}_3\text{H}$ groups formed upon treatment with sulfuric acid. The protons in the $-\text{SO}_3\text{H}$ most likely form strong hydrogen bonding with C=O groups which explains the broadening of the C=O peak.

The IR spectroscopy results verify the hydrolysis of ester groups of the base copolymer upon treatment with strong alkali and hydrolysis of ester groups along with the sulfonation of benzene rings in divinylbenzenes and ethylvinylbenzenes upon treatment with concentrated H_2SO_4 . The assignment of IR signals discussed above are based on earlier literature.²⁷

The $-\text{SO}_3\text{H}$ groups in the resins were quantified based on the analysis of HCl produced in the following reaction:



where " φ " represents the phenyl ring of DVB units. The $-\text{COOH}$ groups of the resins were quantified based on the consumption of NaOH in the following reaction:



The results are listed in Table IV. The highest overall concentration of functional groups was observed in the case of Experiment 4.

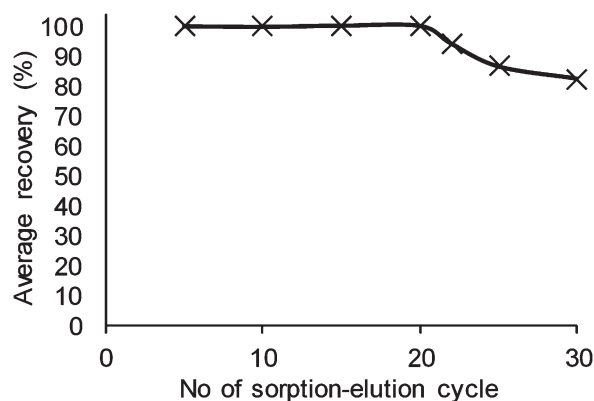


Figure 6. Average percentage recoveries versus number of sorption-elution cycles. Experimental conditions that were kept constant were: resin = 0.2 g, sorbate = 25 mL, $1 \mu\text{g mL}^{-1}$, eluent = 5 mL of 2 mol L^{-1} HCl, loading/elution rate = 7 mL min^{-1} , pH 6.5.

The SC of the bi-functional resins in water (SC_w) was found to decrease with an increase in the crosslinkage as shown in Table IV. The SCs of resins derived from the copolymers synthesized in the presence of *n*-heptane were higher than for diethyl phthalate. The resins have fixed ionic groups (partially ionized $-\text{COO}^- \text{H}^+$ and fully ionized $-\text{SO}_3^- \text{H}^+$ groups) and absorb water due to osmotic pressure. So, the higher the amount of the fixed ions, the greater the swelling is. The swelling stops at a certain point due to stretching at crosslinkage points. So, the higher the crosslinkage, the lower the swelling is. In conclusion, the swelling is dependent on two factors: the number of ionized groups and the degree of crosslinkage. This conclusion is verified by the fact that the highest swelling is observed in the case of Experiment 4 where the combined amount of $-\text{COOH}$ and $-\text{SO}_3\text{H}$ was the highest ($\sim 11 \text{ meq g}^{-1}$) and the crosslinkage was the lowest (10%) among all the resins synthesized in this study. The SC for the change of the resins from H-form to Na-form ($SC_{\text{H-Na}}$) was also found to decrease with an increase in the crosslinkage. The $SC_{\text{H-Na}}$ values were $>4\%$ for all the resins except for Experiment 1 which was a gel type, i.e., without macroporous porosity. A low $SC_{\text{H-Na}}$ is a desirable property with respect to the application of the resins as media in ion-exchange chromatography.

Figure 5 shows that the percentage recoveries of almost all metals from pH 2–10 were $>99\%$ except for Pb. It was observed that at pH >8 , Pb started to precipitate in the solution. The removal of Pb due to precipitation accounts for the decrease in recovery observed in this study.

It is clear from the above discussion that the resin obtained by sulfuric acid treatment of the copolymer from Experiment 4 is best suited for the extraction of toxic metals. This conclusion is based on the fact that this resin has an optimum combination of desirable characteristics, i.e., lower crosslinkage, reasonably good porosity and the highest overall concentration of $-\text{COOH}$ and $-\text{SO}_3\text{H}$ functional groups. It was evaluated for extraction of heavy metals from water samples. The capacities of the resin for some common toxic metals found in wastewater were com-

parable or better than other sorbents reported in literature^{28–33} as shown in Table V.

The concentration of toxic metals and their recoveries from actual wastewater samples are shown in Table VI. The results show that the porous bi-functional resin synthesized in this study is suitable for extraction of toxic metals from wastewater.

To assess re-usability of the resins, thirty sorption–elution cycles were performed. The column can be re-used for up to 20 sorption–elution cycles without any decrease in the recoveries for the selected metals, as shown in Figure 6. The performance of the resin started to decline after 20 cycles of sorption–elution, which may be due to the accumulation of precipitates, such as metal hydroxides, in the pores of the resin.

CONCLUSIONS

The conclusions of this study are the following:

1. Macroporous ethyl acrylate-divinylbenzene copolymer beads can be synthesized by using a diethyl phthalate or *n*-heptane diluent and a 10–30% crosslinkage.
2. The copolymer having a PV of $\sim 0.7 \text{ mL g}^{-1}$ and low crosslinkage (10% crosslinkage) converted to a bi-functional resin after treatment with concentrated sulfuric acid with highest concentration of functional groups compared to other PV and crosslinkage conditions.
3. The bi-functional resin has shown excellent extraction efficiency for heavy metals from water samples. The wide working pH range makes it suitable for the extraction of toxic metals from water samples of various origins.
4. The resin is reusable for an adequate number of cycles and the regeneration process is simple.

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