

Adsorptive Removal of Technetium-99 Using Macroporous Poly(GMA-co-EGDMA) Modified with Diethylene Triamine

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ABSTRACT: The possibility of sorption of technetium-99 in the form of pertechnetate anion (TcO_4^-) and the sorption kinetics for removing TcO_4^- from aqueous solution by chelating polymers based on glycidyl methacrylate (GMA) were investigated. Two samples of macroporous crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGME), with different amount of the crosslinker (ethylene glycol dimethacrylate, EGDMA), were synthesized by suspension copolymerization and functionalized with diethylene triamine (deta). We propose that nonspecific sorption of pertechnetate anion via electrostatic interactions takes place at the protonated amino groups of macroporous crosslinked copolymer. The results of batch experiments per-

formed at pH 1–14 showed fast sorption kinetics for removing TcO_4^- by amino-functionalized PGME-deta in a wide range of pH, that is, from 1.0 to 9.0. Almost complete removal of TcO_4^- (91–98%) was reached within 180 min in the stated pH range (1.0–9.0), with the sorption half-times of under 25 min. The partitioning coefficients of linear adsorption isotherms, with 180-min equilibrium time, reach the high values of 2130 mL g^{-1} and 1698 mL g^{-1} for the two samples of synthesized PGME-deta. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1273–1282, 2012

Key words: macroporous polymers; glycidyl methacrylate based; pertechnetate; adsorption; FTIR

INTRODUCTION

Detection and quantification of technetium-99 radionuclide in the environment are important, because it is one of many hazardous isotopes frequently detected in contaminated groundwater and sediments. Technetium-99 (^{99}Tc) is a long life (half-life of 2.13×10^5 years) pure β -emitter and has a specific activity of 629.0 MBq/g. It is produced in large amounts by nuclear fission of ^{235}U or ^{239}Pu in nuclear reactors and in small amounts by spontaneous fission of ^{238}U in the Earth's crust or by decay of ^{99}Mo in nature.¹ It also occurs environmentally originating from the decay of the short-lived medical radioisotope $^{99\text{m}}\text{Tc}$ (6.0058 h half-life), which decays by isomeric transition to technetium-99.² Over a wide range of oxidic conditions, the predominant form

of technetium is the pertechnetate anion (TcO_4^-).^{3,4} TcO_4^- is poorly sorbed by natural materials, highly soluble in water, and thus readily mobile in the environment.⁵ TcO_4^- can also be involved in anion uptake by plants and has a tendency for bioaccumulation in plants.⁶

Removal of TcO_4^- from contaminated water by sorption has been extensively investigated. Effective removal of ^{99}Tc from contaminated groundwater is very difficult because of strong competition for sorption from the other present anions. Various synthetic and natural materials have been investigated for their potential use for the removal of Tc from the environment. TcO_4^- can be strongly sorbed on activated carbon,^{4,7,8} various synthetic resins and sponges,^{9–12} elemental iron,¹³ strongly magnetic iron sulfide material,⁶ organic polymers,¹⁴ chitin, and chitosan.¹⁵

The acrylic-based resins are almost ideal for the removal of toxic pollutants like Cu, Co, Ni, Zn, and Cd^{16,17} as well as Pb and Hg,^{18,19} because they are very stable in a range of buffers from pH 1.0 to 11.0 and resistant to microbial degradation.²⁰ Macroporous crosslinked copolymers based on GMA are of great interest due to their chemical and structural versatility, owing to the presence of epoxy groups

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(EG) that can rapidly react with various reagents and be easily transformed into iminodiacetate, thiol, azole, pyrazole groups, etc.²¹ The EG can be ring-opened with various amines (ethylene diamine, diethylene triamine, and triethylene tetramine) to yield amino-hydroxyl-functionalized sorbents.²² Functionalization of these copolymers with amines yields specific sorbents with high capacity, fast kinetics, and good selectivity for many metal ions as well as good chemical and mechanical stability.^{17,18,23,24}

The advantage of amino-functionalized macroporous crosslinked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (PGME) over the conventional ion exchange resins lies in the fact that depending on pH, they can both coordinate heavy and precious metals and bind them as chloro complexes.²⁵ Accordingly, in addition to functioning as chelating resins, amino-functionalized macroporous crosslinked PGME can also be used in ion exchange (electrostatic sorption), because they possess weakly basic primary and secondary amino groups.

The choice of diethylene triamine as amination reagent was made on the basis of the results obtained in our earlier previous extensive research. Namely, we observed that the type of amino-ligand strongly influences the heavy metal sorption by macroporous crosslinked amino-functionalized PGME.²⁶ For example, the sorption capacity toward Cu(II) ions decreased in order: PGME-deta > PGME-en > PGME-teta (Note: additional marks -en, -deta, and -teta stand for PGME with attached ethylene diamine, diethylene triamine, and triethylene tetramine, respectively). In earlier works,²⁷⁻²⁹ the sorption rate and the sorption capacity of amino-functionalized macroporous crosslinked copolymers based on glycidyl methacrylate (GMA) for different metal ions have been investigated. We have successfully used PGME functionalized with diethylene triamine for the removal of Cr(VI) anionic species from acidic solutions.³⁰ This lead us to believe that technetium sorption by amino-functionalized copolymers may be possible.

Moreover, Kim et al.¹⁵ demonstrated that ReO_4^- , which is often used as pertechnetate analog, is efficiently sorbed by natural organic polymer chitosan-containing amino groups, while Plevaka et al.³¹ showed that perrhenate binds to fibrous chitosan-carbon materials. Also, Liang et al.⁹ showed that sorption of pertechnetate by Forager sponge can also be attributed to the presence of amino groups. Therefore, on the basis of our previous extensive research as well as on the literature data, we concluded that amino-functionalized copolymers may be used for pertechnetate sorption.

In this work, we investigated the possibility of successful removal of $^{99\text{m}}\text{TcO}_4^-$ from aqueous solutions by the ion exchange media in the form of the synthesized amino-functionalized macroporous crosslinked

copolymers, in batch operation. $^{99\text{m}}\text{Tc}$ is a metastable nuclear isomer of ^{99}Tc with a half-life for γ emission of 6.0058 h and thus easily detectable by scintillation techniques. The sorption rate and the sorption capacity of the synthesized macroporous crosslinked copolymers for TcO_4^- as well as the pH dependence of TcO_4^- sorption are reported here.

EXPERIMENTAL

Materials

All the chemicals used were analytical grade products and used as received: GMA (Merck), EGDMA (Fluka), diethylene triamine (deta) (Merck), 2,2'-azobisisobutyronitrile (AIBN) (Merck), poly(*N*-vinyl pyrrolidone) (Kollidone 90, BASF), cyclohexanol (Merck), 1-tetradecanol (Merck), ethanol (Merck), and toluene (Merck). Saline sodium pertechnetate eluate was obtained from a $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator (Vinča Institute of Nuclear Sciences).

Aqueous buffer solutions were prepared from reagent grade chemicals, and deionized water (Milli-Q Millipore $18\text{M}\Omega\text{ cm}^{-1}$ conductivity) was used for all dilutions. A pH meter, Beckman F40 with a combined Ag/AgCl electrode, was used for adjusting pH values.

For the preparation of pH 1 and 2 solutions, appropriate volumes of 0.1M potassium chloride and 0.1M hydrochloric acid solutions were used. Phosphate buffer solution for pH 3 was prepared by mixing appropriate volumes of 0.2M sodium dihydrogen phosphate solution and 1 : 20 diluted phosphoric acid. Acetate buffer solutions were prepared by mixing appropriate volumes of 0.1M acetic acid and 0.1M sodium acetate solutions for pH 4 and 5. Phosphate buffer solutions were prepared by mixing appropriate amounts of 0.1M NaH_2PO_4 and 0.1M Na_2HPO_4 solutions for pH 6 and 7. Ammonia buffer solutions were prepared by mixing appropriate amounts of 0.1M ammonia and 0.1M ammonium chloride solutions for pH 8–10. By mixing appropriate volumes of 0.1M potassium hydroxide and 0.1M potassium chloride solutions for pH 11, pH 12–14 were obtained.

Synthesis of poly(GMA-*co*-EGDMA)

Two samples of macroporous crosslinked copolymers of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA), PGME, with different amounts of the crosslinker (40% PGME1 and 20% PGME2), were synthesized by suspension copolymerization and modified by ring-opening reaction of the pendant EG with diethylene triamine (deta).

The monomer phase (75.0 g) containing monomer mixture (19.5 g GMA and 13.0 g EGDMA for sample PGME1, and 26.0 GMA and 6.5 g EGDMA for sample PGME2), AIBN as initiator (0.3 g), and 45.2 g of

TABLE I
Porosity Parameters of Initial and Amino-Functionalized Poly(GMA-co-EGDMA) Samples

Sample	S_{Hg} (m ² /g)	V_s (cm ³ /g)	$d_{V/2}$ (nm)	d_p (nm)
PGME1	59 ± 0.4	0.96 ± 0.007	94 ± 0.3	74 ± 0.2
PGME2	40 ± 0.2	0.96 ± 0.009	182 ± 1.5	148 ± 1.1
PGME1-deta	55 ± 0.3	0.91 ± 0.006	107 ± 1.3	96 ± 0.5
PGME2-deta	29 ± 0.2	0.89 ± 0.004	212 ± 2.7	184 ± 1.4

inert component (34.0 g of cyclohexanol and 8.5 g of 1-tetradecanol) was suspended in the aqueous phase consisting of 225.0 g of water and 2.25 g poly(*N*-vinyl pyrrolidone). The copolymerization was carried out at 70°C for 2 h and at 80°C for 6 h with a stirring rate of 300 rpm. After the completion of reaction, the copolymer particles were washed with water and ethanol, kept in ethanol for 12 h, and dried in vacuum at 40°C. The resulting crosslinked beads were sieved and purified by Soxhlet extraction with ethanol. The fraction with the average particle diameter (*D*) in the range of 150 < *D* < 300 μm was used in the subsequent reactions.

Functionalization of poly(GMA-co-EGDMA) with diethylene triamine

A mixture of 7.2 g of poly(GMA-co-EGDMA) (samples PGME1 and PGME2, with particle size 150 < *D* < 300 μm), 31.4 g of diethylene triamine, and 300 mL of toluene was left at room temperature for 24 h and then heated for 6 h at 80°C at a stirring rate of 250 rpm. The modified samples, named PGME1-deta and PGME2-deta, were filtered, washed with ethanol, and dried.

Characterization of copolymers

The copolymer samples were analyzed for their carbon, hydrogen, and nitrogen content using the Vario EL III device (GmbH Hanau Instruments, Germany).

To determine the amine content,³² 0.100 g of the polymer sample was left in contact with 5.0 mL of 0.1M HCl for 10 h. Two milliliters of the supernatant solution were taken, and the acid content of the solution was determined by titration with a 0.051M NaOH solution in the presence of phenolphthalein as a color indicator.

The weak base anion exchange capacity was evaluated by contacting 0.2 g of resin with 50 mL of 0.100M HCl for protonation for 12 h, and then washing the resin with methanol to remove the excess acid. Then, the resin was equilibrated with 50 mL of 0.102M NaOH for 12 h. A 10 mL aliquot of the filtrate was withdrawn, and the excess standardized sodium hydroxide was determined by acid-base titration, using methyl orange as a color indicator.³³

The amino group content and the weak base anion exchange capacity for both amino functionalized copolymers were calculated using mass balance equations.

The pore size distributions were determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200).

Standard errors for porosimetry data calculated from triplicate measurements are reported in Tables I–III, alongside the mean values.

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectra for the initial and the amino-functionalized macroporous crosslinked copolymers were obtained by using a Thermo Nicolet 6700 FTIR spectrometer, equipped with an ATR Smart Orbit accessory (4000–400 cm⁻¹).

The quantification of ^{99m}Tc was determined using scintillation gamma counting technique, with 1282 Compugamma, LKB universal gamma counter (Wallac, Finland). The specific activity of the eluted sodium pertechnetate solution was measured and adjusted using a Capintec CRC-15 beta dose calibrator.

Technetium uptake experiments

^{99m}TcO₄⁻ solution was eluted from ⁹⁹Mo/^{99m}Tc generator, and its specific activity was determined by a Capintec CRC-15 beta dose calibrator and adjusted by adding saline solution to 1.3 MBq/mL. Adsorption of ^{99m}TcO₄⁻ on amino-functionalized poly(GMA-co-EGDMA) samples was performed at room temperature in static (batch) experiments. Fifty milligrams of each sample were contacted with 1 mL of ^{99m}Tc-pertechnetate aqueous solution and 3 mL of the appropriate buffer solution. The pH of the solution was varied from 1.0 to 14.0. For each pH value, a blank without copolymer was prepared in the same manner. After 30, 60, 90, 180 min, and 24 h, 100 μL aliquots from the vials containing no sorbent as well as from the sorbent containing vials were removed. The aliquot activity was measured with an automated gamma counter. Relative measurements of sorbed radioactivity were obtained using the following equation:

$$R = \frac{R_b - R_s}{R_b} \times 100\%$$

where *R* is the sorbed pertechnetate activity (%), *R_b* is the measured activity of the blank aliquot (counts per

min) for a given pH, and R_s is the activity of the supernatant aliquot (counts per min) for the same pH value.

The sorption isotherms were measured at room temperature by mixing 50 mg of copolymer with 3 mL of the pH 3.0 buffer solution and 1 mL of sodium pertechnetate solution. The concentration range studied was between 0.081 and 2.5 mCi/mL for PGME1-deta and 0.067 and 2.3 mCi/mL for PGME2-deta. The solutions were equilibrated for 3 h.

All the uptake experiments were conducted in triplicate, and sometimes repeated again, and the mean values have been reported.

RESULTS AND DISCUSSION

Characterization of PGME and PGME-deta samples

Macroporous crosslinked copolymers are obtained by suspension copolymerization in the shape of regular beads of required size, when the inert component is present in the mixture of monomer and initiator^{19,34,35}. By changing the amount of the crosslinker, EGDMA (40% for PGME1 and 20% for PGME2 synthesis), different porous structures were obtained. The initial samples were amino-functionalized by ring-opening reaction of the pendant EG with diethylene triamine (PGME1-deta and PGME2-deta samples).

The mean values of the porosity parameters from mercury porosimetry (specific surface area, S_{Hg} , specific pore volume, V_s , diameter, which corresponds to half of the pore volume, $d_{V/2}$, and average pore diameter, d_p) for initial and amino-functionalized samples are presented in Table I. Standard errors calculated from triplicate measurements are reported.

The calculation of the specific surface area, S_{Hg} , of initial and amino-functionalized samples is based on the cylindrical pore model.³⁶

From the porosity data in Table I, it can be seen that initial samples with different porosity parameters were synthesized and that the process of amino-functionalization caused modification of the porosity parameters. The reduction of the crosslinker concentration by 20% is accompanied by a large increase of the pore diameter which corresponds to half of the pore volume, $d_{V/2}$, (almost twice the value) and a decrease in the specific surface area (32%). The specific surface area of PGME1-deta and PGME2-deta decreased in comparison with the initial samples (7 and 28%, respectively). The specific pore volume of both amino-functionalized samples decreased (5% for PGME1-deta and 7% for PGME2-deta) compared to the initial samples. The average pore diameter, d_p , of PGME1-deta and PGME2-deta increased in comparison with the initial samples (30 and 24%, respec-

TABLE II
Elemental Analysis^a

Samples	Found			Calculated		
	%C	%H	%N	%C	%H	%N
PGME1	59.0	6.5	—	59.8	7.1	
PGME2	58.7	7.4	—	59.5	7.1	
PGME1-deta	53.8	8.2	7.0	56.3	8.2	8.4
PGME2-deta	52.4	8.1	9.1	55.0	9.0	14.3

^a Elemental analysis was calculated from multiple determinations within $\pm 0.2\%$ agreement.

tively) as well as the diameter, which corresponds to half of the pore volume, $d_{V/2}$, of PGME1-deta and PGME2-deta (10 and 16%, respectively).

The results of elemental analysis of the initial copolymer samples, PGME, and the samples modified with diethylene triamine are presented in Table II. Standard errors calculated from triplicate measurements are reported.

From elemental analysis data, the degree of conversion of EG, the ligand concentration, and the amino group concentration in the samples PGME1-deta and PGME2-deta were calculated and presented in Table III. Also in Table III, the amine contents for the modified samples determined by acid-base titration, as well as the evaluated weak base anion exchange capacities were given.

The higher amount of the crosslinking monomer, EGDMA, in the synthesized sample PGME2 (40%) than in PGME1 (20%), should result in lower content of EG that can be functionalized, because glycidyl methacrylate is the epoxy ring-containing monomer. Indeed, the theoretical content of EG was calculated to be 4.22 mmol g^{-1} for PGME1 (sample with 60% of GMA) and 5.63 mmol g^{-1} for PGME2 (sample with 80% of GMA). However, it was shown that the degree of conversion of EG in reaction with diethylene triamine (deta) was almost the same for both samples, that is, the amino-functionalization results in the following amino group content: 5.01 mmol g^{-1} for PGME1-deta and 6.51 mmol g^{-1} for PGME2-deta are calculated from the elemental analysis data. The possible explanation can be found in different porous structure as well as in different distribution of EG. The obtained percent conversion of EG is the consequence of the fact that some EG usually remain inside the crosslinked copolymer, not being accessible for subsequent reactions and analytical determinations.³⁷

It can be seen from Table III that the results acquired from the amine content determination by titration and for the amount of weak base anion exchanging functional groups are in agreement. However, these values are significantly lower than the content of amino groups calculated from the elemental analysis data. The nitrogen atom that takes part in SN2 nucleophilic attack on the least sterically

TABLE III
Percent Conversion of Epoxy Groups, Ligand Concentration, Amino Group Concentration, and the Weak Base Anion Exchange Capacity of the Amino-Functionalized Poly(GMA-co-EGDMA) Samples

Samples	Conversion of EG (%)	C_{lig} (mmol g^{-1})	C_{AG} (mmol g^{-1} , calculated from elemental analysis)	C_{AG} (mmol g^{-1} ; determined by titration)	IEC (meq g^{-1})
PGME1-deta	39.5 ± 0.2	1.67 ± 0.004	5.01 ± 0.006	3.7 ± 0.21	3.6 ± 0.18
PGME2-deta	38.6 ± 0.2	2.17 ± 0.005	6.51 ± 0.008	4.9 ± 0.35	4.6 ± 0.25

shielded carbon atom of the EG does not participate in bonding protons during the sample equilibration with hydrochloric acid, because it is hydrogen bonded with the H atom of the hydroxyl group, which is bonded to the neighboring C atom. This is the consequence of the functionalized copolymer structure and the proximity of those two groups. Therein lies the explanation for the differing results obtained for the amino group concentration acquired from the elemental analysis data and the titration methods. As can be seen from Table III, the latter methods give the amino group contents and the anion exchange capacities that are roughly equal to two thirds of the numbers calculated from elemental analysis. The results are slightly higher for the determination of amine content by titration than for the weak base anion exchange capacity, due to the drawback of the former method (the excess acid is not washed out of the pores of the resin).

To confirm the structure of the obtained cross-linked copolymers and to identify their functional groups responsible for TcO_4^- sorption, the copolymers were characterized by FTIR-ATR technique. FTIR-ATR spectra of samples were recorded in the frequency range of 4000–400 cm^{-1} . Figures 1 and 2 show the FTIR-ATR spectra of the initial and the amino-functionalized samples. The assignment of FTIR-ATR bands to specific chemical bonds is given in Table IV.

The data clearly show the presence of both EG and ester carbonyl group in the unmodified copolymers and also the amino group in the modified copolymers.

The presence of EG shows that GMA has been incorporated into the copolymer chain. The bands at 2994–2949 cm^{-1} (PGME1) and 2997–2943 cm^{-1} (PGME2) are due to the stretching vibration of C–H bond, the strong bands at 1147 (PGME1) and 1145 (PGME2) cm^{-1} are due to the stretching vibration of the C–O ester bond, and the strong bands at 1720 (PGME1) and 1722 cm^{-1} (PGME2) are due to the stretching vibration of the $>C=O$ bond.

The bands characteristic for crosslinked copolymers were not changed in the modified samples, with the exception of the intensity of the EG vibrations, which indicate that the structure of the copolymer remains unchanged in the process of modification with diethylene triamine.

The bands due to the epoxide ring vibrations at 907 and 844 cm^{-1} in the spectrum of PGME1 have not completely disappeared in the spectrum of modified sample PGME1-deta, although their intensity became very small, and they were shifted to smaller frequencies (from 844 to 815 cm^{-1}). The band in the spectrum of PGME2 at 906 cm^{-1} disappeared entirely in the spectrum of PGME2-deta, while the band at 844 cm^{-1} underwent a shift to 815 cm^{-1} as well as a significant reduction of intensity,

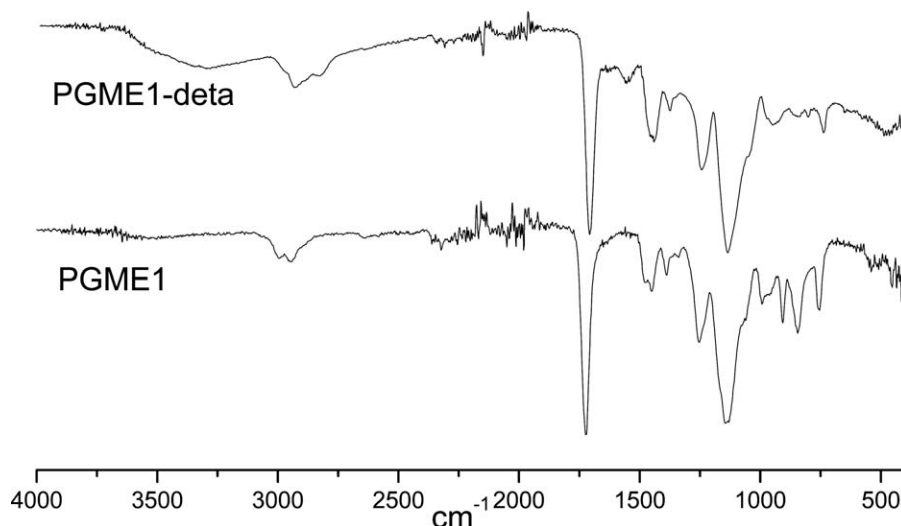


Figure 1 FTIR-ATR spectra of poly(GMA-co-EGDMA) (sample PGME1) and amino-functionalized sample PGME1-deta.

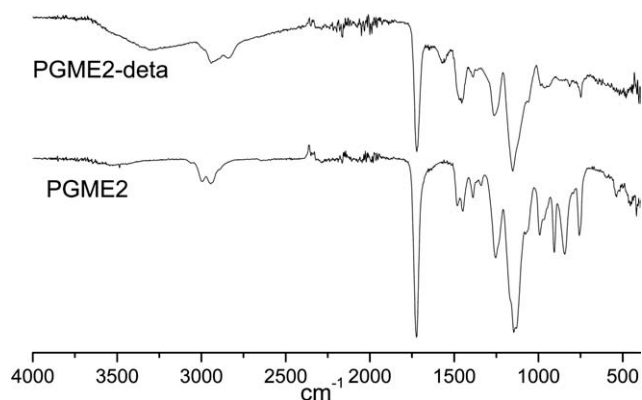


Figure 2 FTIR-ATR spectra of poly(GMA-co-EGDMA) (sample PGME2) and amino-functionalized sample PGME2-deta.

as the consequence of the conversion of EG. The result of the conversion of EG is the appearance of new bands at 3300, 1569, and 1389 cm^{-1} (PGME1-deta) and 3300, 1570, and 1389 cm^{-1} (PGME2-deta) in the spectra of amino-functionalized copolymers, due to the presence of amino groups ($\nu(\text{NH}_2)$, $\delta(\text{NH})$, and $\nu(\text{NH})$). The band at 1643 cm^{-1} due to the bending vibration of NH_2 is present only in the spectrum of PGME2-deta. It is possible that it originates from the larger amino group concentration (Table III) in PGME2-deta than in PGME1-deta.

Sorption of TcO_4^- by PGME-deta

Nuclear facilities include a number of liquid processes and waste streams which require treatment for the removal of the radioactive contaminants³⁸; the most common treatment method is ion exchange. Typically, organic ion exchange resins, which have proved to be reliable and effective, are used, especially in high-purity water applications. Weak base resins exhibit minimum exchange capacity above a pH of 7.0,³⁹ and they are preferred over strong base resins, because they require less regenerant chemical, if reuse is the goal.

The ion exchange process is very effective at transferring the radioactive content of a large volume of

liquid into a small volume of solid, which minimizes disposal costs of this secondary waste.³⁸

Generally, total concentration of salts in solution containing the radionuclide species of interest must generally be low (<1 g/L).³⁸ However, there are factors that increase the affinity of an anion for the resin, which include small charge-to-size ratio and low-hydration energy.⁴⁰ Because TcO_4^- is larger and has a lower hydration energy⁴¹ than most of the other anions encountered in groundwater⁴² (such as nitrate, chloride, bicarbonate, and sulfate) present in ~ 4 – 6 order of magnitude higher concentrations or in tank waste,⁴³ there is a natural bias toward exchanging TcO_4^- preferentially over the other anions in an aqueous solution.⁴⁴ This bias can be enhanced by chemical modification of the resin, including varying the type of the cationic exchange sites and the crosslink density of the copolymer.⁴⁵

Before the selection of a particular ion exchange treatment process, the principal cost components to be considered are as follows: the capital costs, the initial cost of the ion exchange media, the operating costs and the cost associated with the treatment and disposal of the spent ion exchanger.³⁸

The effect of pH on of TcO_4^- sorption

The sorption capability of both synthesized crosslinked copolymers was measured as a function of the solution pH. The pH-dependent sorption of TcO_4^- on crosslinked copolymers was studied in the range of pH 1.0–14.0. The percent uptake of TcO_4^- was measured after 30, 60, 90, 180 min, and finally after 24 h. The curves displaying the amount sorbed TcO_4^- after 30, 60, and 180 min versus pH are presented in Figure 3(a–c), respectively. The maximum standard deviation calculated from triplicate activity measurements was $\pm 4\%$. Standard errors are presented in Figures 3–5 in the form of error bars.

It can be seen from Figure 3 that the sorption of TcO_4^- anions on the copolymers is strongly dependent on the pH of the solution. For both investigated copolymers, sorption was inversely correlated with increasing pH. The amount of sorbed TcO_4^- varied

TABLE IV
FTIR-ATR Spectra Assignments

Sample	Epoxy ring vibration (cm^{-1})		$\delta(\text{CH})$ epoxy (cm^{-1})		Crosslinked copolymers vibrations (cm^{-1})			$\nu(\text{NH}_2)$ (cm^{-1})	$\delta(\text{NH})$ (cm^{-1})	$\nu(\text{NH})$ (cm^{-1})	$\delta(\text{NH}_2)$ (cm^{-1})
	907	844	1253	1453	N (CH)	$\nu(\text{CO})$	$>\text{C}=\text{O}$				
PGME1	907	844	1253	1453	2994–2949	1147	1725				
PGME1-deta	854	815	1257	1452	2955	1149	1725	3300	1569	1389	
PGME2	906	844	1254	1449	2997–2943	1145	1722				
PGME2-deta		815	1262	1453	2955	1152	1725	3300	1570	1389	1643

δ -bending vibration, ν -stretching vibration.

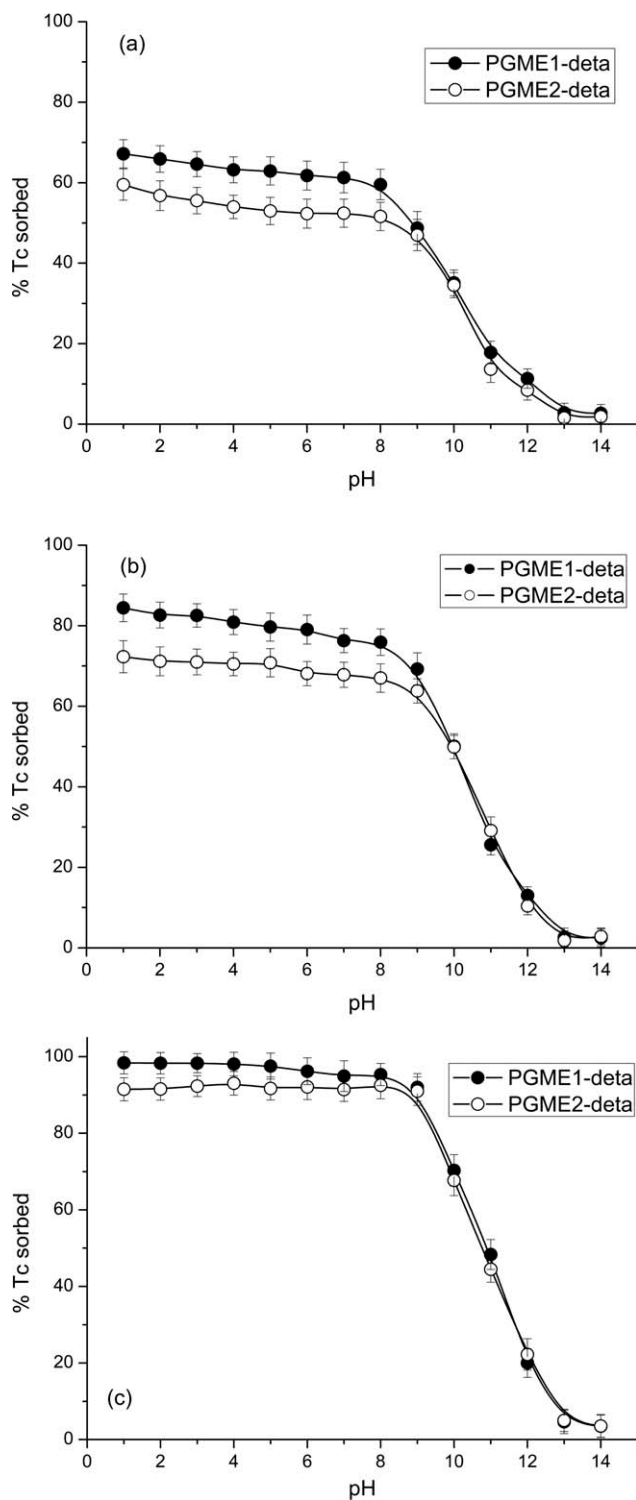


Figure 3 Effect of pH on TcO_4^- sorption on PGME1-deta and PGME2-deta after (a) 30 min, (b) 60 min, and (c) 180 min. Vertical error bars represent standard errors.

from 99 to 2% as pH increased from 1.0 to 14.0, indicating a lowering of the sorption capacity of copolymers as pH increases. Up to pH of ~ 3 , a large number of amino groups are in their protonated form and can interact with the negatively charged per-

technetate anion TcO_4^- via electrostatic interactions; consequently, the sorption capacity is large. pK values of the amino groups in weak base anion exchangers are in the range of 8–10. Under neutral and weak alkaline conditions, protonated amino groups still exist, but hydrogen bonding between partially protonated and free amino groups prevails. The consequence is a decrease in TcO_4^- binding via electrostatic interactions, and the sorption capacity decreases slowly in the pH range from 1.0 to 8.0. At higher pH values (>8), the amount of protonated amino groups decreases rapidly, sorption of TcO_4^- is limited, and the amount of sorbed pertechnetate anions declines to under 40% at pH values higher than 10, with negligible sorption at $pH > 11$.

The curves in Figure 3 also show that PGME1-deta always sorbs more TcO_4^- than PGME2-deta. The results of elemental analysis (Table III) and the intensity of the IR bands due to the amino groups of the copolymers indicate that PGME2-deta has more amino groups than PGME1-deta. On the basis of these results and taking into account that the TcO_4^- anions are binding to protonated amino groups of the copolymers, it was expected that PGME2-deta would be a better adsorbent for TcO_4^- than PGME1-deta. However, the results of our experiments showed the opposite to be the case. The explanation may be in fact that, apart from the content of attached amine ligands in copolymers, the sorption of pertechnetate anions depends on the structural properties of the copolymers (copolymer particle size, specific surface area, pore diameter, and specific pore volume). The main structural difference between these two polymers (Table I) is in their specific surface areas, namely, the surface area of PGME1-deta is approximately twice that of PGME2-deta. The pore size of both polymers (Table I) is

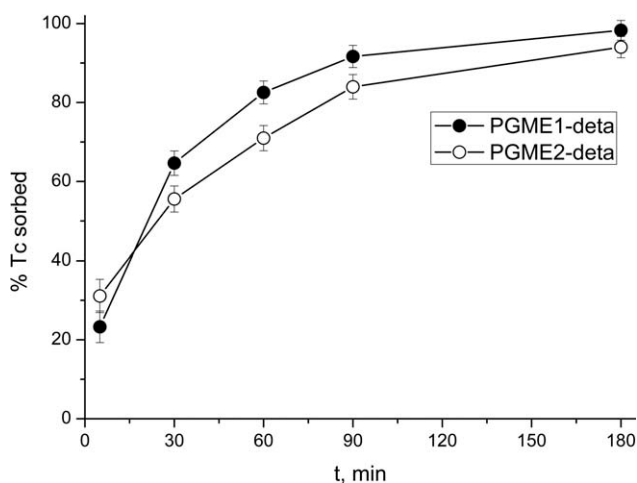


Figure 4 Sorption of TcO_4^- versus time on PGME1-deta (a) and PGME2-deta (b), $pH = 3.0$. Vertical error bars represent standard errors.

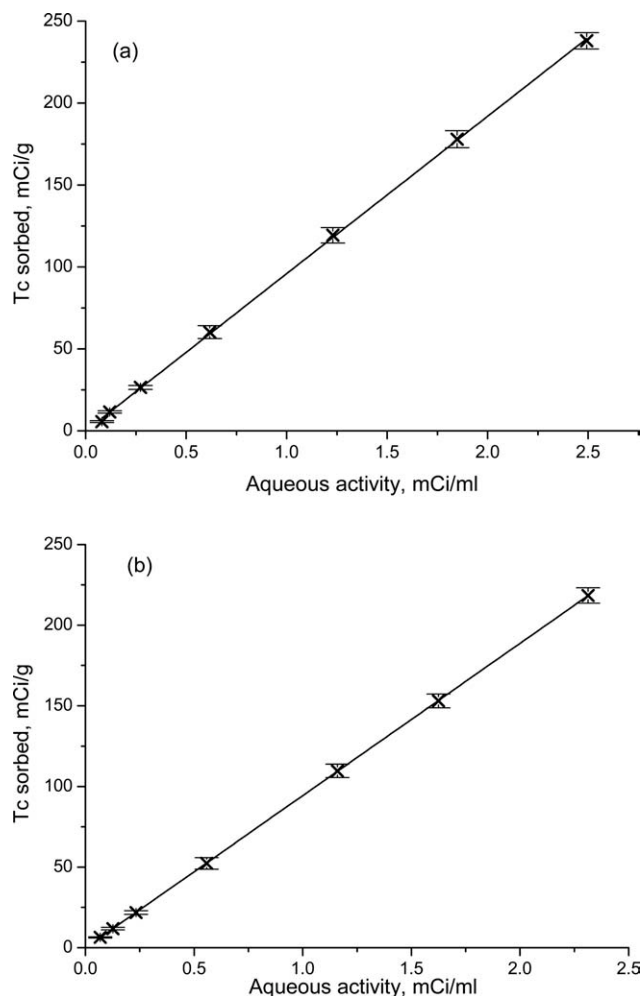


Figure 5 Sorption isotherms of TcO_4^- on PGME1-deta (a) and PGME2-deta (b) from aqueous solution at pH = 3.0. Solutions were equilibrated for 180 min. Standard errors are shown as vertical error bars.

sufficient for the penetration of TcO_4^- , which has the hydrated ionic radius of 0.24 nm in aqueous solutions.⁴⁶ The interaction between amino groups and TcO_4^- anions occurs in the bulk volume of copolymer. Internal surface of macroporous materials such as these crosslinked copolymers is small in comparison with their external one. The fact that PGME1-deta is a better adsorbent for TcO_4^- than PGME2-deta indicates that sorption primarily occurs at the external surface, where larger amount of amino groups on PGME1-deta are capable of electrostatic interaction with TcO_4^- anions. In conclusion, the sorption of TcO_4^- anions on investigated copolymers depends on both the amount of protonated amino groups and the specific surface area of the copolymers.

Sorption kinetics

Figure 4 presents the plot of TcO_4^- uptake versus contact time for PGME1-deta and PGME2-deta. It can be seen from Figure 4 that the sorption processes

reached equilibrium within ~ 180 min. The sorption half-time, $t_{1/2}$, defined as the time required to reach 50% of the total sorption capacity, was 21 min for PGME1-deta and 24 min for PGME2-deta. After ~ 30 min, the sorption rates declined. Seventy percent of maximum TcO_4^- uptake was reached on PGME1-deta after 47 min and after 69 min on PGME2-deta. After 180 min, the amounts of sorbed TcO_4^- anions were nearly 100% for both amino-functionalized copolymers. Obviously, PGME1-deta has higher sorption capacity and higher rate of sorption of TcO_4^- anions than PGME2-deta. Under the stated experimental conditions (pH = 3.0), both copolymers have a sufficient amount of protonated amino groups for sorption of pertechnetate anions, and the higher specific surface area of PGME1-deta compared to PGME2-deta determines the sorption kinetics.

The literature data regarding sorption of pertechnetate from aqueous solutions vary considerably, because it pertains to a wide range of experimental conditions. For the sake of comparison, we will mention some of these results. Cul et al.¹³ reported that the adsorption of TcO_4^- on Dowex-SRB-OH resin and Reillex resins took more than 6 weeks to reach equilibrium, while Hughes et al.¹² found that 20-min time was sufficient to achieve more than 95% removal of the radioactivity from solution on Dowex $1 \times 8-400$ (Cl^-). The results of studies of Liang et al.⁹ indicated that for the removal of TcO_4^- by Forager sponges, the reaction rate reached an equilibrium after 3 days, while for the removal of TcO_4^- by zero valence iron filings, the observed reaction half-life was ~ 8 h, and the reaction rate reached its equilibrium after 24 h. On the other hand, Holm et al.⁸ reported that the *in situ* sorption of technetium using activated carbon reached equilibrium in about 5 h.

Adsorption isotherms

Amino-functionalized poly(GMA-co-EGDMA), that is, PGME1-deta and PGME2-deta were studied for TcO_4^- sorption at varying concentrations of solution, that is, the range of aqueous activities studied, was between 0.081 and 2.5 mCi/mL for PGME1-deta and 0.067 and 2.3 mCi/mL for PGME2-deta (Fig. 5). The reaction of TcO_4^- with these polymers yielded linear adsorption isotherms, with excellent correlation coefficients of $R^2 = 0.9998$ for PGME1-deta and $R^2 = 0.9999$ for PGME2-deta and the partitioning coefficients of 2130 mL g^{-1} and 1698 mL g^{-1} for PGME1-deta and PGME2-deta, respectively. The partitioning coefficients, K_d (mL/g), were calculated according to the equation $S = K_d C$, where S represents the adsorbed concentration on adsorbent surface (Tc activity per gram of polymer) and C is the equilibrium aqueous concentration (activity per milliliter of solution). The Oak Ridge National Laboratory investigated

several synthetic resins⁴⁷ for the removal of pertechnetate from contaminated wastewater and also found linear adsorption isotherms, with partitioning coefficients ranging from 902 to 2370 mL g⁻¹.

Possible treatment options for spent ion exchange resins

Regeneration processes are likely to produce a liquid waste that has higher treatment and disposal costs than the costs saved by a reuse of the media. Also, in theory, ion exchange process is reversible, but the medium is typically not completely regenerated, with typical restoration rates of up to 90%, that is, nuclear grade quality is maintained only until the first regeneration.³⁸

Ion exchange processes can be implemented in a variety of ways, including in batch systems, in column operations, and in membrane processes. Batch operation is simple to construct and operate, good for small scale applications, and easily customized for specific treatment problems.³⁸ In addition, bead-type media are easily removed by filtration.

There are two main methods for the treatment spent ion exchange resins³⁸: the destruction of organic compounds to produce inorganic intermediate product that may or may not be further conditioned for storage and/or disposal and direct immobilization, which produces a stable end product. Available pretreatment options include⁴⁸: dewatering (by pressure, vacuum filtration, and centrifugation), drying, and heating (fluidized bed dryers, vertical thin film dryers, and cone dryers), foam preparation, crushing, and grinding. These processes include thermal and nonthermal treatments. Thermal treatments encompass pyrolysis, incineration, vitrification, wet oxidation, thermochemical treatments, etc.³⁸

One of the most interesting from the point of view of organic ion exchangers, such as PGME-deta, is probably pyrolysis, which is a low-temperature thermal process (500–700°C), during which resins are degraded in an inert atmosphere. Pyrolysis experiments in Canada⁴⁹ and Japan⁵⁰ have demonstrated the potential of this process. Solid residue typically is about one-third the resin weight, and the rest is a gas-vapor fraction. The advantages of pyrolysis are volume reduction factors on the order of magnitude of 10, a biologically and geochemically stable end product, and a retention factor of nonvolatile radioactivity in the pyrolysis residue of 10⁶.³⁸ The literature data support the conclusion that pyrolysis may be an ideal solution for the used ion exchanger, because there seems to be a general consensus that at temperature ~ 500°C, the mass percent of solid residue of GMA-based polymers (barring those containing aromatic substituents) is less than 6%.^{51–53}

Spent organic exchangers may also be incinerated solely⁵⁴ or in combination with other combustible waste.⁵⁵ The incineration of spent resins in atmosphere rich in oxygen brings about oxidation of the initial feed material and a volume reduction factor in the range of 30–100. It is a well-known fact that conventional incineration of organic matter in the presence of oxygen, which is conducted at temperatures 650–1650°C, yields gaseous products only.

Typical acceptance criteria for the properties of immobilized waste forms are given in cited reference.⁵⁶

CONCLUSIONS

Macroporous crosslinked poly(GMA-co-EGDMA) copolymers with different porosity parameters were synthesized by suspension copolymerization and modified to amino-functionalized copolymers, poly(GMA-co-EGDMA)-deta, by ring-opening reaction of the pendant EG with diethylene triamine (deta). Synthesized samples were characterized by mercury porosimetry, elemental analysis, and FTIR-ATR spectroscopy.

Sorption of TcO₄⁻ on amino-functionalized poly(GMA-co-EGDMA) samples was investigated at room temperature in static (batch) experiments. It is found that the high sorption capabilities of synthesized copolymers for the removal of pertechnetate ions from aqueous solutions are due to nonspecific electrostatic interactions between negatively charged TcO₄⁻ ions and positively charged protonated amino groups of the modified macroporous polymers. The sorption of TcO₄⁻ is found to be influenced by pH and specific surface area of the copolymers. The sorption capacity for TcO₄⁻ decreases slowly in the pH range from 1.0 to 8.0. At pH 9.0, the quantity of TcO₄⁻ sorbed remained relatively high, about 90% of the maximum observed sorption capacity at pH 3.0. Above pH 9.0, the TcO₄⁻ uptake became lower than 40%.

The results of this work suggest that it is possible to almost completely remove TcO₄⁻ (91–98%) with macroporous poly(GMA-co-EGDMA)-deta from aqueous solutions in a wide range of pH values. The maximum sorption capacity of obtained macroporous polymers for TcO₄⁻ anions was reached within 180 min, with the sorption half times of under 25 min. The high affinity of macroporous poly(GMA-co-EGDMA)-deta for TcO₄⁻ was confirmed by their high partitioning coefficients, 2130 mL g⁻¹ for PGME1-deta and 1698 mL g⁻¹ for PGME2-deta.

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