Sorption of Uranyl Ions from Aqueous Solutions Using Crosslinked Maleic Anhydride-Octene-Styrene Terpolymer

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ABSTRACT: Maleic anhydride-octene-styrene terpolymer has been modified with allylic alcohol and methylmethacrylate to prepare a new crosslinked functional polymer sorbent. The sorption behaviors of uranyl ions on the optimum sorption conditions were determined. The synthesized crosslinked polymer sorbent has a network structure and contains carboxylic acid, carbonyl, and ester groups, all of which are capable of interacting with metal ions. The maximum experimental sorption capacity of the sorbent for uranyl ions has been measured as 1.25 mmol g^{-1}. Langmuir and Freundlich isotherm constants and correlation coefficients for the present system have been calculated and compared. Uranyl ions are desorbed from the sorbent by treatment with hydrocholric and nitric acids at various concentrations. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3570–3575, 2010

Key words: terpolymer; adsorption; copolymerization; uranyl ions; crosslinking

INTRODUCTION

Uranium is a potential environmental pollutant, especially in mining industry wastewater, and the migration of uranium in Nature is important in this context. In view of the anticipated exhaustion of terrestrial uranium reserves in the near future, research has been directed toward the recovery of uranium from nonconventional sources, such as coal and natural water.[1] Many types adsorbents have been developed and studied for the recovery and removal of uranium from aqueous media. Immobilized siloxane polymers have been used as sorbents for the sorption uranyl and other heavy metal ions from aqueous solutions.[2,3] Sorbents have contained amine, carboxylic acid, phosphinic acid, and other functional groups. Sorption can be explained in terms of complexing of metal ions with the functional groups of the sorbent. The extraction of uranyl ions by structured hydrogels composed of acrylamide-maleic acid and acrylamide –acrylic acid systems has been studied.[4,5] The sorption of uranyl ions on modified chitosan resins has been studied by atomic absorption spectroscopy,[6,7] whereby the sorption degree was found to be 90–93%. The sorption of urany ions on polyethylene glycol-methylacrylic acid hydrogels has been compared with that on polymethylacrylic acid homopolymer.[8] The effect of uranyl ion concentration on the sorption efficiency of the hydrogels was demonstrated. A new kind of copolymeric hydrogel adsorbent containing hydrophilic groups that provided both swelling in water and chelation of uranyl ions has been synthesized, and its adsorptive ability for recovering uranium from aqueous media was investigated.[9] The uranyl adsorption capacities of poly (2-hydroxyethyl methacrylate/ maleic acid) hydrogels were determined by a polarographic technique to be 3.2–4.8 mg UO_2^{2+}/g dry gel from a 15 ppm uranyl nitrate solution at pH 6, depending on the molar content of maleic acid in the hydrogel. Polyelectrolyte N-vinyl-2-pyrrolidone-g-tartaric acid hydrogels have been prepared and the effect of external stimuli, such as the solution pH, ionic strength and temperature, on uranyl adsorption by these hydrogels was investigated.[10] Uranyl adsorption capacites of the hydrogels were determined to be 53.2–72.2 mg UO_2^{2+}/g dry gel at pH 1.8 and 36.3–60.7 mg UO_2^{2+}/g dry gel at pH 3.8. The interaction of uranyl ions with interpenetrating polymer networks based on amidoximated poly (acrylonitrile)poly(vinyl-2-pyrrolidone) has also been examined.[11] The adsorption capacity of hydrogels, the adsorption kinetics and the effect of temperature on uranyl ion adsorption were investigated. Thermodynamic quantities and kinetic parameters were calculated from the adsorption isotherm data. The adsorption enthalpy, entropy, and free energy of the uranyl ion with hydrogels were calculated on the basis of thermodynamic relationships. The sorption of uranyl ions on acrylonitrile copolymers modified by NH_2OH, $NaOH$, and $NH_2NH_2 \cdot HCl$ has been

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investigated.[12] Sorption can be explained in terms complexing of uranyl ions with the functional groups of the sorbent. A water-soluble polymer of acrylic acid has also been used for the sorption of uranyl and other heavy metal ions.[13]

In this work the sorption of uranyl ions on a synthetic sorbent based on a maleic anhydride-octene-styrene terpolymer has been investigated. The analytical characteristics of the sorbent, such as pH, sorption degree, and sorption capacity have been established and the optimum sorption conditions have been determined.

EXPERIMENTAL

Materials and methods

All chemicals used were of analytical reagent grade. Maleic Anhydride (MA) was purified before use by recrystallization from benzene and by sublimation under vacuum. Octene-1 (OC), styrene (St), allyl alcohol (AA), and methylmethacrylate (MMA) were distilled before use and had the following characteristics: OC : b.p. 121–122°C; St : b.p. 144–145°C, AA : b.p. 97°C and MMA : b.p. 100°C. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. The sulfate salt was used for the preparation of a stock solution of uranyl ions. A pH-meter (model "Water Quality Checker U-10) was used for pH measurements. Infrared spectra of allylic ester films and sorbent were recorded in the range 450–4000 cm^{-1} using a Varian 3600 FTIR spectrometer. ^{1}H NMR spectra of the terpolymer were recorded on a spectrometer Bruker AC-300 (300 MHz). The sorbent degree and sorption capacity of the sorbent were calculated by the following equations:

$$\text{Sorption degree} = \frac{(C_0 - C_e)}{C_0} \times 100\%$$
$$\text{Sorption capacity} = \frac{(C_0 - C_e) \times V_{\text{sol}}}{m_{\text{sorb}}}$$

Where C_0 and C_e (mmol L^{-1}) are initial and equilibrium concentrations of uranyl ions solutions, respectively, V_{sol} (L) is the volume of the uranyl solution submitted to sorption, and m_{sorb} (g) is the weight of sorbent. The optimum sorption conditions like pH of media, weight of sorbent and initial concentration of uranyl ions has been determined using batch equilibriation technique at statical conditions. Dried samples of sorbent were placed in 40 mL of uranyl solution in a 100 mL single-necked round flack and left for 24 h at 25°C. Then the sorbent filtered out and the concentration of the remaining uranyl ions were determined. Uranyl ion concentrations were determined according to change in ^{235}U-isotope activity, which was determined from peak at 185.7 KeV in the gamma-spectra of the uranyl solutions (gamma – spectrometer "Canberra" with an HPGe germanium detector).

PREPARATION OF THE CROSSLINKED TERPOLYMER

The sorbent has been prepared by consecutive reactions, which was illustrated on the Scheme 1.

Synthesis of maleic anhydride-octene-styrene terpolymer

Maleic anhydride-octene-styrene terpolymer (TPL) was synthesized by free-radical terpolymerisation in acetic anhydride (Ac$_2$O) solution in the presence of AIBN as an initiator. AIBN (50 mg), MA (9.8 g), OC (5.6 g, 7.8 mL) and St (5.2 g, 5.7 mL), (molar ratio MA/OC/St = 2 : 1 : 1) were dissolved in Ac$_2$O (30 mL). After heating the mixture at 70°C for 1 h the polymer precipitated in ethanol and dried at 40°C in a vacuo (72.6% yield). The monomer contents were determined by chemical analysis and the ^{1}H NMR – spectrum. It was established that the molar contents of MA, OC, and St in the terpolymer were 51.2, 18.0, and 30.8 mol %, respectively. The intrinsic viscosity 0.65 dl g^{-1} (methyl ethyl ketone, 20°C).

Preparation of TPL monoallyl ester

Monoallylic ester of TPL (MeTPL) was prepared by following technique: TPL (8.2 g) and AA (3.5 g, 4.1 mL) were dissolved in methylcyclohexanone (25 mL) and heated at 80°C for 3 h. The MeTPL precipitated in heptane and dried at 40°C in a vacuo. Double bond of allylic group was identified by IR spectra (916 and 1636 cm^{-1}).

Copolymerisation of the MeTPL with MMA

A mixture of MeTPL (5.3 g), MMA (3.0 g, 3.2 mL), and AIBN (0.166 g, 2%) was heated at 80°C for 3 h. The obtained crosslinked polymer was then washed repeatedly with chloroform to remove of residual MMA and poly-MMA. The sorbent was dried in vacuum at 30°C.

RESULT AND DISCUSSION

Characterization of the crosslinked polymer

The prepared crosslinked polymer proved to be insoluble in water and organic solvents. The crosslinked terpolymer has a network structure and contains various functional groups (—COOH, —OCO, =CO). Figure 1 shows FTIR spectra of synthesized sorbent. It shows clearly that the characteristic peak at 3419 cm^{-1} the strong and broad absorption band
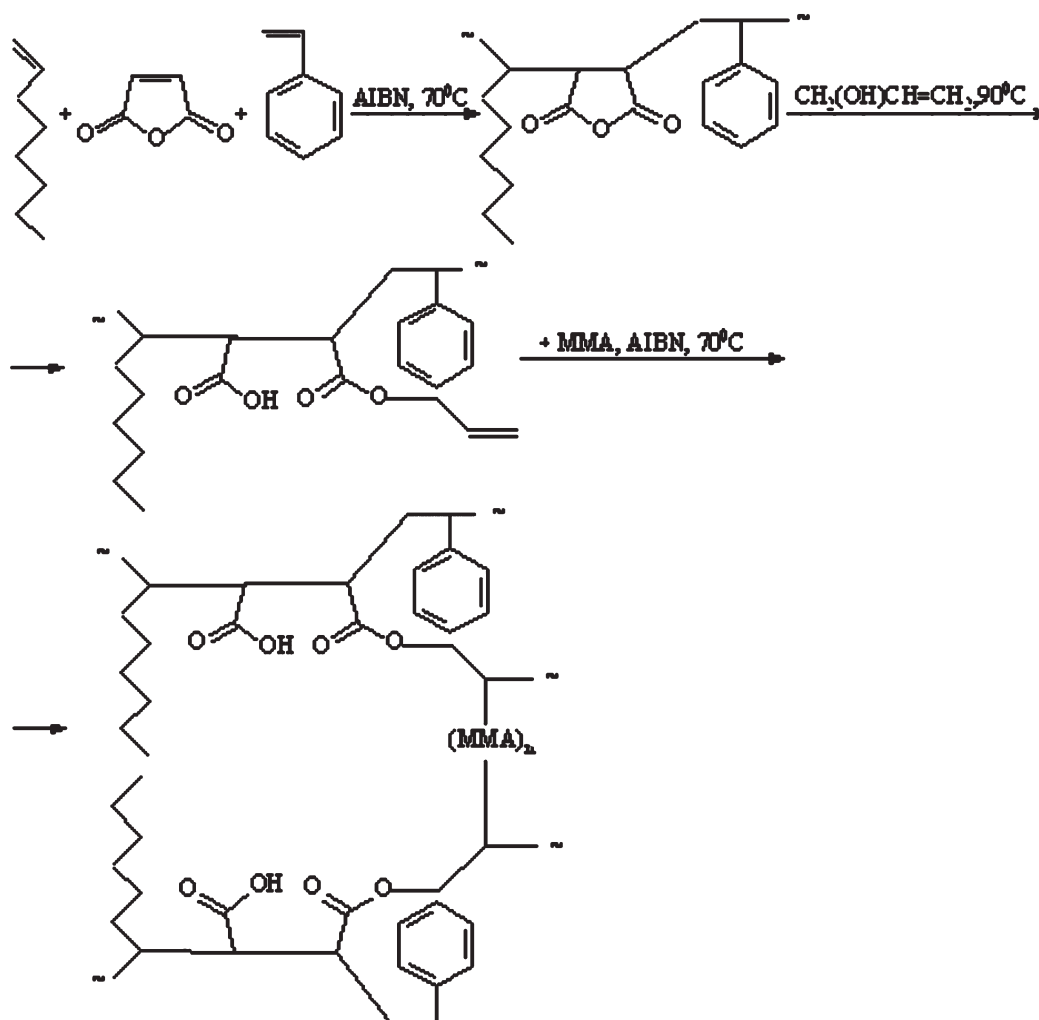
Scheme 1 Synthetic pathway used to obtain crosslinked terpolymer.

of stretching vibration of hydroxyl group of carboxylic acid. The peaks 1112 and 1043 cm^{-1} are related to asymmetry and symmetry vibrations of C—O—C, respectively. It is very important that the absorption band peaking at 1637 cm^{-1} corresponds to structure characteristic of carbonyl group. The absorption
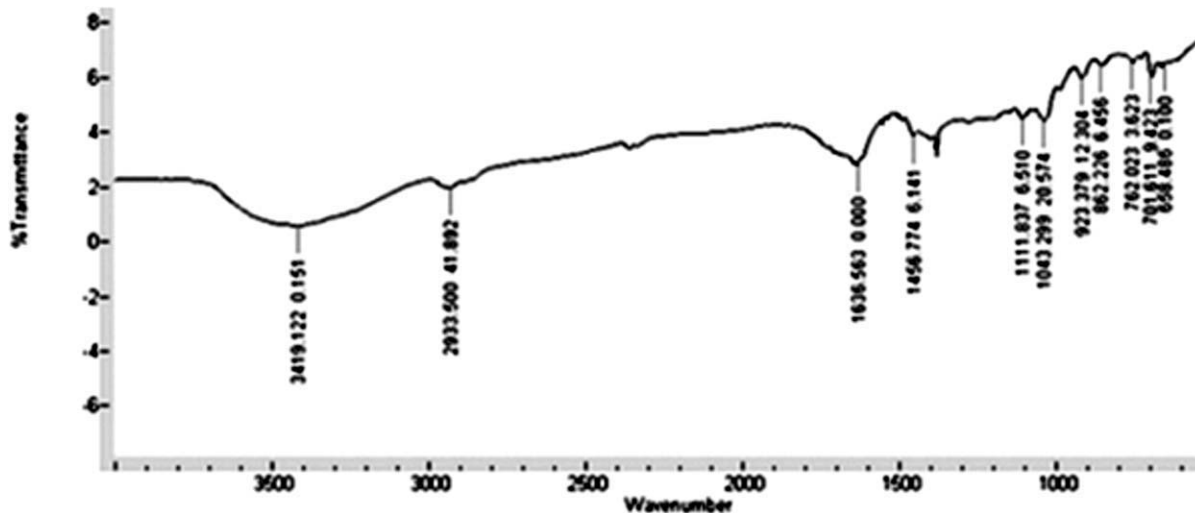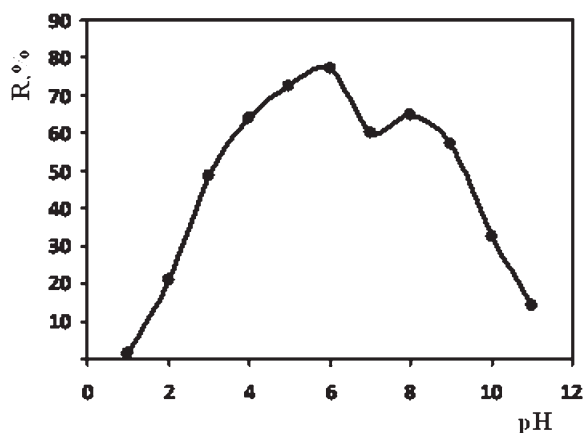

Figure 1 FTIR spectra of sorbent.

Figure 2 Effect of pH on the sorption of uranyl ions (C_0 = 0.98 mmol L^{-1}, V_{sol} = 0.04 L, m_{sorb} = 0.05 g, 25°C, 24 h).

peaks at 2933 cm^{-1} belong to the stretching vibration of C—H bonds of octene-1 units. Overall, it can be deduced logically that the TPL, modified by allyl alcohol and MMA has definitely crosslinked structure. In the complexation, which is associated with sorption, depending on the sorption conditions, carboxylic acid, ester, and carbonyl groups can participate.

Effect of the pH medium

Figure 2 shows the sorption degree for uranyl ions as a function of pH using the prepared sorbent. The results indicate that the sorption process is most favorable at pH 5–6. As is evident from the values obtained for a strongly acidic medium (pH 1–2) uranyl ion sorption proceeds only very slowly (sorption degree 1–20%), which may be ascribed to the equilibrium being displaced toward desorption owing to replacement of uranyl ions by hydrogen ions on the one hand, and blocking of sorbent coordination cen-
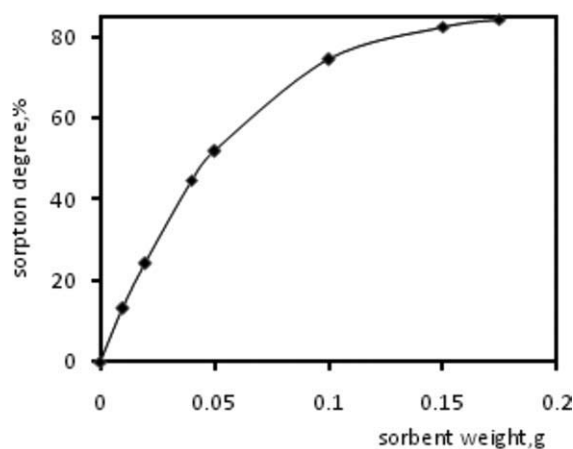
Figure 3 Effect of sorbent weight on the sorption of uranyl ions (C_0 = 2.94 mmol L^{-1}, V_{sol} = 0.04 L, pH 6, 25°C, 24 h).
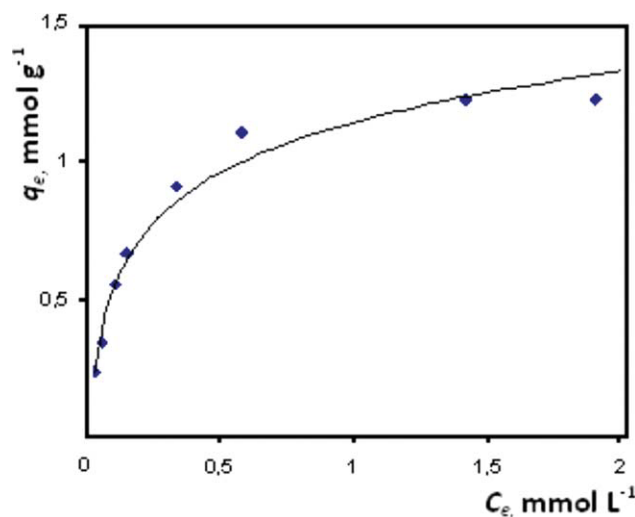
Figure 4 Adsorption isotherm of sorbent (pH 6, V_{sol} = 0.04 L, m_{sorb} = 0.05 g, 25°C, 24 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ters by hydrogen ions on the other. As the acidity is decreased, the sorption degree increases and reaches maximum at pH 5–6 (72–77%). At higher pH (pH 8–11) the percentage removal of uranyl ions decreases owing to formation of insoluble $UO_2(OH)_2$ and hydrolysis of uranyl ions forming complex hydroxy anions, such as $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$, $(UO_2)_3(OH)_7^-$, $(UO_2)_3(OH)_8^{2-}$, $(UO_2)_3(OH)_{10}^{4-}$ and $(UO_2)_3(OH)_{11}^{5-}$. Formation of products of hydrolysis of uranyl ions has been studied by Nguyen Trung and et al.[14]

Effect of sorbent weight

Figure 3 shows the dependence of sorption degree on sorbent weight. The sorbent weight was varied from 0.01 up to 0.175 g at a concentration of uranyl ions of 2.94 mmol L^{-1} and pH 6. Application of a
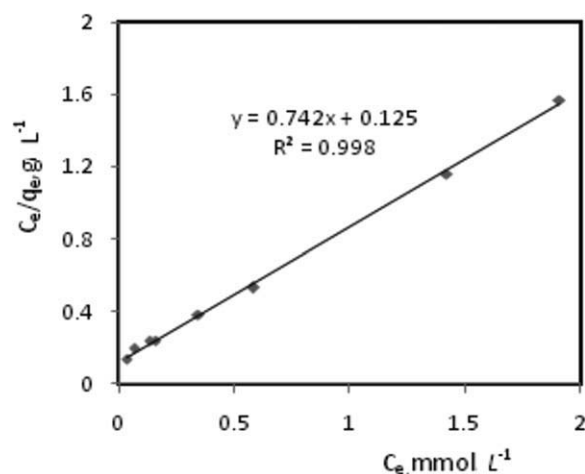
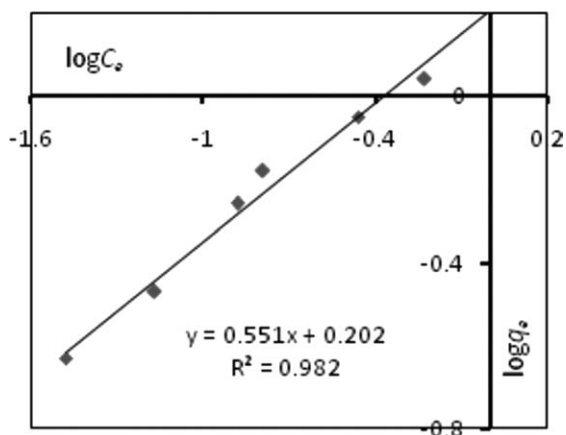**Figure 5** Langmuir plot for sorption of uranyl ions.

Figure 6 Freundlich plot for sorption of uranyl ions.

more concentrated solution is associated with providing the capacity for maximum sorption with rather large amount of sorbent. From Figure 3, it can be seen that with increasing of sorbent weight the sorption degree increases and reaches 85% at 0.15–0.175 g of sorbent. The results indicate that near-complete extraction of uranyl ions from more concentrated solutions under static conditions, a rather large quantity of sorbent is required.

Adsorption isotherm of sorbent

The metal uptake mechanism is dependent on the initial heavy metal concentration: at low concentrations metals are adsorbed at specific sites, whereas with increasing of metal ion concentration the specific sites are saturated and the exchange sites are filled.[15] Figure 4 shows the adsorption isotherm of uranyl ions by synthesized sorbent at 25°C. The experimental results show that the equilibrium adsorption capacity of sorbent increases rapidly with the increasing of equilibrium concentration of uranyl ions. However, when the uranyl ion concentration increased to a certain extent, the increasing trend of adsorption capacity became slower. We can conclude that the maximum equilibrium adsorption

TABLE I
Langmuir and Freundlich Sorption Constants Obtained from the Langmuir and Freundlich Sorption Isotherms at 25°C

| Langmuir constants			Freundlich constants		
q_{max} (mmol g^{-1})	K_L(L mol^{-1})	R^2	K_F	n	R^2
1.35	5.94	0.998	1.59	1.81	0.982

capacity of sorbent toward to uranyl ions is 1.25 mmol g^{-1}. Figure 4 also shows that in the studied interval of concentration of uranyl ions the adsorption process occurs on a monomolecular layer and is described by Langmuir model. But, it is possibly that at higher concentration of uranyl ions character of adsorption can vary and experimental value of the sorption capacity will differ from its limiting value found on dependence $C_e/q_e = f(C_e)$.

Langmuir and Freundlich models

The adsorption isotherm can be approximately expressed as a mathematical equation when it obeys an adsorption model. In other words, it is possible that the correlation between equilibrium concentration (C_e), obtained from experiments and the equilibrium adsorption capacity (q_e) would accord with certain mathematical formula. Actually, the Langmuir equation and Freundlich equation are the most usual calculation formula for experimental data of liquid phase adsorption if the sorption of solvent is neglected. The verification of linear relationship by substituting the experimental data into eq. (1) is the way to estimate whether they truely obey Langmuir model

$$C_e/q_e = 1/K_L q_{max} + C_e/q_{max} \qquad (1)$$

where C_e (mmol L^{-1}) is the equilibrium concentration of metal ions in the solution, q_e (mmol g^{-1}) the equilibrium adsorption capacity of metal ion on
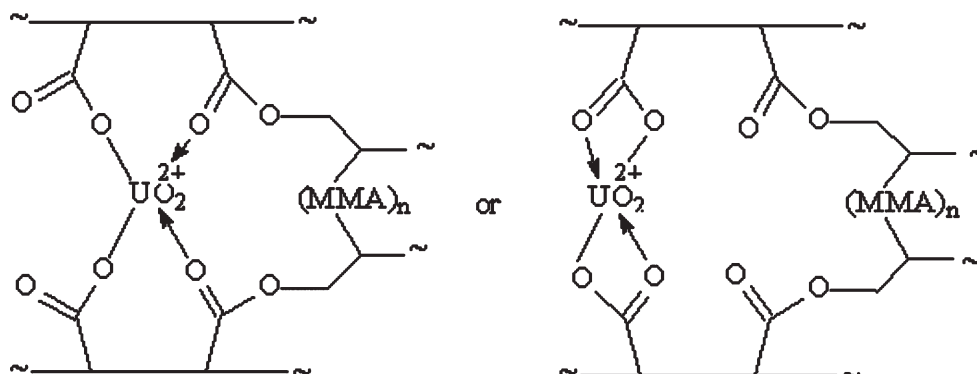
Scheme 2 Probable complexation modes of uranyl ions with carboxylic acid and carbonyl groups of the sorbent.

TABLE II
Desorption Degree (R) at Various Concentrations of HCl and HNO$_3$ (m_{sorb} = 0.05 g, 25°C, 24 h)

Concentration of HCl or HNO$_3$ (%)		0	5	10	15	20	25
R (%)	HCl	2.4	52.8	62.3	88.9	92.5	93.5
	HNO$_3$	2.4	14.1	34.1	51.7	90.5	95.9

sorbent, q_{max}(mmol g^{-1}) the saturated (maximum) capacity, K_L is a Langmuir constant. In the same way, the confirmation of linear relationship of eq. (2) substitution method is the way to evaluate whether the experimental data fit the Freundlich model.

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (2)$$

where, K_F and n are the adsorption constants.

The linear plot of specific sorption (C_e/q_e) versus equilibrium concentration of uranyl ions in solution (C_e) and the logarithmic plot of the Freundlich equation for the equilibrium adsorption capacity (log q_e) and equilibrium concentration (log C_e) are given in Figures 5 and 6, respectively. The values of q_{max}, K_L, K_F, and n were calculated from the slope and intersept of the plots and are shown in Table I. The obtained values of parameters of the Langmuir equation specify high enough sorption activity of the synthesized sorbent toward to uranyl ions. The high value of K_L (5.94) is connected probably with uranyl ions strong attraction on the sorbent surface owing to chemical interaction uranyl ions with functional groups of sorbent chelate center. The most probable complexation mode of uranyl ions with polymer sorbent is presented in the following Scheme 2.

From Table I, $n = 1.81$ and $(1/n) = 0.552$ that satisfies requirement of the Freundlich equation (in usual $0 < (1/n) < 1$). It means that the sorption process in the investigated interval concentration of the uranyl ions is enough described by Freundlich model.

Desorption of uranyl ions from the sorbent

After the sorption experiments, the sorbent was collected by filtration and washed with deionized water. The treated sorbent was placed in distilled water, hydrochloric and nitric acids of various concentrations were added, and the mixtures were left for 24 h. The results are given in Table II. As can be seen from Table II, migration of uranyl ions to the neutral aqueous medium was practically unobserv-

able (R = 2.4%), whereas nearly full extraction of uranyl ions from the sorbent took place in 20% aqueous HCl and HNO$_3$ solutions. The results further confirmed the above-stated assumption that in strongly acidic media sorption–desorption equilibrium is displaced to the desorption side.

CONCLUSIONS

The preparation, characterization, and application of a crosslinked maleic anhydride-octene-styrene terpolymer containing various functional groups have been elaborated. The new sorbent has been used for the removal of uranyl ions from aqueous solutions. The sorption properties of the sorbent have been determined under different conditions by varying the pH of medium, the weight of sorbent and the initial concentration of uranyl ions. Sorption isotherms of uranyl ions on the prepared polymer sorbent have been measured and the equilibrium data fitted well to the Langmuir and Freundlich isotherm models. Using 20% aqueous solutions of HCl and HNO$_3$ the feasibility of regeneration of the prepared polymer sorbent has been demonstrated. This study has provided the theoretical basis for sorbent synthesized on the basis TPL, to be applied in adsorption systems, such as wastewater treatment, ion exchange, etc.

References

1. Kavakli, P.; Guven, O. J Appl Polym Sci 2004, 93, 1705.
2. El-Nahhal, I. M.; Zaggout, F. R.; El-Ashgar, N. M. Anal Lett 2000, 33, 3373.
3. Zaggout, F. R.; El-Nahhal, I. M.; El-Ashgar, N. M. Anal Lett 2001, 34, 247.
4. Kavakli, P.; Guven, O. J Appl Polym Sci 2000, 78, 284.
5. Chanshyam, S. J Appl Polym Sci 2008, 110, 3795.
6. Atia Asem, A. Hydrometallurgy 2005, 69, 13.
7. Minamisawa, H.; Iwanaki, H.; Arai, I. Anal Chim Acta 1992, 378, 279.
8. Mun, G. A.; Nurkeeva, Z. C.; Irmukhametova, G. S.; Guven, O. Nucl Instrum Methods Phys Res 2007, 265, 379.
9. Caykara, T.; Recai , I.; Cengiz, O. J Polym Sci A 2001, 39, 277.
10. Oren, S.; Caykara, T.; Kantoglu, O.; Olgun , C. J Appl Polym Sci 2000, 78, 2219.
11. Pekel, N.; Sahiner, N.; Olgun, G. J Appl Polym Sci Part B: Polym Phys 2004, 42, 986.
12. Godjevaryova, T.; Simeonova, A.; Dimov, A. J Appl Polym Sci 2001, 79, 283.
13. Bakircioglu, J.; Sergen, G.; Akman, S. Spectrochim Acta 2000, 55, 1129.
14. Nguyen-Trung, C.; Begun, G. M.; Peiffert, C.; Mesmer, R. E.; Palmer, D. A. J Solution Chem 2000, 29, 101.
15. Patel, M.; Karadia, M.; Patel, G. Joshi, J. React Funct Polym 2007, 67, 74.