Radiochim. Acta **97**, 709–717 (2009) / **DOI** 10.1524/ract.2009.1668
© by Oldenbourg Wissenschaftsverlag, München

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

Kinetic and thermodynamic studies on the adsorption of U(VI) ions on densely crosslinked poly(methacrylic acid) from aqueous solutions

By C. Özeroğlu* and G. Keçeli

İstanbul University, Faculty of Engineering, Department of Chemistry, 34320 Avcılar İstanbul, Turkey

(Received January 10, 2009; accepted in final form June 16, 2009)

Uranium(VI) ion / Adsorption / Methacrylic acid / Isotherm / Kinetic equations

Summary. In this study, densely crosslinked poly(methacrylic acid) was used to adsorb uranium(VI) ions from aqueous solution. For this purpose, the crosslinked copolymer of ethylene glycol dimethacrylate (EGDM) and methacrylic acid (MA) containing 25% (w/w) methacrylic acid (MA) was synthesized by using dibenzoyl peroxide-*N*,*N*-dimethylaniline (BPO-DMA) initiator system at room temperature. The adsorption of uranium(VI) ions on the copolymer sample (0.02 g copolymer/5 mL solution of U(VI) ions) was carried out in a batch reactor. The parameters which effect the uranium adsorption process, such as, contact time, pH of solution, initial uranium(VI) concentration and temperature were investigated. It was observed that an increase in these parameters enhanced the removal of U(VI) ions from aqueous solution. The adsorption data were modelled by the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms. The adsorption capacity of the crosslinked copolymer and free energy change were calculated by using D–R isotherms. Thermodynamic parameters (ΔH°, ΔS° and ΔG°) were determined for the adsorption of U(VI) ions from aqueous solutions by the crosslinked copolymer bearing methacrylic acid functional groups. Experimental adsorption data were analyzed using sorption kinetic models of the pseudo-first order and pseudo-second order kinetic models. It was observed that pseudo-second order kinetic model provided a high goodness of fit with experimental data for the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups. The densely crosslinked poly(methacrylic acid) might be of interest in large scale uranium removals from aqueous solution, since it had high uranyl sorption capacities ranging from 0.16 to 2.37 mmol/g copolymer at pH 2.7 (293 K).

1. Introduction

Uranium and its compounds like other toxic or radioactive metals are highly toxic causing progressive or irreversible renal injury, and in acute cases, may lead to kidney failure and dead [1–9]. It was reported that the tolerable daily intake of uranium is 0.6 μg/kg of body weight per day [9, 10]. Therefore, there is a need for removal/separation of toxic or radioactive metal ions from aqueous waste solutions or wastes by using organic and inorganic adsorbents. Chemical precipitation, ion exchange, solvent extraction and sorption on the solid are the commonly used methods for the removal of toxic or radioactive metal ions from waste solutions or wastes [9, 11–16]. It is also known that the use of polymeric adsorbents has advantages for controlling adsorption capacity and may present selective adsorption of metal ions from waste solutions [17–21]. Therefore, in the previous studies, polymers or polymer networks having functional groups, such as, amidoxime, phosphorous acid, methacrylic and iminoacetic acids and hydroxamic acid have been used to remove the metal ions from the waste solutions. Ethylene glycol dimethacrylate has been chosen deliberately, due to reasonably high hydrolytic stability of the ester linkage. Obviously, any functional vinyl monomer can be preferred as the crosslinker. However, copolimerizability of dimethacrylate units of this compound with methacrylic acid is known to be better achieved than those of other crosslinkers such as divinyl benzene. Methacrylic acid has been chosen as chelating compound because of its well-known chelating ability with uranium as mentioned previously [22, 23]. The mechanism of adsorption involves chemical reaction between functional groups on the adsorbents and the metal ions or mass-transport processes, such as, transport in bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles and diffusion in macropores or micropores. By using inorganic or polymeric adsorbents, adsorption isotherms and adsorption kinetics have been studied to determine the constants of adsorption isotherms and of the kinetic equations [1, 24–29]. It has been commonly observed that the adsorption rate is very rapid at the beginning of process, then it gets slower as described by first or second order kinetic reactions and sometimes by two or three order kinetics [1, 26–29].

The main objective of this work is to study the feasibility of uranium adsorption on the crosslinked copolymer bearing methacrylic acid functional groups from aqueous solutions. The uranium(VI) adsorption by using batch method was analyzed as a function of the following parameters: contact time, pH of solution, initial uranium(VI) concentration and temperature. U(VI) uptake experiments were performed

*Author for correspondence (E-mail: ozeroglu@istanbul.edu.tr).

in non-buffered conditions in which pH = 2.7–2.8, except for the effect of pH on the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups. It was observed that an increase in these parameters enhanced the removal of U(VI) ions from aqueous solutions. The adsorption features were evaluated on the basis of adsorption parameters derived from the compatibility of adsorption isotherms to the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) models. The adsorption capacity of the crosslinked copolymer, free energy change and thermodynamic parameters (ΔH°, ΔS° and ΔG°) were also calculated. This study also compares the suitability of several kinetics models for describing the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups. The adsorption rate constants for the removal of U(VI) ions on the crosslinked copolymer from aqueous solution were calculated using the pseudo-first order and pseudo-second order kinetic models [1, 24–29].

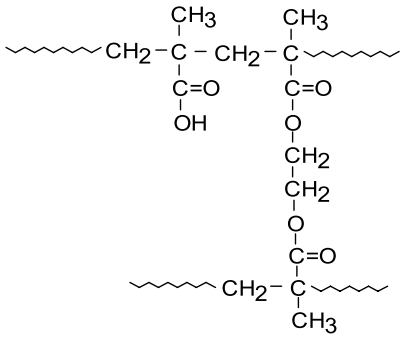
2. Experimental

2.1 Reagent

Ethylene glycol dimethacrylate (Merck), methacrylic acid (Merck), *N*,*N*-dimethyl aniline (Fluka), dibenzoyl peroxide paste in dibutyl phthalate (Lucidol BT-50, Akzo Nobel) and uranium nitrate hexahydrate (Merck) were used without further treatment, and hereafter, noted as EGDM, MA, DMA, BPO and U(VI), respectively.

2.2 The synthesis of crosslinked copolymer

Polymers bearing carboxylate functional groups, such as, methacrylic acid or imino acetic acid were synthesized for metal uptakes from solutions, using different initiator system [19–24]. Peroxide and hydroperoxide can be used for free radical polymerization or copolymerization reactions. Decomposition of an organic peroxide or hydroperoxide is accomplished either thermally or by the addition of chemical reducing agents. Tertiary amines are used as promoters or copromoters for polymerization reactions especially for the systems utilizing benzoyl peroxide or methyl ethyl ketone peroxide/cobalt octoate initiator systems, respectively [21–23, 30–32]. From this point, we aimed to synthesize an insoluble copolymer bearing carboxylate groups to use in the adsorption measurements of metal ions from solutions and dibenzoyl peroxide-*N*,*N*-dimethylaniline initiator system was used to initiate copolymerization of methacrylic acid and ethylene glycol dimethacrylate at room temperature.



Scheme 1. The structure of synthesized crosslinked copolymer.

For this purpose, 75 g EGDM and 25 g MA were mixed in 250 mL beaker and 2.2 g BPO paste was added to the this mixture and then the mixture were stirred. While stirring, 0.2 mL DMA was added to start copolymerization of EGDM and MA at the room temperature. Finally, a crosslinked copolymer given in Scheme 1 was synthesized.

The structure of crosslinked copolymer was examined by the FT-IR measurement and the carboxyl content in the copolymer was determined by the titrimetric method.

The FT IR spectrum of crosslinked copolymer is given in Fig. 1. In this figure, the broad absorption band observed in the range of 3200–3500 cm^{-1} is O–H stretching vibration in the –COOH group. The C=O of ester is observed at 1730 cm^{-1}. The bands at 1400 cm^{-1} and 1460 cm^{-1} indicate O–H bending and the vibration bending of C–O in C–O–H plane. CH_3 bending of methacrylic acid group also appears at 1400 cm^{-1}. The C–O–C asymmetric stretching

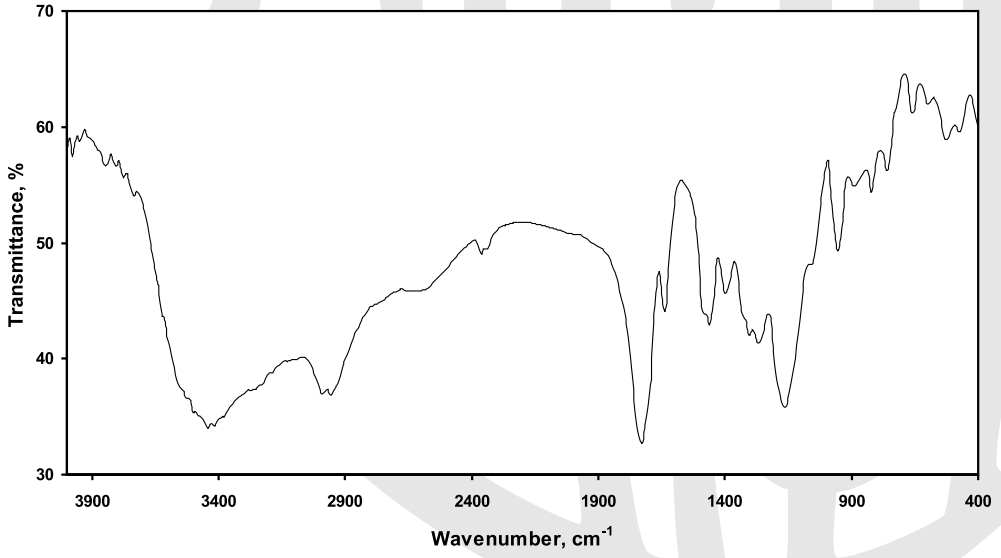


Fig. 1. FT IR spectrum of copolymer synthesized from EGDM and MA by using BPO-DMA initiator system at room temperature.

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

in ester groups is observed at the wave number of 1280 cm^{-1} and 1170 cm^{-1}.

For the titrimetric determination of carboxyl groups in copolymer, 1 g of copolymer sample was treated with 20 mL of 2 M NaOH solution for 4 h. Then, it was filtered and three times washed with 20 mL distilled water to remove excess NaOH. Then, 0.4 g dried copolymer sample in 10 mL distilled water was titrated with 0.105 M HCl solution. The volume of HCl solution at neutralization point was 5.85 mL and the titration was completed in 30 min. The amount of carboxyl groups of copolymer was found to be 1.53 mmol/g copolymer.

2.3 Uranium sorption experiments

The solid polymer was ground into powder for adsorption experiments and the particles of smaller than 160 μm of diameter were used in the adsorption measurements of U(VI) ions. The batch method was used for the adsorption of uranium ions on the copolymer sample (0.02 g copolymer/5 mL solution of uranium ions). U(VI) uptake experiments were performed in non-buffered conditions (pH = 2.7–2.8). The dependence of adsorption on the uranium concentration ($C_{U(VI)} = 1\times10^{-3}$, 2×10^{-3}, 5×10^{-3}, 1×10^{-2} and 2×10^{-2} mol/L), the temperature (T = 283, 293, 303 and 323 K), the time (t = 1, 3, 6, 10, 15, 30, 45 and 60 min) and pH ranging from 0.5 to 4 was investigated.

0.02 g polymer sample was immersed in 5 mL U(VI) solution to measure U(VI) sorption on the crosslinked copolymer. The mixture was shaken for 60 min. The samples of polymer were separated by centrifugation (3500 rpm for 20 min). The uranium sorptions were assigned by monitoring the beta activity of solution with ERG Mullard G-M type MX123. The percentage (Ads. %) of adsorption, distribution coefficients (K_d), the concentrations of C_t and C_e and the amounts of q_t and q_e were calculated using following relationships.

$$\text{Ads.}\,\% = \frac{A_i - A_f}{A_i}100 \quad (1)$$

$$K_d = \frac{A_i - A_f}{A_f}\frac{V}{m} \quad (2)$$

$$q_t = (C_0 - C_t)\frac{V}{m} \quad (3)$$

$$q_e = (C_0 - C_e)\frac{V}{m} \quad (4)$$

$$C_t = (1 - \text{Ads.}\,\%/100)C_0 \quad (5)$$

where A_i and A_f are the initial and final activity (Bq/cm^3) of solution (mL), C_0 is the initial U(VI) concentration (mol/L), K_d is the batch distribution coefficient, C_t and C_e are the U(VI) concentrations (mol/L) in solution at time t and at the equilibrium at t = 60 min, respectively. q_t and q_e are the amounts of adsorbed uranium in terms of mmol/g on the crosslinked copolymer at time t and at equilibrium (t = 60 min), respectively. V is the volume of U(VI) solution (mL) in the experiment, and m is the amount the adsorbent (g).

3. Result and discussion

3.1 The effect of concentration

Adsorption of U(VI) ions on the copolymer bearing methacrylic acid functional groups has been examined as a function of U(VI) concentration at different temperatures (283–323 K) and at constant contact time (t = 60 min). The results were illustrated in Fig. 2. As seen from Fig. 2, an increase in the uranium concentration in the adsorption experiments resulted in a decrease in the percentage of the adsorbed U(VI) ions over the crosslinked copolymer (Fig. 2, curves 1–4). However, the amount of uranium adsorption increased (Fig. 2, curves 5–8) with an increasing initial U(VI) concentration from 1×10^{-3} to 2×10^{-2} mol/L, respectively. At the low initial uranium concentrations, there are available unoccupied carboxyl groups (the number of available carboxyl groups in 0.02 g crosslinked copolymer, $n_{COOH} = 0.02\text{ g}\times1.53\text{ mmol/g} = 3.06\times10^{-2}$ mmol) for the adsorption of all uranium ions in solution. The reason of the low binding capacity of the crosslinked copolymer is largely due to the following equilibrium (Eq. (6)):

$$Ⓟ\text{–COOH} + UO_2^{2+} \rightleftharpoons (Ⓟ\text{–COO})_2UO_2 + 2H^+ . \quad (6)$$

When initial uranium concentration equals to 1×10^{-3} mol/L, this equilibrium follows 64.38% percentage of uranium adsorption at 293 K on the crosslinked poly(methacrylic acid). The sorption quantities have been estimated by differences of the beta activities of uranyl ions in solutions before and after adsorption (Eq. (1)). It was observed that when temperature increased, the amount and percentage of the adsorbed U(VI) ions on the crosslinked copolymer also increased. This increase might be due to the increased dif-

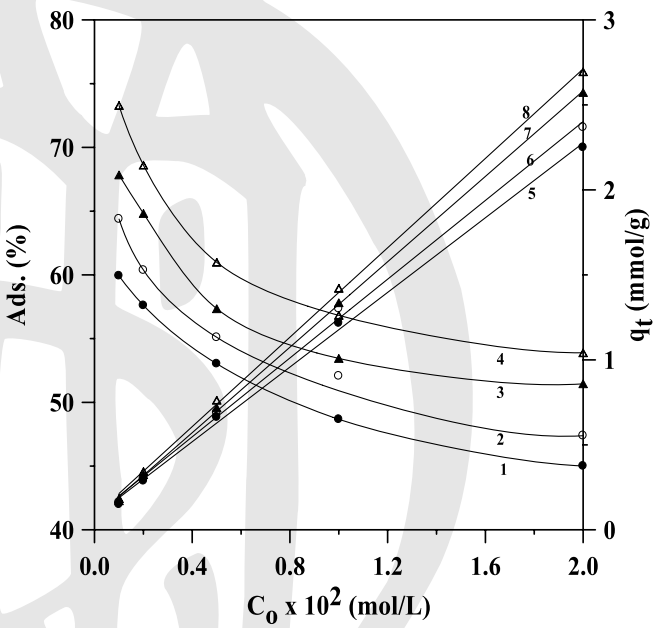


Fig. 2. The effect of the initial uranium concentration on the percentage (T = 10 °C (1), 20 °C (2), 30 °C (3) and 50 °C (4)) and the amount (T = 10 °C (5), 20 °C (6), 30 °C (7) and 50 °C (8)) of U(VI) ions adsorbed on the crosslinked copolymer containing methacrylic acid functional groups. The contact time is 60 min. The pH range of initial U(VI) solutions: 2.7–2.8.

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

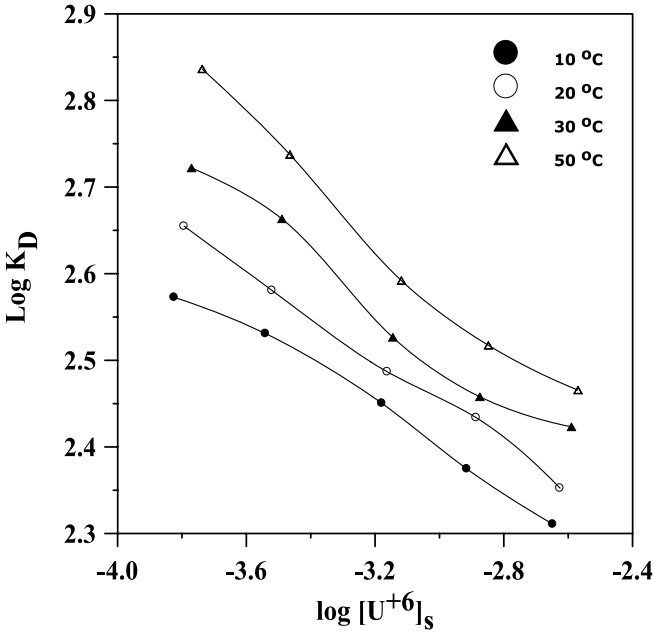


Fig. 3. The loading curves of U(VI) adsorption on the crosslinked copolymer at different temperatures. $T = 283\,\mathrm{K}$ (●), 293 K (○), 303 K (▲) and 323 K (△).

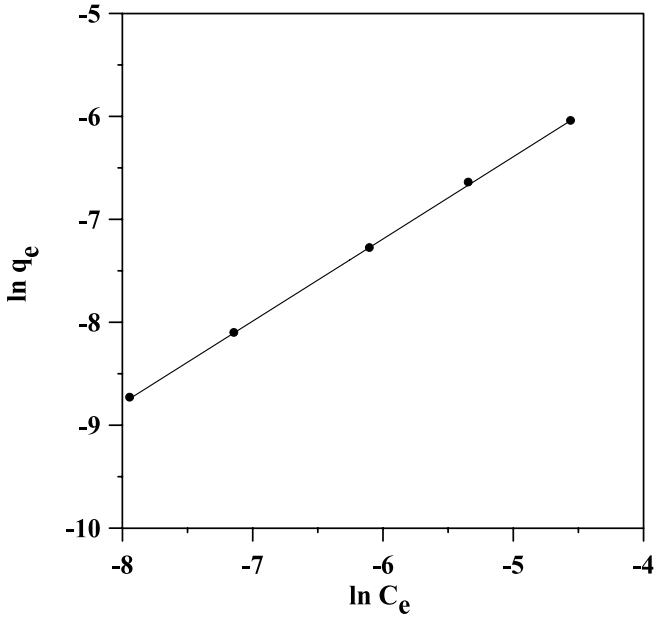


Fig. 4. Freundlich adsorption isotherm for the adsorption of U(VI) on the crosslinked copolymer containing methacrylic acid functional groups at 293 K.

fusibility of U(VI) ions on polymer matrix or the ionization of carboxyl groups by increase temperature.

For adsorption of U(VI) ions on the crosslinked copolymer, the loading curve was constructed by plotting $\log K_d$ values against to log[U(VI)] as illustrated in Fig. 3. The units of K_d and U(VI) are given in L/g and mol/g, respectively. It would appear that the high distribution coefficient in dilute solution is due to equilibrium of ion-exchange as stated above. At the higher temperatures, high K_d values can be ascribed to increased dissociation of carboxyl groups.

3.1.1 The adsorption isotherms

An isotherm is a functional expression for the variation of adsorption with concentration to adsorbate in bulk solution at constant temperature. The models for the uptake processes were checked using the Freundlich, the Langmuir and the D–R isotherm models.

The fitting of adsorption data on the Freundlich adsorption isotherm was studied at constant temperature of 293 K using Eq. (7).

$$q_e = K_F C_e^{n_F} \tag{7}$$

Where q_e is the amount of U(VI) adsorbed at equilibrium (mol/g) and C_e is the equilibrium solution concentration as mol/L. n_F and K_F are the Freundlich adsorption constants. Fig. 4 shows that the $\log q_e$ *vs.* $\log C_e$ plot shows a straight line given in Eq. (8) for the adsorption of U(VI) ions on the crosslinked copolymer.

$$\log q_e = \log K_F + n_F \log C_e \tag{8}$$

The concentration of U(VI) ions was between 2.0×10^{-2} and 1.0×10^{-3} mol/L. n_F and K_F values of the Freundlich constants were calculated from the slope and intercept of this line and calculated to be 0.798 and 0.090, respectively. The correlation coefficient (R) of the straight line was found to be 0.999. The slope value of n_F (0.798) was lower than 1. This indicated that heterogeneous adsorption reaction occured. The previous literature results revealed that if $0 < n < 1$, then, the surface of adsorbent was heterogeneous [22, 33, 34].

The fitting of adsorption data on the Langmuir adsorption isotherm was examined and the following linearized Langmuir equation was used to describe the equilibrium data:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{b}{K_L} C_e \tag{9}$$

where q_e is the amount of uranium concentration absorbed on the crosslinked copolymer at equilibrium (mol/g), C_e is the equilibrium solution concentration as mol/L, the constants of K_L and b are the characteristics of the Langmuir equation. Fig. 5 shows the plot of C_e/q_e *vs.* C_e indicating the relationship between the C_e/q_e and C_e values was not linear, implying that the adsorption data did not show a fitting to Langmuir adsorption isotherm. The deviation from the linearity of Langmuir isotherm could be due to the fact that these type isotherms have originally been deviated from the adsorption of gases on adsorption surfaces and thus have been limitation in the extrapolation to adsorption of other compounds [22, 35, 36] as in the current study.

It was reported that the D–R isotherm model was applicable at low concentration ranges and could be used to describe sorption on both homogeneous and heterogeneous surfaces. The D–R isotherm model was represented by the following equation:

$$q_e = q_m \exp(-K\varepsilon^2) \tag{10}$$

where ε is the polany potential given as $RT \ln(1 + 1/C_e)$ (kJ/mol), R is the ideal gas constant (8.314 J/(mol K)), T is

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

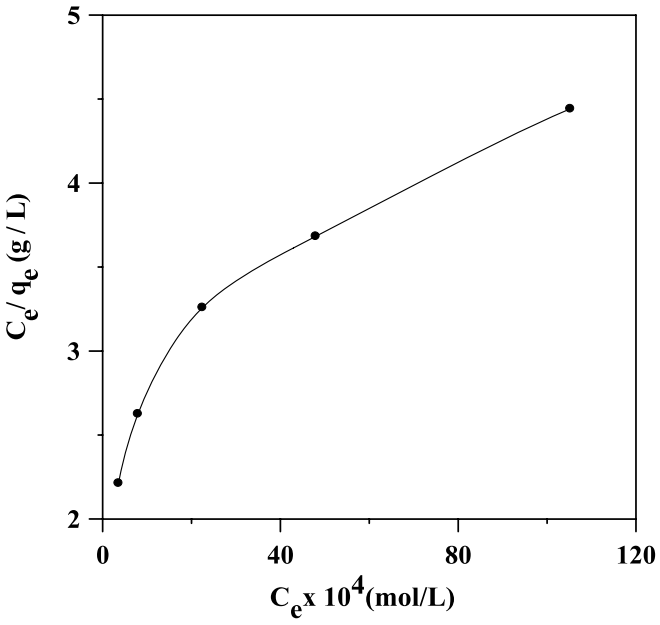


Fig. 5. The dependence of adsorption data on the Langmuir adsorption isotherm at 293 K.

the absolute temperature (K), q_m is the adsorption capacity of adsorbent per unit weight (meq/g).

The linear form of the D–R equation was

$$\ln q_e = \ln q_m - K\varepsilon^2 . \tag{11}$$

The value of q_m and K were determined by plotting $\ln q_e$ *vs.* ε^2 as given in Fig. 6 and found to be 8.11×10^{-3} and 1.15×10^{-2}, respectively. The correlation coefficient (R) of the straight line was found to be 0.994.

The value of K $(\text{mol/kJ})^2$ was the constant related to the adsorption mean free energy, E (kJ/mol) which was defined as the free energy change required to transfer one mole of ions from the infinity of solution to the solid surface can be calculated using following equation:

$$E = (-2K)^{-1/2} . \tag{12}$$

E was found to be 6.607 kJ/mol for the adsorption of U(VI) ions on the crosslinked copolymer at 293 K. According to Kundu *et al.* and Sari *et al.* [37, 38], the adsorption energy could be employed to estimate the type of adsorption and an energy adsorption based on ion-exchange mechanism was around 8–16 kJ/mol. 6.607 kJ/mol of adsorption energy found in present study was close to the above energy range of ion-exchange. Therefore, the adsorption by crosslinked copolymer with methacrylic acid has been of ion-exchange type.

3.2 The effect of temperature

Temperature dependence of adsorption of U(VI) ions on the crosslinked copolymer was studied at different uranium concentration from 1×10^{-3} to 2×10^{-2} mol/L in the temperature range from 283 to 303 K. The following equation was used to calculate ΔH° and ΔS° values

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{13}$$

where K_d is the distribution coefficient (cm^3/g), ΔS° is the standard entropy, ΔH° is the standard enthalpy, T is the absolute temperature (K) and R is the gas constant (kJ/(mol K)). Fig. 7 shows the relation between $1/T$ of absolute temperature and $\ln K_d$.

The standard free energy values were calculated by using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

where ΔG° is the standard free energy. The calculated results of ΔH°, ΔS° and ΔG° values were given in Table 1.

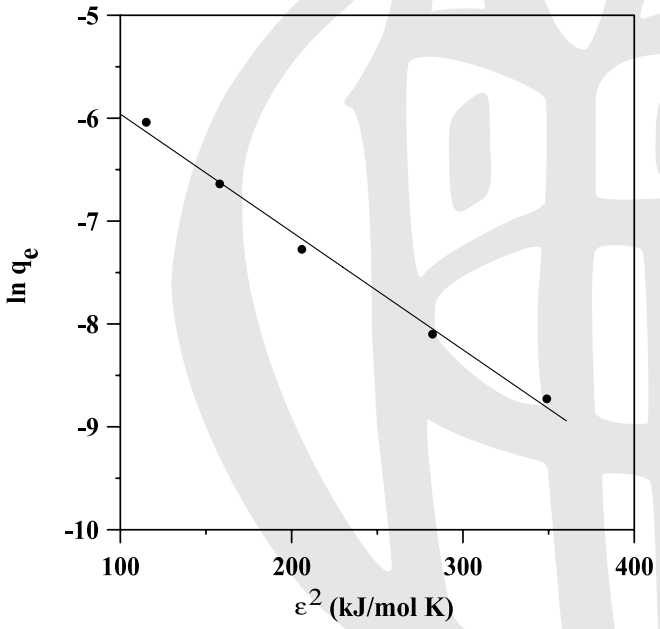


Fig. 6. D–R adsorption isotherm for the adsorption of U(VI) on the crosslinked copolymer containing methacrylic acid functional groups at 293 K.

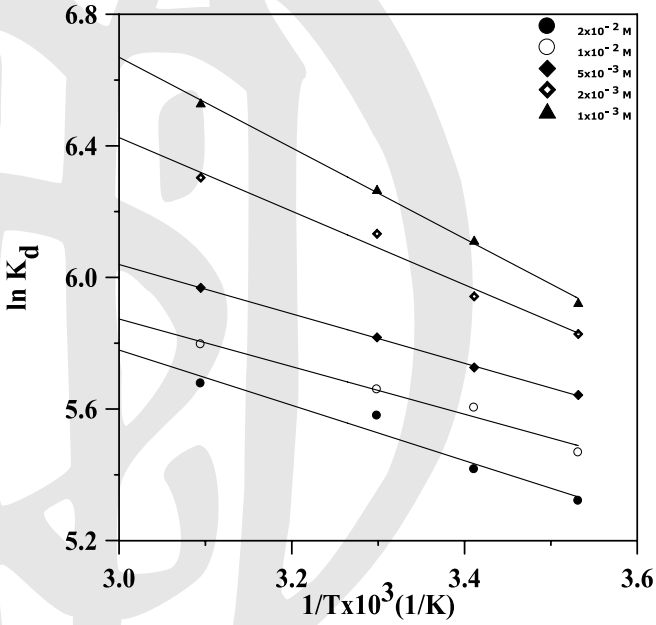


Fig. 7. Variation of $\log K_d$ *vs.* $1/T$ for the adsorption U(VI) by crosslinked copolymer containing methacrylic acid functional groups.

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

Table 1. The calculated values of thermodynamic parameters for the adsorption of U(VI) ions on the crosslinked copolymer containing methacrylic acid functional groups.

C_0	ΔH°	ΔS°	$-\Delta G^\circ$ (kJ/mol)				
(mol/L)	(kJ/mol)	(kJ/(mol K))	283 K	293 K	303 K	323 K	R
2×10^{-2}	6.992	6.90×10^{-2}	11.68	13.23	13.92	15.30	0.954
1×10^{-2}	6.014	6.69×10^{-2}	12.67	13.33	13.99	15.31	0.977
5×10^{-3}	6.241	6.89×10^{-2}	13.29	13.98	14.67	16.05	0.999
2×10^{-3}	9.173	8.13×10^{-2}	13.63	14.44	15.25	16.87	0.981
1×10^{-3}	11.484	8.98×10^{-2}	13.73	14.62	15.51	17.29	0.998

All the values except for C_0 were obtained by average of three measurements with ±0–3% errors.

The positive value of enthalpy (ΔH°) corresponded to the endothermic adsorption process. The values of free energy were negative and indicated a decrease in ΔG° values with increase in the temperature. Positive entropy (ΔS°) reflected the affinity of the crosslinked copolymer with methacrylic acid functional groups as adsorbent towards uranium ions in solution and the results indicated that the contribution of entropic term made the free adsorption energy negative as explained in the earlier studies [38–40].

3.3 The effect of contact time

Fig. 8 shows that as adsorption duration increased, the amount of U(VI) ions absorbed on the crosslinked copolymer was increased and reached to an equilibrium after 30 min. As was common in most adsorbents, a rapid initial adsorption of U(VI) ions on the copolymer has been followed by a steady and later stages which finally reached an apparent plateau in 30 min.

In order to investigate the mechanism of adsorption potential rate controlling steps, such as, mass-transport and chemical reaction processes, the kinetics models including the pseudo-first order and the pseudo second order equations were tested [1, 23–29, 41, 42]. The adsorption data determined under equilibrium conditions were used for the analysis of kinetic models.

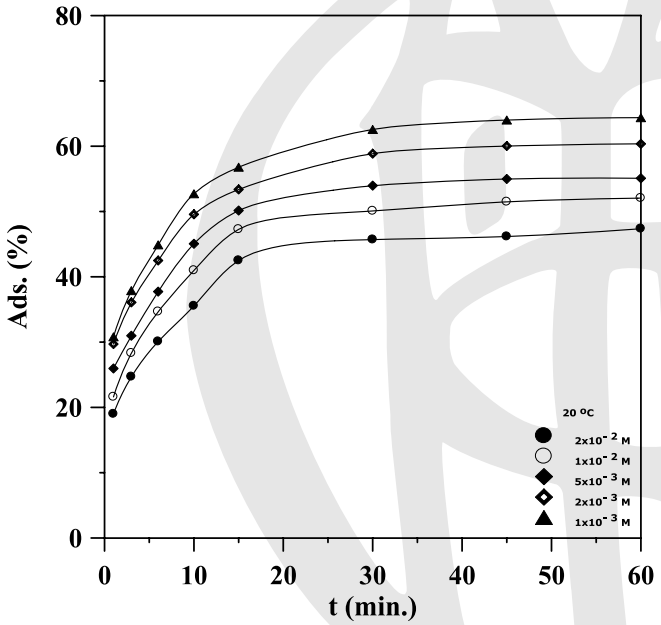


Fig. 8. The dependence of adsorption of U(VI) ions on the time for various U(VI) concentrations. $C_{U(VI)} = 1 \times 10^{-3}$ mol/L (▲), 2×10^{-3} mol/L (◇), 5×10^{-3} mol/L (◆), 1×10^{-2} mol/L (○) and 2×10^{-2} mol/L (●). The pH range of initial U(VI) solutions: 2.7–2.8.

3.3.1 Pseudo-first order kinetic model

The kinetic models for uranyl sorption were studied based on the Elovich and modified Freundlich kinetic models. However, these models were found to be inconsistent with our kinetic results.

The pseudo first order kinetic equation can be written as follows [26, 27, 41]:

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{15}$$

where q_e and q_t are the amounts of uranium ions absorbed by the crosslinked copolymer at equilibrium and a time t, respectively. The k (1/min) is the rate constant for pseudo-first order kinetic equation. The linearized first order kinetic Eq. (15) can be given below.

$$\ln(q_e - q_t) = \ln q_e - kt \tag{16}$$

The results for the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups from aqueous solutions were given in Fig. 9 and Table 2 for various initial U(VI) concentrations. A linear relationship between $\ln(q_e - q_t)$ and t has been established with a fairly good correlation coefficient (minimum R value > 0.959). The rate constant (k) decreased with increasing the initial U(VI) concentration at constant temperature (293 K).

3.3.2 Pseudo-second order kinetic model

In order to describe U(VI) adsorption on the crosslinked copolymer for various initial U(VI) concentrations at constant temperature of 293 K, the modified pseudo-second order kinetic equation can be written as below [28, 29, 41]

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{17}$$

where q_e and q_t are the adsorbed U(VI) ions on the crosslinked copolymer from aqueous solutions at equilibrium and a time t respectively and k is the rate constant for pseudo-second order kinetic adsorption model. For the

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

Table 2. The kinetic constants obtained from pseudo-first order and pseudo-second order kinetic equations for the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups.

C_0 (mol/L)	Pseudo-first order kinetic model		Pseudo-second order kinetic model			
	k (min^{-1})	R	q_e (mmol/g)	k (g/(min mmol))	h (mmol/(min g))	R
2×10^{-2}	0.146	0.959	2.477	0.137	0.840	0.999
1×10^{-2}	0.161	0.973	1.358	0.283	0.521	0.999
5×10^{-3}	0.143	0.991	0.718	0.607	0.320	0.999
2×10^{-3}	0.121	0.998	0.313	1.452	0.142	0.999
1×10^{-3}	0.123	0.997	0.167	2.627	0.076	0.999

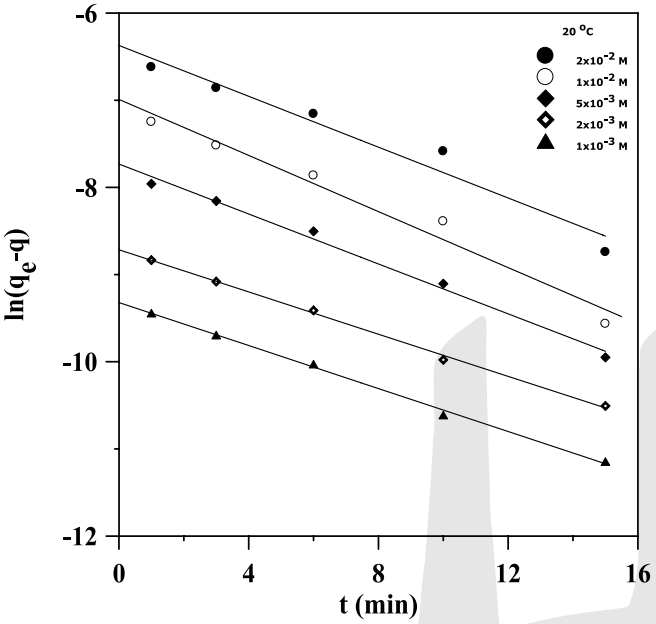


Fig. 9. The dependence of $\ln(q_e - q_t)$ to time t, using pseudo-first order kinetic model as function of various initial uranium concentrations at constant temperature (293 K).

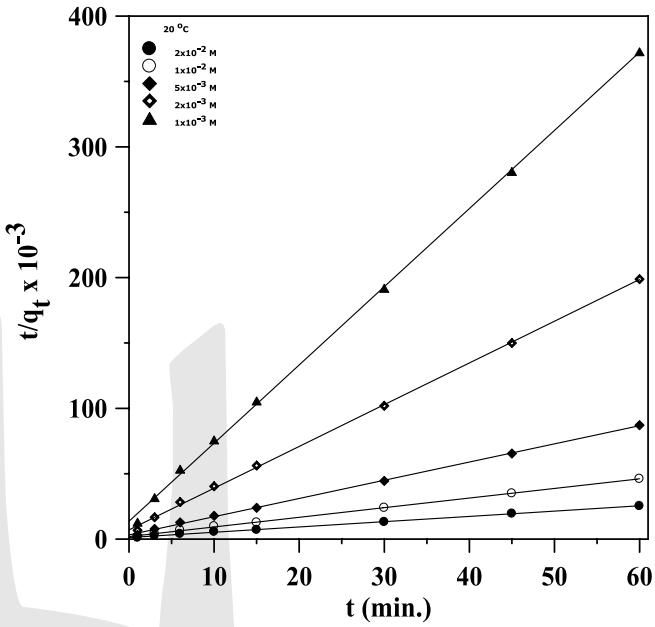


Fig. 10. The fitting of adsorption data on the pseudo-second order kinetic equation for adsorption of U(VI) ions on the crosslinked copolymer containing methacrylic acid functional groups at various initial U(VI) concentrations at 293 K.

boundary conditions from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (17) takes the form:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{18}$$

The linearized form of the Eq. (18) can be written as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{19}$$

Here kq_e^2 equaled to the initial adsorption rate [43] given as h (mmol/g min) in Table 2. When a plot of t/q_t against to t of Eq. (19) was performed, a linear relationship was found between t/q_t and t. The slope and intercept of equation were $1/q_e$ and $1/kq_e^2$ respectively. The goodness of fit to pseudo-second order kinetic model was given in Fig. 10. As seen from Fig. 10, the data-fits have revealed very high correlation coefficient ($R \geq 0.999$), when the pseudo-second order model was employed to the experimental results. The results given in Table 2 indicated the initial adsorption rate constant (k), initial adsorption rate (h) and equilibrium adsorption capacity as a function of initial uranium concentration (C_0, mol/L). With increasing the initial U(VI) concentration from 1×10^{-3} to 2×10^{-2} mol/L, the adsorption capacity, q_e increased from 0.167 to 2.477 mmol/g. The result indicated that our data fitted better than other kinetic models.

3.4 The effect of pH

It was known that pH was an important factor on the adsorption of metal cations on the adsorbents. Initial pH of each mixture of U(VI) solution (2×10^{-3} M and 5 mL) and 0.02 g copolymer was 2.7–2.8. pH values of the mixtures were adjusted by adding 2 N HCl and 0.1 N NaOH solutions. The effect of pH for the adsorption of U(VI) on the crosslinked copolymer containing methacrylic acid functional groups was given in Fig. 11. The amount of U(VI) adsorbed on the crosslinked copolymer showed a marked influence with increasing pH from 0.5 to 2.0 and it reached to an equilibrium after pH = 2.5. Considering uranyl adsorption by amidoxime functional polymers [44, 45] and iron oxide based matrix sorbents [46, 47] operating in neutral or in alkaline medium, uranyl adsorption by densely crosslinked poly(methacrylic acid) under highly acidic con-

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

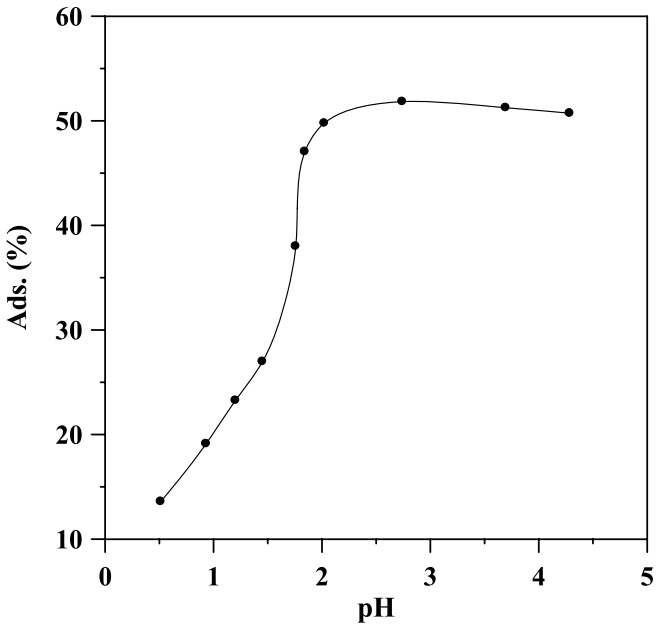
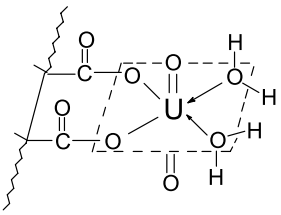


Fig. 11. The effect of pH on the adsorption of U(VI) ions on crosslinked copolymer at 293 K. Initial U(VI) concentration: 2×10^{-2} mol/L; contact time 60 min. Initial pH of the mixture of U(VI) solution containing 0.02 g copolymer was 2.7.

ditions (pH = 0.5–2.5) was significant achievement. Since ideal pH range for adsorption of common metal ions by chelating polymers was in neutral or weakly alkaline. Uranyl sorption ability of crosslinked poly(methacrylic acid) made it superior in comparison to other sorbent materials. Since most of other ions can not be adsorbed in range of pH = 0.5–2.5, capacity of the crosslinked copolymer would have enhanced virtually. It was reported that in the adsorption of Sr(II) ions on this crosslinked copolymer, the maximum adsorption was achieved in the range of pH = 6–8 [23]. In this study, the adsorption of U(VI) ions took place at lower pH values. This indicated that U(VI) and Sr(II) ions in waste solution may separate from each other using adsorption process at different pH values. According to the pH results and our observations of U(VI) ions in solution, metal ions were able to bind chemically with carboxyl groups in copolymer and metal bonding mechanism of copolymer containing methacrylic acid groups were shown in Scheme 2.

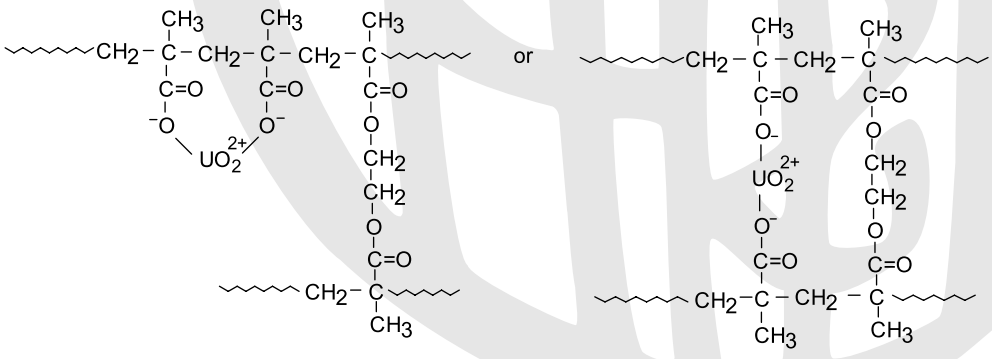
Since the uranyl was a four-coordinating ion [48], additional two water molecules were expected to involve in the coordination to form a planar geometry as illustrated in Scheme 3.



Scheme 3. The expected geometric structure of adsorbed UO_2^{2+} ions on the crosslinked copolymer bearing methacrylic acid functional groups.

4. Conclusion

The densely crosslinked copolymer of methacrylic acid was efficient adsorbent for the removal of radioactive U(VI) ions from aqueous solution. Since this adsorbent was produced from commercially available starting materials, the procedure described here was a cost effective alternative of the removal of radioactive U(VI) ions from wastes. Experiments indicated that the adsorption capacity increased with increasing initial uranium concentration and reached to 2.37 mmol/g copolymer for initial U(VI) concentration of 2×10^{-2} mol/L at 293 K with a contact time ($t = 60$ min). With increasing adsorption temperature from 283 to 323 K, the amount of uranium ions adsorbed on the crosslinked copolymer increased from 2.25 to 2.70 mmol/g copolymer, respectively for initial U(VI) concentration of 2×10^{-2} mol/L. The results obtained at the various temperatures for the adsorption of U(VI) ions on the crosslinked copolymer showed that the amount of absorbed uranium ion increased, due to the increase in the mobility of ionic species in solution and acceleration of some originally slow steps at higher temperatures which resulted in an increase in U(VI) adsorption. At low initial uranium concentration (1×10^{-3} mol/L), 64.38% of the amount in solution containing U(VI) ions at 293 K was adsorbed which accounted for about 38 g uranium per kilogram adsorbent. This makes this adsorbent a good candidate for removal uranium ions from highly diluted solution. The sorption data were evaluated by the Freundlich, Langmuir and the D–R isotherms. The n_F value in the Freundlich isotherm was founded lower than 1. This meant that the surface of adsorbent was heterogeneous. It was important to note that enthalpy (ΔH°) of adsorption was found to be slightly positive in all experiments indicating that the adsorption was mainly entropy driven process. The contribution of en-



Scheme 2. Metal bonding mechanism of the crosslinked copolymer containing methacrylic acid functional groups.

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.

tropic term made the free adsorption energy (ΔG°) negative. The Fitting of data values to the pseudo-first order and the pseudo-second order kinetic models indicated that the data values obtained from experimental results for the adsorption of U(VI) ions on the crosslinked copolymer bearing methacrylic acid functional groups provided much better fitting for the pseudo-second order kinetic equation with high correlation coefficient ($R \geq 0.999$). Adsorption rate constants, initial adsorption rates and equilibrium adsorption capacities were determined for various initial U(VI) concentrations by using pseudo-second order kinetic model. The increase in the initial U(VI) concentration for the adsorption of U(VI) ions on the crosslinked copolymer containing methacrylic acid functional groups resulted in an increase in the initial adsorption rate (h) and equilibrium adsorption capacity (q_e) but resulted in a decrease in the adsorption rate constant (k).

Acknowledgment. This work was supported by the Research Fund of University of Istanbul. Project numbers: 591/14082006 and UDP-1324; BYP-2180.

References

1. Quadeer, R. Hanif, J.: Radiochim. Acta **65**, 259 (1994).
2. Malleh, A., Chegrouche, S., Barkat, M.: J. Colloid Interface Sci. **296**, 434 (2006).
3. Pantchev, I., Farquet, P., Surbeck, H., Meyer, Th.: React. Funct. Polym. **67**, 127 (2007).
4. Korob, R. O., Nuno, G. A. B.: Radiat. Isot. **64**, 525 (2006).
5. Akkaya, R., Ulusoy, U.: Talanta **151**, 380 (2008).
6. Singh, B. N., Maiti, B.: Talanta **69**, 393 (2006).
7. Křepelová, A., Sachs, S., Bernhard, G.: Radiochim. Acta **94**, 825 (2006).
8. Denizli, A., Say, R., Garipcan, B., Patır, S.: React. Funct. Polym. **58**, 123 (2004).
9. Rao, T. P., Metilda, P., Gladis, J. M.: Talanta **68**, 1047 (2006).
10. Gilman, A. P., Villencuve, D. C., Seccours, V. E.: Toxicol. Sci. **41**(1), 117 (1998).
11. Aksoyluoğlu, S.: J. Radioanal. Nucl. Chem. **34**(2), 393 (1989).
12. Lu, N., Mason, C. F. V.: Appl. Geochem. **16**, 1653 (2001).
13. El-Shahat, M. E., Moamed, E. A., Farag, A. B.: Talanta **71**(1), 236 (2007).
14. Choi, S. H., Choi, M. S., Park, Y. T., Lee, K. P., Kang, H. D.: Radiat. Phys. Chem. **67**, 387 (2003).
15. Özcan, M., Akman, S., Özeroğlu, C.: Anal. Lett. **35**(6), 1075 (2002).
16. Tokman, N., Akman, S., Özeroğlu, C.: Talanta **63**, 699 (2003).
17. Metilda, P., Sanghamitra, K., Gladis, J. M., Naidu, G. R. K., Rao, T. P.: Talanta **65**, 192 (2005).
18. Svec, F.: Acta Polym. **31**, 68 (1980).
19. Bıçak, N., Şenkal, B. F., Yarbaş, T.: Macromol. Chem. Phys. **199**, 2731 (1998).
20. Kalalova, E., Beiglova, V., Kalal, J., Svec, F.: Angew. Makromol. Chem. **72**, 143 (1978).
21. Baysal, A., Tokman, N., Akman, S., Özeroğlu, C.: J. Hazard. Mater. **150**, 804 (2008).
22. Özeroğlu, C., Keçeli, G.: J. Radioanal. Nucl. Chem. **268**(2), 211 (2006).
23. Özeroğlu, C., Keçeli, G.: Radiochim. Acta **95**(8), 459 (2007).
24. Hsu, C. N., Liu, D. C., Chuang, C. L.: Acta Physicochim. URSS **1**(3–4), 449 (1934).
25. Chabani, M., Amrane, A., Bensmaili, A.: Desalination **206**, 560 (2007).
26. Lagergren, S.: Handlingar **24**(4), 1 (1898).
27. Ho, Y. S.: Scientometrics **59**(1), 171 (2004).
28. Ho, Y. S., McKay, G.: Water Res. **34**(3), 735 (2000).
29. Ho, Y. S.: J. Hazard. Mater. **136**(3), 681 (2006).
30. Özeroğlu, C.: Polym.-Plast. Technol. **43**(3), 661 (2004).
31. Kalenda, P.: Eur. Polym. J. **31**(11), 1099 (1995).
32. Misra, G. S., Bajpai, U. D. N.: Prog. Polym. Sci. **8**, 111 (1982).
33. Mishra, S. P., Tiwari, D. J.: J. Radioanal. Nucl. Chem. **253**(3), 421 (2002).
34. Mishra, S. P., Tiwary, D.: Appl. Radiat. Isot. **51**, 359 (1999).
35. Shahwan, T., Erten, H. E.: J. Radioanal. Nucl. Chem. **253**(1), 115 (2002).
36. Escrig, I., Morell, I.: Water Air Soil Pollut. **105**, 507 (1998).
37. Sari, A., Tuzen, M., Citak, D., Soylak, M.: J. Hazard. Mater. **149**, 283 (2007).
38. Kundu, S., Gupta, A. K.: Colloid Surf. A Physicochem. Eng. Asp. **273**, 121 (2006).
39. Yue, Q. Y., Li, Q., Gao, B. Y., Yuan, A. J., Wang, Y.: Appl. Clay Sci. **35**, 268 (2007).
40. Önal, Y.: J. Hazard. Mater. **B137**, 1719 (2006).
41. Ho, Y. S., McKay, G.: Adsorp. Sci. Technol. **20**(8), 797 (2002).
42. Low, M. J. D.: Chem. Rev. **60**, 267 (1960).
43. Ho, Y. S., McKay, G.: Chem. Eng. J. **70**(2), 115 (1998).
44. Zhang, A., Uchiyama, G., Asakura, T.: React. Funct. Polym. **63**, 143 (2005).
45. Lin, W., Lu, Y., Zeng, H.: J. Appl. Polym. Sci. **47**, 45 (1993).
46. Bargar, J. R., Reitmeyer, R., Lenhart, J. J. Davis, J. A.: Geochim. Cosmochim. Acta **64**(16), 2737 (2000).
47. Dodge, C. J., Francis, A. J., Gillow, J. B., Halada, G. P., Eng, C., Clayton, C. R.: Environ. Sci. Technol. **36**, 3504 (2002).
48. Clark, D. L., Conradson, S. D., Donohoe, R. J., Keogh, D. W., Morris, D. E., Palmer, P. D., Rogers, R. D., Tait, C. D.: Inorg. Chem. **38**(7), 1456 (1999).

This article is protected by German copyright law. You may copy and distribute this article for your personal use only. Other use is only allowed with written permission by the copyright holder.