

# Synthesis and uranyl ion adsorption study of cross-linked allyl propionate-maleic anhydride-styrene terpolymer

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Allyl propionate-maleic anhydride-styrene terpolymer has been modified with glycerin in order to prepare a new cross-linked functional polymer sorbent. The synthesized cross-linked polymer sorbent has a network structure and contains carboxylic acid, carbonyl, hydroxy, and ester groups, all of which are capable of interacting with metal ions. The sorption behavior of  $\text{UO}_2^{2+}$  ions under optimum sorption conditions was determined. The sorption properties of the sorbent were determined under different conditions by varying of the pH of medium, the sorbent weight, and the initial concentration of uranyl ions. The maximum experimental sorption capacity of the sorbent for uranyl ions was measured as  $1.63 \text{ mmol g}^{-1}$  ( $440 \text{ mg UO}_2^{2+} \text{ g}^{-1}$ ). Langmuir and Freundlich isotherm constants and correlation coefficients for the present system were calculated and compared. Uranyl ions are desorbed from the sorbent by treatment with hydrochloric and nitric acids at various concentrations.

**Key Words:** Adsorption; sorption degree; sorption isotherms; cross-linked terpolymer; uranyl ions.

## 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 unconventional sources, such as coal and natural water.<sup>1</sup> Many types of 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 of uranyl and other heavy metal ions from aqueous solutions.<sup>2,3</sup> Sorbents contain amine, carboxylic acid, phosphinic acid, and other functional groups. Sorption can be explained in terms of complexing

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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.<sup>4,5</sup> The sorption of uranyl ions on modified chitosan resins has been studied by atomic absorption spectroscopy,<sup>6</sup> whereby the sorption degree was found to be 90%–93%. The sorption of uranyl ions on polyethylene glycol-methylacrylic acid hydrogels has been compared with that on polymethylacrylic acid homopolymer.<sup>7</sup> The effect of uranyl ion concentration on the sorption efficiency of the hydrogels has been 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 has been investigated.<sup>8</sup> The uranyl ion adsorption capacities of poly (2-hydroxyethyl methacrylate/maleic acid) hydrogels have been 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 has been investigated.<sup>9</sup> Uranyl adsorption capacities of the hydrogels have been 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.<sup>10</sup> The adsorption capacity of the hydrogels as well as the adsorption kinetics and the effect of temperature on uranyl ion adsorption have been 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. A water-soluble polymer of acrylic acid has also been used for the sorption of uranyl and other heavy metal ions.<sup>11</sup>

In the present work, the sorption of  $UO_2^{2+}$  ions on a synthetic sorbent, synthesized on the basis of allyl propionate-maleic anhydride-styrene terpolymer was investigated. The analytical characteristics of the sorbent, such as pH, sorption degree, and sorption capacity, were established and the optimum sorption conditions were determined.

## Experimental

### Materials and instruments

All chemicals used were of analytical reagent grade. Maleic anhydride (MA) was purified before use by recrystallization from benzene and by sublimation under vacuum. Allyl propionate (AP) and styrene (St) were distilled before use and had the following characteristics: AP: b.p. 122–123 °C; St: b.p. 144–145 °C. Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. The sulfate salt was used for the preparation of the ions stock solution. The pH values were checked by means of a pH-meter (model “Water Quality Checker U-10”). Infrared spectra of the terpolymer and sorbent on a KBr pellets were recorded in the range 450–4000  $cm^{-1}$  using a Varian 3600 FTIR spectrophotometer. <sup>1</sup>H-NMR spectra of the terpolymer were recorded on a Bruker AC-300 (300 MHz) spectrometer at room temperature in acetone d<sub>6</sub>. Uranyl ion concentrations were determined according to change in <sup>235</sup>U-isotope activity, which was determined from the peak at 185.7 KeV in the gamma spectra of the uranyl solutions (gamma - spectrometer “Canberra” with an

HPGe germanium detector). The sorption degree and sorption capacity of the sorbent have been calculated by the following equation:

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

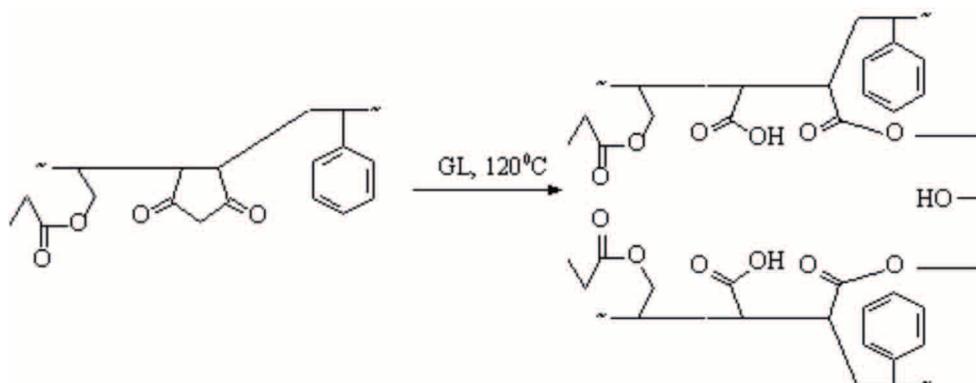
where  $C_0$  and  $C_e$  ( $\text{mmol L}^{-1}$ ) are initial and equilibrium concentrations of uranyl ions solutions, respectively,  $V_{sol}$  (L) is the volume of the uranyl solution submitted to sorption, and  $m_{sorb}$  (g) is the weight of sorbent.

### Synthesis of allyl propionate-maleic anhydride-styrene terpolymer



Allyl propionate-maleic anhydride-styrene terpolymer (TPL) was synthesized by free-radical terpolymerization in acetic anhydride ( $\text{Ac}_2\text{O}$ ) solution in the presence of AIBN as an initiator. MA (9.8 g), AP (5.7 g, 6.0 mL), St (5.2 g, 5.7 mL) (molar ratio MA/AP/St = 2:1:1), and AIBN (50 mg) were dissolved in  $\text{Ac}_2\text{O}$  (30 mL). After heating the mixture at 70 °C for 1 h, the terpolymer was precipitated in ethanol and dried at 40 °C in a vacuum oven (85.0% yield). The monomer contents were determined by chemical analysis and the  $^1\text{H-NMR}$  spectrum. It was established that the molar contents of MA, AP, and St in the terpolymer were 49.2, 16.3, and 34.5 mol %, respectively. The intrinsic viscosity was measured as 0.75 dL  $\text{g}^{-1}$  (methyl ethyl ketone, 20 °C).

### Preparation of the cross-linked terpolymer

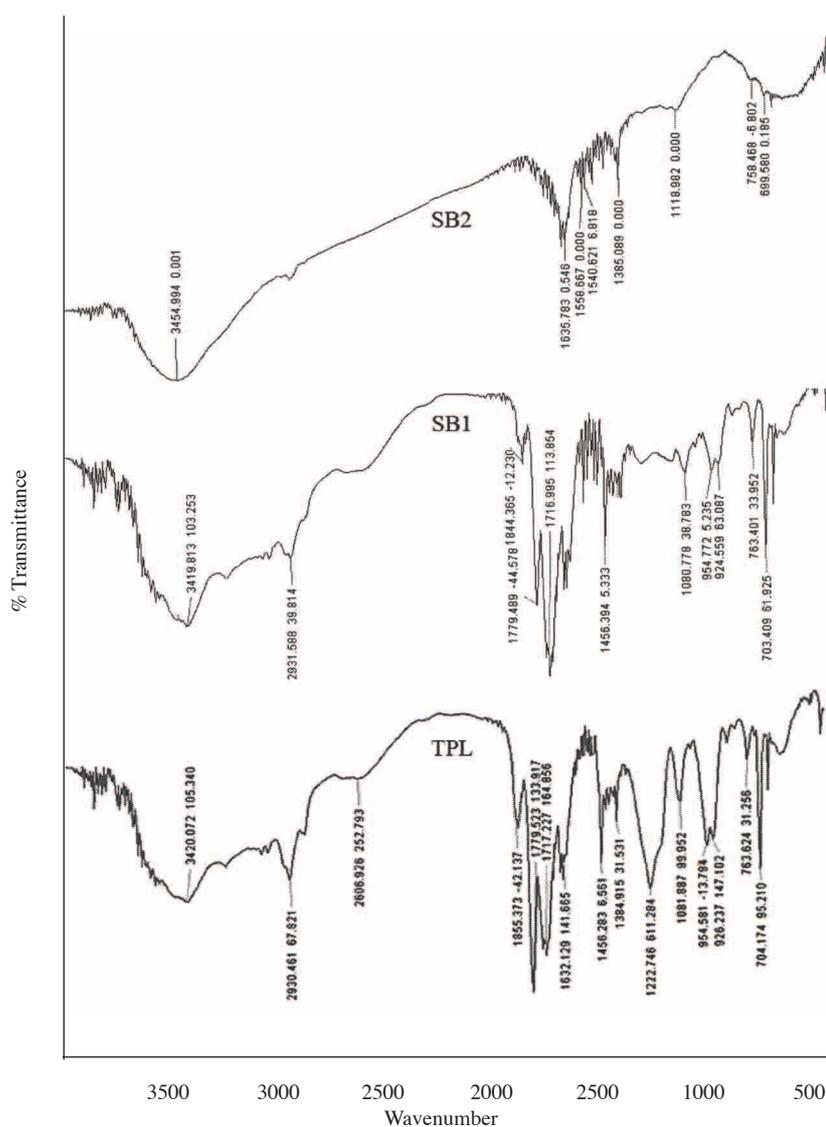


A mixture of TPL (4.1 g) and glycerin (GL) (2.8 g, molar ratio 1:3) was heated at 120 °C for 3 h. The obtained cross-linked polymer was washed repeatedly with distilled water and acetone to remove residual GL and TPL. The sorbent was dried at 30 °C in a vacuum oven. The prepared sorbent proved to be insoluble in water and organic solvents, had a network structure, and contained various functional groups ( $-\text{COOH}$ ,  $-\text{OCO}$ ,  $=\text{CO}$ ,  $-\text{OH}$ ).

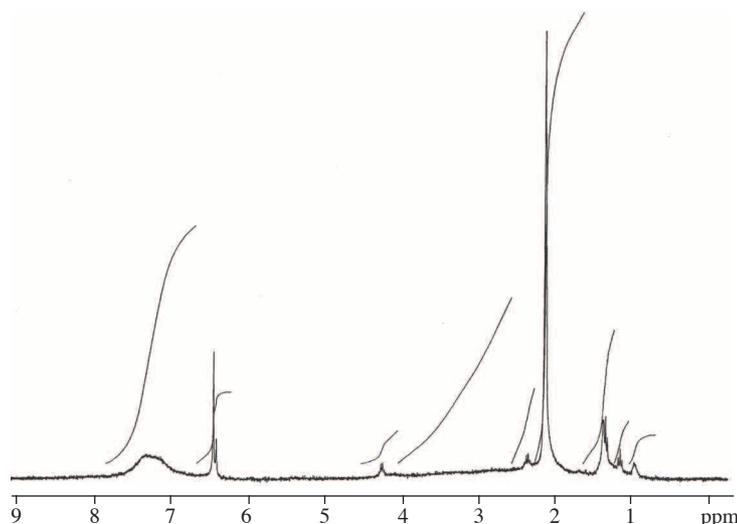
## Results and discussion

### FT-IR and <sup>1</sup>H-NMR spectroscopy

The synthesized TPL was characterized by FT-IR (Figure 1) and <sup>1</sup>H-NMR (Figure 2) spectroscopy. The IR spectrum of the TPL shows 2 bands at 1779 cm<sup>-1</sup> and 1855 cm<sup>-1</sup>, which are assigned to C=O stretching vibrations, and the absorption band at 1222 cm corresponds to the C-O-C stretching vibration in the cyclic anhydride structure. The peak around 2930 cm<sup>-1</sup> was due to the stretching vibration of C-H bonds of AP units. The peaks at 704 and 763 cm<sup>-1</sup> are related to C-H bonds of the benzene ring of St units. The peaks at 1717 and 3420 cm<sup>-1</sup> are related to the carboxyl group, which was obtained in the TPL synthesis process.



**Figure 1.** FT-IR spectra of terpolymer and sorbent before and after adsorption.



**Figure 2.**  $^1\text{H-NMR}$  spectra of terpolymer.

In the  $^1\text{H-NMR}$  spectrum of TPL characteristic peak signals corresponding to  $\delta$ -0.9 ppm for  $-\text{CH}_3$ ,  $\delta$ -1.1 ppm for  $-\text{CH}_2$ , and  $\delta$ -4.2 ppm for  $-\text{OCH}_2$  groups in AP units. The peak at  $\delta$ -1.2 ppm and peaks between  $\delta$ -7.0 and 7.6 ppm are due to methylene/methine and aromatic ring hydrogen of St, respectively. The characteristic peak signal corresponding to  $\delta$ -2.3 ppm was for  $-\text{HC-CH-}$  in MA units.

The ring-opening reaction of MA units by TEA resulted in the formation of crosslinked polymer with carboxylic groups and ester bonds. The FT-IR spectra of the crosslinked sorbent (SB1) are given in Figure 1. As expected, in the conversion of the anhydride cycle to carboxylic and ester groups after the reaction of TPL with TEA the anhydride absorption intensity peaks at  $1855$  and  $1779\text{ cm}^{-1}$  were decreased, and instead new carboxyl and ester groups peaks appeared in the range  $1700$ - $1727\text{ cm}^{-1}$ . Peaks relating to unreacted anhydride groups ( $1844$ ,  $1779$ ,  $1222\text{ cm}^{-1}$ ) in the FT-IR spectrum are clearly seen. The peak at  $3420\text{ cm}^{-1}$  is relevant to stretching vibration of the hydroxyl group of  $-\text{COOH}$  and  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$  groups. The FT-IR spectrum of the sorbent after adsorption process (SB2) is given in Figure 1. The intensity of the  $\text{C}=\text{O}$  bands associated with the  $-\text{COOH}$  group at  $1700\text{ cm}^{-1}$  disappeared while the asymmetric bands of the  $\text{COO}^-$  (carboxylate) structure in the  $1540$ - $1560\text{ cm}^{-1}$  region were formed. The broad peak at  $1636\text{ cm}^{-1}$  is relevant to the ester group at chelate form.<sup>12</sup> These spectral data show that the uranyl ion enters into a complex with sorbents carboxylic and ester groups sorbent. The comparison of sorbent IR spectra before and after adsorption also shows that absorption bands  $1222$ ,  $1779$ , and  $1844\text{ cm}^{-1}$  carried to unreacted anhydride groups disappear as a result of hydrolysis in the water medium. The broad band in the  $3500\text{ cm}^{-1}$  region is relevant to the  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$  fragment of the sorbent.

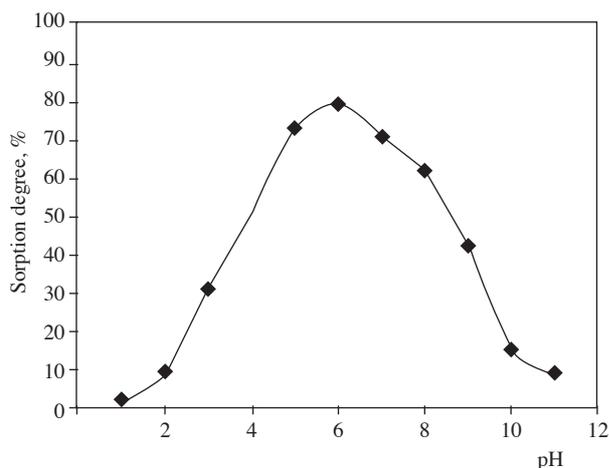
### Effect of the pH of medium

In Figure 3 the sorption degree for uranyl ions is shown as a function of pH using the prepared sorbent. The results indicate that the sorption process is most favorable at pH 6. As is evident from the values obtained for a strong acid medium (pH 1–2), uranyl ion sorption proceeds very slowly (sorption degree 1.6%-9.4%), which may be ascribed to the equilibrium that has been displaced towards desorption owing to replacement

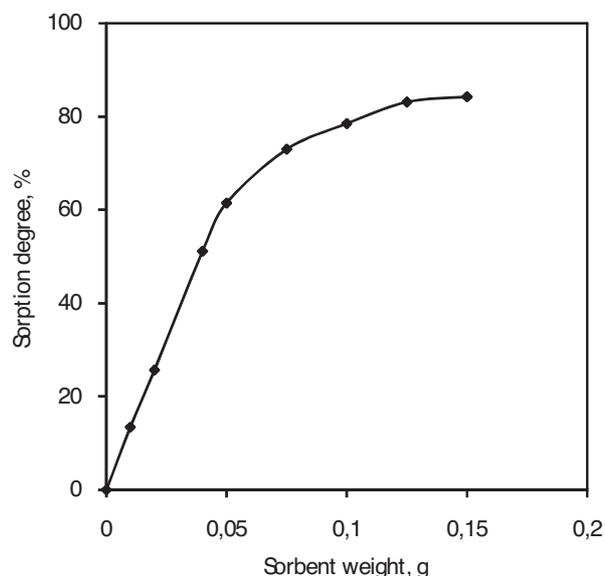
of uranyl ions by hydrogen ions on the one hand, and blocking of sorbent coordination centers by hydrogen ions on the other. As the acidity has been decreased, the sorption degree increases and reaches a maximum at pH 6 (82.3%). At higher pH values (7-11), the percentage removal of uranyl ions decreases owing to formation of insoluble  $UO_2(OH)_2$  and  $UO_2(OH)_3^-$ ,  $UO_2(OH)_4^{2-}$ ,  $(UO_2)_3(OH)_7^-$ ,  $(UO_2)_3(OH)_8^{2-}$ ,  $(UO_2)_3(OH)_{10}^{4-}$ , and  $(UO_2)_3(OH)_{11}^{5-}$  as a result of the hydrolysis of uranyl ions.<sup>13</sup>

### Effect of sorbent weight

Figure 4 shows the dependence of sorption degree on sorbent weight. The sorbent weight was varied from 0.01 up to 0.15 g at the concentration of uranyl ions of  $3.14 \text{ mmol L}^{-1}$  and pH 6. Application of a more concentrated solution is associated with providing the capacity for maximum sorption with a rather large amount of sorbent. From Figure 3 it can be seen that with increasing sorbent weight the sorption degree increases too and reaches 83.1%-85.0% at the weight of sorbent 0.125–0.15 g. The results indicate that for near-complete extraction of uranyl ions from more concentrated solutions under static conditions a rather large quantity of sorbent was required.



**Figure 3.** Effect of pH on the sorption of uranyl ions ( $C_0 = 0.98 \text{ mmol L}^{-1}$ ,  $V_{sol} = 0.04 \text{ L}$ ,  $m_{sorb} = 0.05 \text{ g}$ ,  $25 \text{ }^\circ\text{C}$ , 24 h).



**Figure 4.** Effect of sorbent weight on the sorption of uranyl ions ( $C_0 = 3.14 \text{ mmol L}^{-1}$ ,  $V_{sol} = 0.04 \text{ L}$ , pH = 6,  $25 \text{ }^\circ\text{C}$ , 24 h).

### Adsorption isotherms study

The metal uptake mechanism depends on initial heavy metal concentration: under low concentrations the metals were adsorbed at specific sites, whereas with increasing metal ion concentration the specific sites were saturated and exchange sites were filled.<sup>14</sup> Uranyl ions adsorption was studied at an initial uranyl concentration of  $0.39\text{-}4.71 \text{ mmol L}^{-1}$  and equilibrium adsorption capacity of sorbent was calculated. Figure 5 shows the

adsorption isotherm of uranyl ions by synthesized sorbent at 25 °C. The experimental results show that the adsorption capacity of sorbent increases rapidly with the increasing of equilibrium ion concentration. However, when the uranyl ion concentration reached a certain level, the upward trend of adsorption capacity became slower. We can conclude that the maximum experimental value of adsorption capacity of sorbent towards uranyl ions is 1.63 mmol g<sup>-1</sup> (440 mg UO<sub>2</sub><sup>2+</sup> g<sup>-1</sup>). As shown from Figure 5, in the studied interval of uranyl ion concentration the adsorption process occurs on a monomolecular layer and was described using the Langmuir model. However, it is possible that at higher initial concentrations of uranyl ions the character of adsorption may vary and the experimental value of the sorption capacity will differ from its limiting value found from dependence  $C_e/q_e = f(C_e)$ . 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 a certain mathematical formula. Actually, the Langmuir equation and Freundlich equation are the most usual calculation formulae for experimental data of liquid phase adsorption if the sorption of solvent is neglected. Verification of the linear relationship by substituting the experimental data into Eq. (1) is the way to estimate whether they truly obey the Langmuir adsorption model

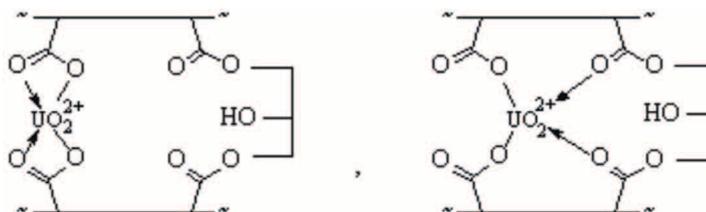
$$C_e/q_e = 1/K_L q_{max} + C_e/q_{max} \quad (1)$$

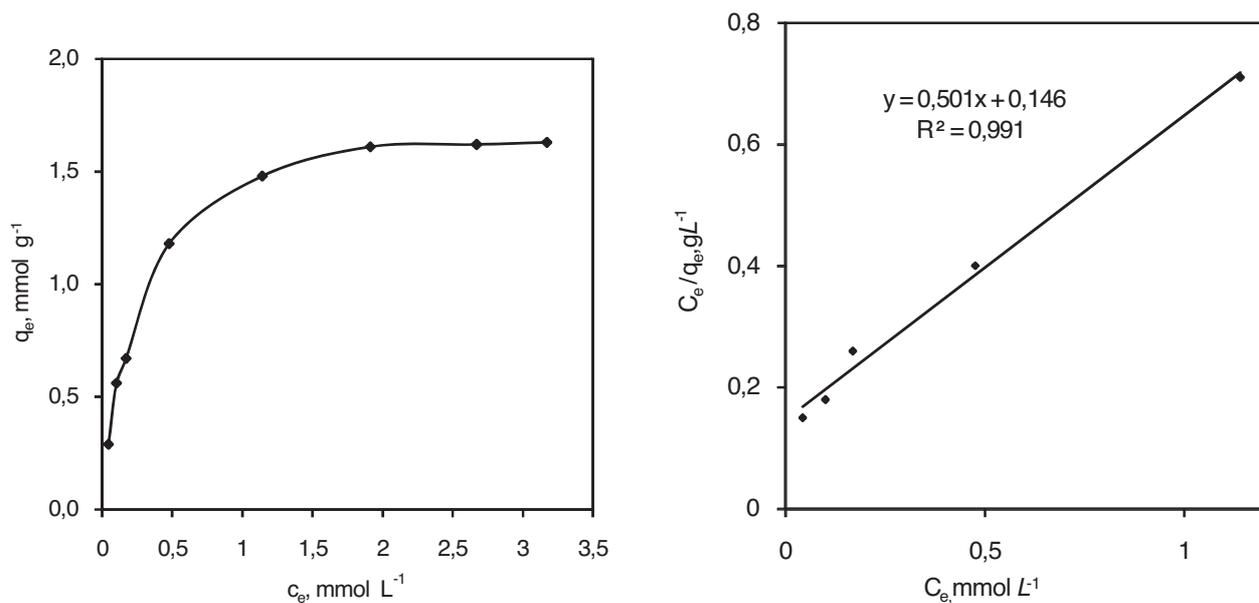
where  $C_e$  (mmol L<sup>-1</sup>) is the equilibrium concentration of metal ions in the solution,  $q_e$  (mmol g<sup>-1</sup>) the equilibrium adsorption capacity of metal ion on sorbent,  $q_{max}$  (mmol g<sup>-1</sup>) is the saturated (maximum) capacity, and  $K_L$  is a Langmuir constant. In the same way, confirmation of the linear relationship of Eq. (2) substitution method is the way to evaluate whether the experimental data fit the Freundlich model

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

where  $K_F$  and  $n$  are the adsorption constants.

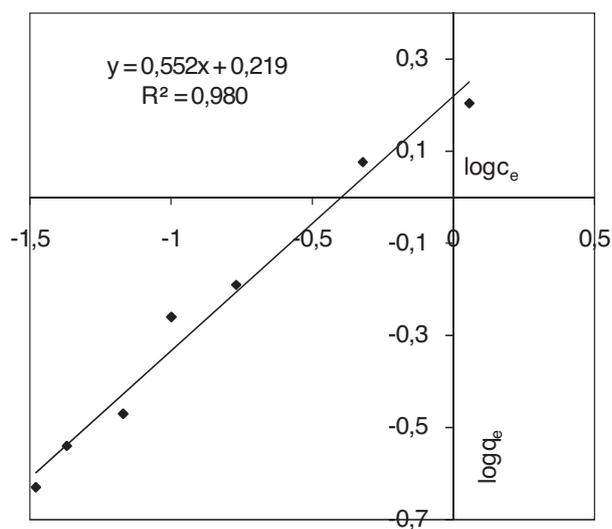
The linear curve of specific sorption ( $C_e/q_e$ ) versus equilibrium concentration of uranyl ions in solution ( $C_e$ ) and the logarithmic curve of the Freundlich equation for the equilibrium adsorption capacity ( $\log q_e$ ) and equilibrium concentration ( $\log C_e$ ) are given in Figure 6 and Figure 7, respectively. The values of  $q_{max}$ ,  $K_L$ ,  $K_F$ , and  $n$  were calculated from the slope and intercept of the plots and are shown in Table 1. The obtained values of the Langmuir equation parameters specify the sufficiently high sorption activity of the synthesized sorbent towards uranyl ions. The high value of  $K_L$  (3.43) is probably connected with uranyl ions' strong deduction on a sorbent surface owing to chemical interaction of uranyl ions with functional groups of sorbent chelate center. The most probable complexation modes of uranyl ions with polymer sorbent are presented in the Scheme





**Figure 5.** Adsorption isotherm of sorbent (pH = 6,  $V_{sol} = 0.04$  L,  $m_{sorb} = 0.05$  g, 25 °C, 24 h).

**Figure 6.** Langmuir plot for sorption of uranyl ions.



**Figure 7.** Freundlich plot for sorption of uranyl ions.

As shown in Table 1,  $n = 1.81$  and  $(1/n) = 0.55$ , which satisfy the requirement of the Freundlich equation (value  $0 < (1/n) < 1$ ). It is possible to conclude that the studied adsorption process can be described by the Langmuir and Freundlich models.

## 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, given in Table 2, show that migration of uranyl ions to the neutral aqueous medium was practically unobservable ( $R = 2.4\%$ ), whereas nearly full desorption of uranyl ions from the sorbent took place in 20% HCl and HNO<sub>3</sub> aqueous solutions. The results further confirmed the above-stated assumption that in strongly acidic media the sorption-desorption equilibrium is displaced to the desorption side.

**Table 1.** Langmuir and Freundlich sorption constants at 25 °C.

Langmuir constants			Freundlich constants		
$q_{max}$ (mmol g <sup>-1</sup> )	$K_L$ (L mol <sup>-1</sup> )	$R^2$	$K_F$	$n$	$R^2$
2.00	3.43	0.991	1.66	1.81	0.980

**Table 2.** Desorption degree ( $R$ ) at various concentrations of HCl and HNO<sub>3</sub> ( $m_{sorb} = 0.05$  g, 25 °C, 24 h).

Concentration of HCl or HNO <sub>3</sub> , %		0	5	10	15	20	25
$R$ , %	HCl	2.4	28.8	59.1	82.7	98.7	96.5
	HNO <sub>3</sub>	2.4	25.6	51.7	68.7	95.5	95.0

## Conclusions

The preparation, characterization, and application of a cross-linked allyl propionate-maleic anhydride-styrene terpolymer containing various functional groups are described. The new sorbent was used for the removal of uranyl ions from aqueous solutions. The sorption properties of the sorbent were determined under different conditions by the varying the pH of medium, the weight of sorbent, and the uranyl ions' equilibrium concentration. Sorption isotherms of uranyl ions onto synthesized polymer sorbent were measured and the equilibrium data fitted well to the Langmuir and Freundlich isotherm models. Using 20% HCl and HNO<sub>3</sub> aqueous solutions the prepared polymer sorbent regeneration was demonstrated.

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