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Adsorption of uranium ions by crosslinked polyester resin functionalized with acrylic acid from aqueous solutions

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Abstract In this paper, the crosslinked polyester resin containing acrylic acid functional groups was used for the adsorption of uranium ions from aqueous solutions. For this purpose, the crosslinked polyester resin of unsaturated polyester in styrene monomer (Polipol 353, Poliya) and acrylic acid as weight percentage at 80 and 20%, respectively was synthesized by using methyl ethyl ketone peroxide (MEK_p, Butanox M60, Azo Nobel)-cobalt octoate initiator system. The adsorption of uranium ions on the sample (0.05 g copolymer and 5 mL of U(VI) solution were mixed) of the crosslinked polyester resin functionalized with acrylic acid was carried out in a batch reactor. The effects of adsorption parameters of the contact time, temperature, pH of solution and initial uranium(VI) concentration for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid were investigated. The adsorption data obtained from experimental results depending on the initial U(VI) concentration were analyzed by the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) adsorption isotherms. The adsorption capacity and free energy change were determined by using D–R isotherm. The obtained experimental adsorption data depending on temperature were evaluated to calculate the thermodynamic parameters of enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy change ($\Delta G°$) for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions. The obtained adsorption data depending on contact time were analyzed by using adsorption models such as the modified Freundlich, Elovich, pseudo-first order and pseudo-second-order kinetic models.

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Keywords Acrylic acid · Polyester resin · Adsorption isotherms and kinetics · Uranium ions

Introduction

The radioactive or toxic metal ions contributed from neutral or industrial resources indicate environmental effects due to their possible detrimental effects associated with radioactivity and/or toxicity to the biological systems even they are present trace levels [1–6]. Uranium which is one of radioactive metal ions such as cesium [7–9] and strontium [10–13] are highly toxic, causes progressive or irreversible renal injury and in acute cases may lead to kidney failure and death [1–4]. The daily in take of uranium is 0.6 μg/kg of body weight per day [1, 4]. Therefore there is a need for removal/separation of toxic or radionuclide metal ions from aqueous waste solutions or wastes by using organic or inorganic adsorbents. Many separation and preconcentration techniques such as chemical precipitation, ion-exchange, solvent extraction and sorption on the solid have been developed to remove metal ions from wastes or waste solutions [12–16]. Nowadays, there is an increasing effort for removing toxic or radionuclide contaminants from aqueous waste solutions or wastes by using various polymeric adsorbents [17–20]. 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. For this reason, many studies have been performed using polymer or polymer networks having various functional groups such as amideoximes and phosphinic, methacrylic, itaconic, succinic, imminoacetic and hydroxamic acids for removal metal ion from waste solutions [21–32].

Unsaturated polyester polymer containing reactive monomer can be copolymerized into infusible, insoluble tree dimensional networks by using an organic peroxide or hydroperoxide [33, 34]. Decomposition of peroxide or hydroperoxide is accomplished either thermally or by addition of chemical reducing agents such as *N*,*N*-dimethyl aniline or cobalt octoate [35–38]. In this study, the unsaturated polyester resin containing styrene monomer was chosen deliberately due to reasonability of high hydrolytic stability of its ester linkage and it is commercially available cheap compound in the market. The copolymer bearing acrylic acid functional groups has been chosen as chelating compound because of its well-known chelating ability with metal ions [12, 20, 28].

Adsorption mechanism between uranium ions and the functional groups of acrylic acid in the crosslinked copolymer involves chemical reaction or mass-transport processes such as in bulk of liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in macropores and micropores. The sorption data have been analyzed by different sorption isotherms of the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) adsorption isotherms. The adsorption capacity and free energy change were determined by using the D–R isotherm. Various kinetic models such as the modified Freundlich, Elovich, pseudo-first order and pseudo-second-order kinetic models have been used to characterize the adsorption kinetics of different ion-exchangers as describe in previous studies [39–43].

The purpose of this work is to study the feasibility of U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions. The U(VI) adsorption was analyzed as a function of adsorption parameters such as contact time, initial uranium concentration, pH of solution and temperature. The equilibrium adsorption values were used to analyze the adsorption isotherms of the Freundlich, Langmuir and D–R isotherms. Adsorption data obtained from experimental results depending on time have been tested for a number of kinetic models (the modified Freundlich, Elovich, pseudo-first order and pseudo-second-order kinetic models). The constants in the adsorption isotherms and kinetic equations have been examined. The adsorption free energy (E) was determined by applying D–R isotherm to the equilibrium adsorption data and thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) were calculated by using adsorption data changing on temperature.

Experimental

Reagents

Standard polyester resin (Polipol 353, Poliya), acrylic acid (Merck), cobalt octoate solution containing 1%Co as weight percentage in toluene (Ege Kimya), methyl ethyl ketone peroxide (MEKp) (Butanox M60, Akzo Nobel) and uranium nitrate hexahydrate(U(VI)) (Merck) were used without further treatment.

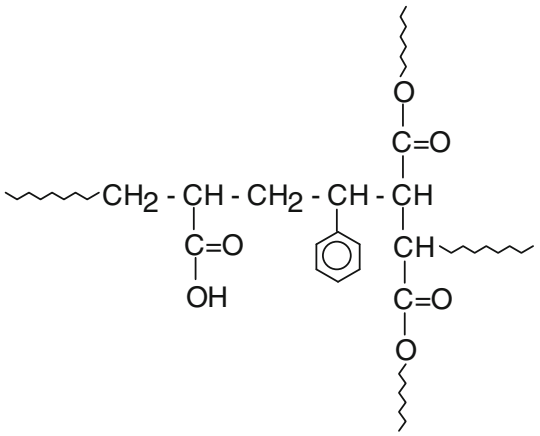
The synthesis of crosslinked polyester resin functionalized with acrylic acid

Chelating resins bearing various functional groups such as pyrrolidone [23] amideoxime [24, 25] groups and hydroxamic [26], methacrylic [12, 28], phosphinic [29], itaconic [30], succinic [31] and imminoacetic [32] acids were synthesized in previous investigations.

The mixtures of unsaturated polyester resin and styrene monomer have been copolymerized to produce some devices or tools to use them in industry or housing by using peroxide-*N*-*N*-dimethyl aniline or hydroperoxide-cobalt octoate initiator systems [33, 34].

The aim of this study is to synthesize an insoluble copolymer functionalized with acrylic acid. For this purpose, 80 g of standard unsaturated polyester resin dissolved in styrene monomer (Polipol 353) and 20 g of acrylic acid were mixed in 250 mL plastic beaker and 0.5 mL of cobalt octoate solution containing 1% Co as weight percentage in toluene was added to the this mixture. Then the mixture was stirred. While stirring, 1 mL of methyl ethyl ketone peroxide (Butanox M60) was added into this mixture of unsaturated polyester resin dissolved in styrene and acrylic acid to start copolymerization at room temperature. The chemical structure of the synthesized crosslinked polyester resin has been presented in Scheme 1.

The structure of the crosslinked polyester resin functionalized with acrylic acid was examined by FT-IR measurements. Figure 1 shows the FT-IR spectrum of the crosslinked polyester resin functionalized with acrylic acid. As can be seen from Fig. 1, the band observed at



Scheme 1 The chemical structure of synthesized unsaturated polyester resin

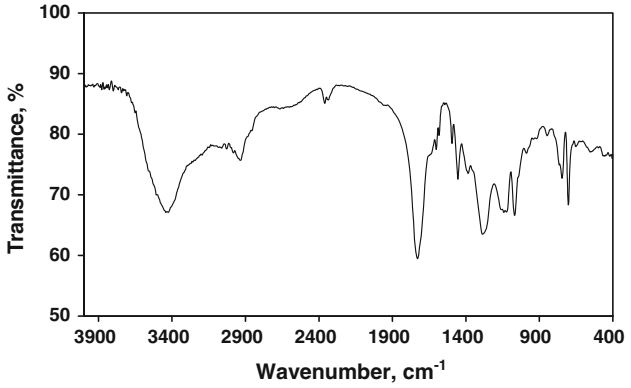


Fig. 1 The FT-IR spectrum of crosslinked polyester resin containing acrylic acid functional groups

3,550 cm^{-1} shows the O–H stretching vibration in –COOH group. The C=O in ester linkage or carbonyl group are observed at 1,730 cm^{-1}. The bands at 1,397 and 1,460 cm^{-1} indicate O–H bending and vibration bending of C–O in C–O–H plane. The C–O–C asymmetric stretching in ester group is observed at 1,150 cm^{-1}.

Uranium adsorption experiments

The crosslinked polyester resin synthesized in solid form was ground into powder to use it in adsorption measurements and the particles which are smaller than 150 μm of diameter were separated to use them in the adsorption measurements of U(VI) from aqueous solutions. Figure 2 shows the picture of scanning electron microscope of crosslinked copolymer functionalized with acrylic acid. As seen from Fig. 2, the biggest particle diameter is lower than 150 μm.



Fig. 2 SEM imagine of particles of the crosslinked polyester resin functionalized with acrylic acid used in U(VI) adsorption measurements

The effect of initial U(VI) concentration ($C_{U(VI)} = 5 \times 10^{-4}$, 1×10^{-3}, 5×10^{-3} and 1×10^{-2} mol/L), contact time ($t = 1$, 3, 6, 10, 15, 30, 45 and 60 min) and temperature ($T = 293$, 313 and 323 K) for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid were investigated.

The batch method was used for the adsorption of U(VI) on the crosslinked polyester resin functionalized with acrylic acid. For this purpose, 0.05 g of copolymer bearing acrylic acid groups was immersed in 5 mL of each uranium solution. U(VI) removal measurements were carried out in non-buffer condition. The pH of the mixture of 1×10^{-3} mol/L U(VI) solution (5 mL) and 0.05 g of adsorbent equaled to 3.75. The mixture was shaken for 60 min. The samples of copolymer were separated by centrifugation (3,500 rpm for 20 min). The uranium adsorption was assigned by monitoring the beta activity of solution with ERG Mullard G-M type MX123. The percentage (% Ads.), the concentration of C_t and C_e and the amounts of q_t and q_e were calculated using following equations.

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

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

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

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

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

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 per gram 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).

Result and discussion

Effect of initial U(VI) concentration

The effect of initial U(VI) concentration ranging from 5×10^{-4} to 1×10^{-2} mol/L on the percentage and amount of U(VI) ions adsorbed on the crosslinked polyester resin functionalized with acrylic acid was studied for various temperatures ($T = 293$, 313 and 323 K at constant contact time ($t = 60$ min). The obtained result plotted in

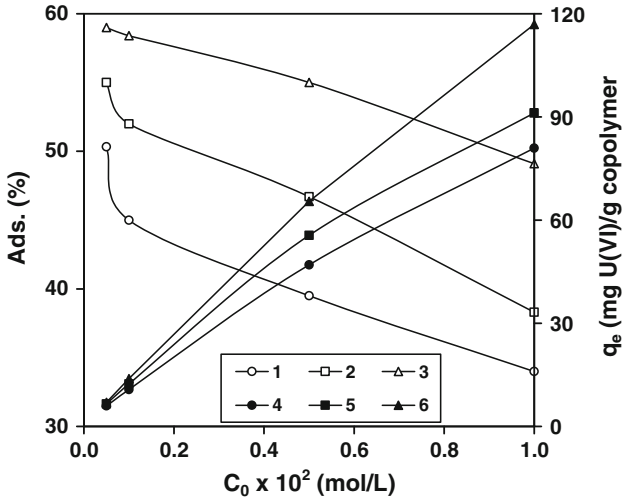


Fig. 3 The effect of initial U(VI) concentration ranging from 5×10^{-4} to 1×10^{-2} mol/L on the percentage (curves 1–3) and amount (curves 4–6) of adsorbed U(VI) on the crosslinked polyester resin functionalized with acrylic acid at different temperatures of $T = 293$, 313 and 323 K at $t = 60$ min)

Table 1 The dependence of percentage and equilibrium adsorption capacity on the initial U(VI) concentration ranging from 5×10^{-4} to 1×10^{-2} mol/L at different temperatures ($T = 293$, 313 and 323 K) for U(VI) adsorption on the crosslinked polyester resin bearing acrylic acid groups from aqueous solutions

T (K)	C_0 (mol/L)	Ads. (%)	q_e (mg U(VI)/g copolymer)
293	1×10^{-2}	34.00	80.93
	5×10^{-3}	39.50	47.01
	1×10^{-3}	45.00	10.71
	5×10^{-4}	50.33	5.99
313	1×10^{-2}	38.30	91.16
	5×10^{-3}	46.70	55.58
	1×10^{-3}	52.00	12.38
	5×10^{-4}	55.00	6.55
323	1×10^{-2}	49.10	116.87
	5×10^{-3}	55.00	65.46
	1×10^{-3}	58.40	13.91
	5×10^{-4}	59.00	7.02

Fig. 3. As can be seen from Fig. 3, The percentage of U(VI) ions adsorbed on the crosslinked polyester resin decreased with increasing the initial U(VI) concentration (Fig. 3, curve 1–3). However the amount of the adsorbed U(VI) ions increased with a rise in initial U(VI) concentration (Fig. 3, curve 4–6).

It was also observed that when temperature in adsorption measurement increased from 293 to 323 K, the percentage and amount of adsorbed U(VI) ions on the crosslinked polyester resin functionalized with acrylic acid increased from 34.00 to 49.10% and 80.93 mg U(VI)/g copolymer to 116.87 mg U(VI)/g copolymer for 1×10^{-2} mol/L initial U(VI) concentration, respectively (Table 1) due to diffusibility of U(VI) ions on the polymer matrix or more ionization of carboxyl groups by increase in temperature described in previous studies [12, 20, 28].

The adsorption isotherms

The equilibrium relationship between concentration in the liquid phase and the concentration in the adsorbent particles at constant temperature and pH has been studied by adsorption isotherms such as the Freundlich, Langmuir and D–R as defined in the literature [27, 28, 38–43]. The fitting of adsorption data to the Freundlich, Langmuir and D–R isotherms was examined for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid at initial U(VI) concentrations ranging from 5×10^{-4} to 1×10^{-2} mol/L at various temperatures ($T = 293$, 313 and 323 K) at constant adsorption time ($t = 60$ min).

The Freundlich equation is a suitable model for describing the surface heterogeneity, exponential distribution of active sites and infinite surface coverage as given in following equation:

$$q_e = K_F \times C_e^{n_F} \tag{6}$$

where q_e is the amount of U(VI) adsorbed on the crosslinked copolymer 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 which relates adsorption intensity and adsorption capacity. The Linear equation has been presented as follows:

$$\log q_e = \log K_F + n_F \log C_e \tag{7}$$

Figure 4 depicts that the $\log q_e$ against $\log C_e$ plots shows a straight line given in Eq. 7 for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid as chelating agent at 293 K. The n_F and K_F constants in the Freundlich equation were calculate from the slope and intercept of the lines for the range of initial U(VI) concentration from 5×10^{-4} to 1×10^{-2} mol/L at different temperatures of $T = 293$, 313 and 323 K at $t = 60$ min listed in Table 2. As seen from Table 2, the slope of n_F value which found as $0.810 < n_F < 0.884$ was lower than 1 for temperature range from 293 to 323 K. The correlation coefficient for the Freundlich plot was found to be of $0.996 \leq R \leq 0.999$ indicating that the fit of adsorption data to the Freundlich isotherm was better. These results indicate that heterogeneous adsorption reaction has occurred and higher n value has meant the higher heterogeneous surface as described in previous investigations [27, 28, 44, 45].

The Langmuir model which is widely used for modeling adsorption data at equilibrium is valid for monolayer adsorption on a surface. The fitting of adsorption data on

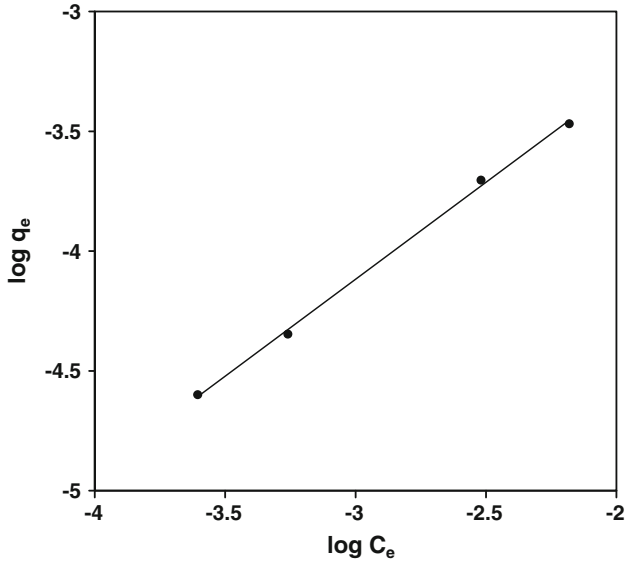


Fig. 4 The relation between log q_e against log C_e for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid at 293 K at $t = 60$ min

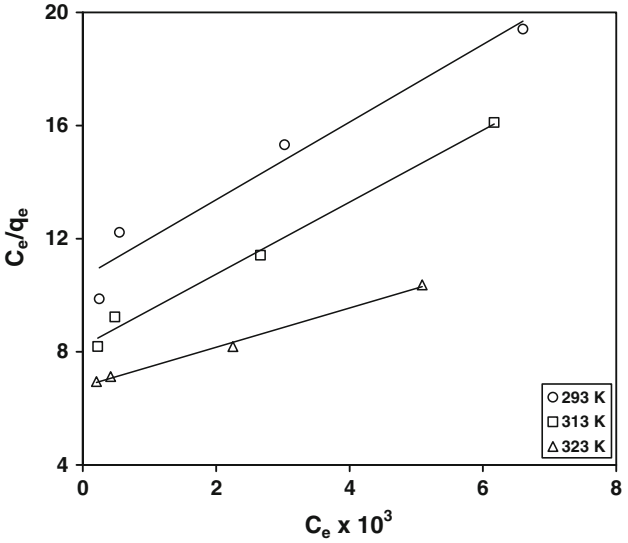


Fig. 5 The fitting of adsorption data on the Langmuir isotherm for initial U(VI) concentration changing from 5×10^{-4} to 1×10^{-2} mol/L at different temperatures of $T = 293$ K (*open circle*), 313 K (*open square*) and 323 K (*open triangle*) and at $t = 60$ min

Table 2 The n_F and K_F values determined at different temperatures ($T = 293$, 313 and 232 K) by applying the Freundlich adsorption isotherm to the adsorption data

T (K)	n_F	K_F	R
293	0.810	0.020	0.999
313	0.812	0.026	0.996
323	0.884	0.056	0.998

Table 3 The b and K_L values determined at different temperatures ($T = 293$, 313 and 232 K) by applying the Langmuir adsorption isotherm to the adsorption data

T (K)	$K_L \times 10^4$	$b \times 10^4$	R
293	7.29	77.45	0.955
313	7.85	64.34	0.992
323	14.42	97.69	0.996

the Langmuir isotherm for different temperatures ($T = 293$, 313 and 323 K) at initial concentration changing from 5×10^{-4} to 1×10^{-2} mol/L was examined and the following linearized Langmuir equation was used to describe the equilibrium data.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{b}{K_L} C_e \tag{8}$$

where q_e is the amount of U(VI) adsorbed on the crosslinked copolymer at equilibrium (mol/g), C_e is the equilibrium solution concentration as mol/L, the constant K_L and b are the characteristic of the Langmuir equation. A plot of C_e/q_e versus C_e would result in straight lines with a slope (b/K_L) and intercept of $1/K_L$ as given in Fig. 5. Langmuir parameters for fitting adsorption data were listed in Table 3. As can be seen from Fig. 5 and Table 3, with increasing adsorption temperature from 293 to 323 K, the correlation coefficient for Langmuir plot increased from 0.955 to 0.996. This result indicates that the goodness of fitting of U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid is more favorable at higher temperature.

The D–R isotherm has been applied to the low concentration ranges of solution and is used to describe the sorption on both homogeneous and heterogeneous surfaces [46–49]. The D–R isotherm model was represented by the following equation:

$$q_e = q_m \exp -(K\varepsilon^2) \tag{9}$$

where ε is the polany potential given as $RT \ln(1 + 1/C_e)$(kJ/mol), R is the ideal gas constant (8.314 kJ/mol K), T is absolute temperature (K) and q_m is adsorption capacity per unit weight (meq/g).

Linearized form of D–R equation was

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{10}$$

The values of q_m and K at different adsorption temperature ($T = 293$, 313 and 323 K) were determined by plotting ln q_e versus ε^2 shown in Fig. 6. The correlation coefficient (R) of straight lines was found to be in the range of $0.996 \leq R \leq 0.999$. The K and q_m values in the linearized D–R equation at different adsorption temperatures were

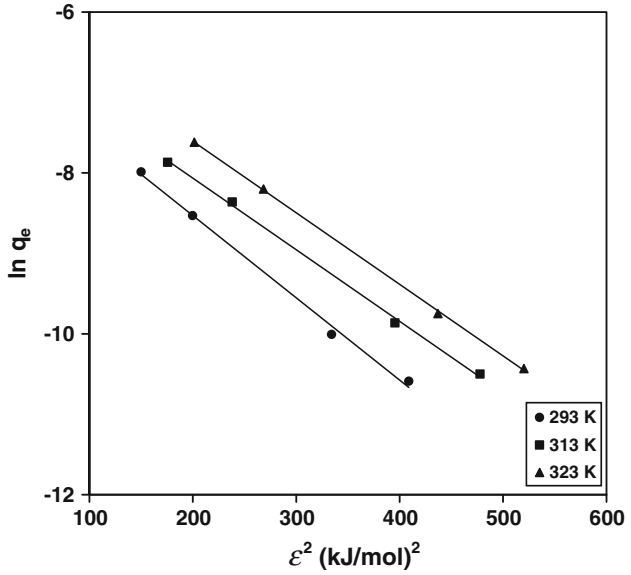


Fig. 6 Application of adsorption data on the D–R isotherm for adsorption on the crosslinked polyester resin functionalized with acrylic acid at different temperatures of $T = 293$ K (*filled circle*), 313 K (*filled square*) and 323 K (*filled triangle*). The contact time, $t = 60$ min

found as -1.02×10^{-3} and 1.526 mmol/g copolymer at 293 K, -0.89×10^{-2} and 1.860 mmol/g copolymer at 313 K and -0.89×10^{-2} and 2.953 mmol/g copolymer at 323 K, respectively for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid. The apparent free energy of adsorption (E, kJ/mol) which is the energy change when 1 mol of ion is transferred to the surface of solid from infinity in the solution was calculated using the following relationship [20, 27, 28, 46–49]:

$$E = (-2\,\mathrm{K})^{-1/2} \tag{11}$$

The E values for the adsorption of U(VI) ions on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions at different temperatures of $T = 293$, 313 and 323 K were found as 7.0, 7.5 and 7.5, respectively by using Eq. 11 [20, 27, 28, 46–49]. It was reported in previous investigations [27, 28, 46–49], the adsorption energy could be employed to estimate the type of adsorption based on ion-exchange mechanism is around 8–16 kJ/mol. The average adsorption energy, E which equals to 7.33 kJ/mol determined in present study was close the above energy ranges of ion-exchange. Therefore, the adsorption by crosslinked polyester resin functionalized with acrylic acid has been of ion-exchange.

The effect of temperature

It was reported that the increase in the temperature has generally increased the adsorption of metal ions on adsorbent containing carboxylate functional groups due to the increase in mobility of ionic species in solution and acceleration of some originally slow steps at higher temperature [12, 20, 28]. The effect of temperature ranging from 293 to 323 K on the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions were studied for various initial U(VI) concentration from 5×10^{-5} to 1×10^{-2} mol/L (Table 4). As can be seen from Table 4, when temperature of adsorption reaction increased, the amount and percentage of the adsorbed U(VI) ions on the crosslinked polyester resin functionalized with acrylic acid increased.

Table 4 The dependence the amount and percentage on the temperature for various initial U(VI) concentrations for the adsorption U(VI) ions on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions

C_0 (mol/L)	T (K)	Ads. %	q_e (mmol/g)
1×10^{-2}	293	34.00	34.00×10^{-2}
	313	38.30	38.30×10^{-2}
	323	49.10	49.10×10^{-2}
5×10^{-3}	293	39.50	19.80×10^{-2}
	313	46.70	23.40×10^{-2}
	323	55.00	27.50×10^{-2}
1×10^{-3}	293	45.00	4.50×10^{-2}
	313	52.00	5.20×10^{-2}
	323	58.40	5.84×10^{-2}
5×10^{-4}	293	50.33	2.52×10^{-2}
	313	55.00	2.75×10^{-2}
	323	59.00	2.95×10^{-2}

The contact time, $t = 60$ min

In order to determine the thermodynamic parameters, the temperature dependence of U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid was examined at different U(VI) concentration from 5×10^{-4} to 1×10^{-2} mol/L in the temperature range from 293 to 323 K. The following equation was used to calculate $\Delta H°$ and $\Delta S°$ values

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{12}$$

where K_D is the distribution coefficient (cm^3/g), $\Delta S°$ is the standard entropy, $\Delta H°$ is the standard enthalpy, T is the absolute temperature (K) and R is the gas constant (kJ/mol K). Figure 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:

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

where $\Delta G°$ is the standard free energy. The calculated results of $\Delta H°$, $\Delta S°$ and $\Delta G°$ values were given in Table 5. The positive value of enthalpy ($\Delta H°$) corresponds to the endothermic adsorption process. The values of free energy

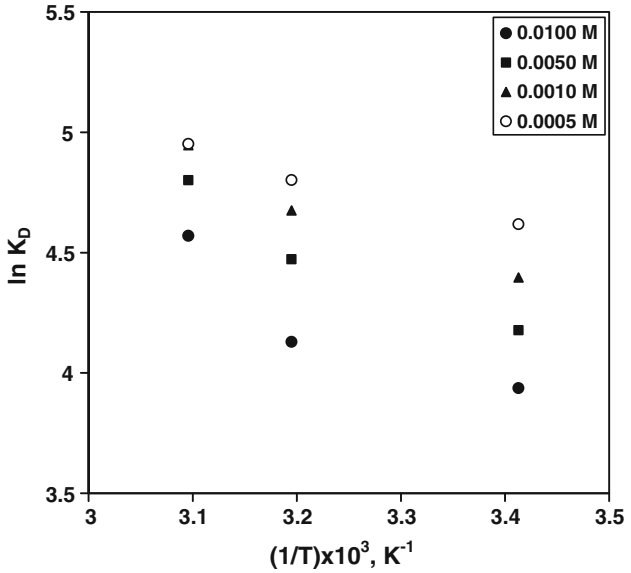


Fig. 7 The plot of ln K_D versus $1/T$ for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid at different initial U(VI) concentration from 5×10^{-4} to 1×10^{-2} mol/L at 293 K

are negative and indicate a decrease in $\Delta G°$ values with increase in the temperature. Positive entropy ($\Delta S°$) reflects the affinity of the crosslinked copolymer with acrylic acid functional groups as adsorbent towards uranium ions in solution and the results indicate that the contribution of entropic term makes the free adsorption energy negative as explained in the earlier studies [28, 47, 50, 51].

The effect of contact time

The effect of contact time for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid from aqueous solutions at 293 K was given in Fig. 8. With increasing contact time, the percentage of the adsorbed U(VI) on the crosslinked copolymer increased and reached an equilibrium value after 30 min. As described in previous investigations, a rapid initial U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid has been followed by a steady and later stages which finally reach 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 kinetic models including the Elovich, the modified Freundlich, the pseudo-first order and pseudo-second order kinetic equations were tested. Adsorption data determined under equilibrium conditions were used for analysis of kinetic models.

The modified Freundlich kinetic model

The modified Freundlich or fractional power kinetic equation for this model can be described by the Eq. 14 given below [7, 27, 52]:

$$q_t = at^b \tag{14}$$

The linearized form of Eq. 14 can be written by following Eq. 15.

$$\ln q_t = \ln a + b \ln t \tag{15}$$

where q_t is the amount of U(VI) adsorbed by crosslinked polyester resin bearing acrylic acid functional groups at time, t. The a and b are the constant for the modified Freundlich kinetic equation. Figure 9 shows a plot of q_t against ln t of the modified Freundlich kinetic equation for the result of adsorption of U(VI) on the crosslinked polyester resin at initial U(VI) concentration of 5×10^{-3} and 1×10^{-3} mol/L at constant temperature (293 K). As seen from Fig. 9, there is a linear relationship between ln q_t and ln t values. The values of a, b and correlation coefficient (R) were calculated and found to be 2.134×10^{-5}, 0.723 and 0.997 for initial U(VI) concentration of 5×10^{-3} mol/L and 4.859×10^{-5}, 0.573 and 0.970 for initial U(VI) concentration of 1×10^{-3} mol/L, respectively. When the modified Freundlich kinetic model was applied to the adsorption data, the slightly low correlation coefficients have been obtained.

Table 5 The calculated values of thermodynamic parameters for the adsorption of U(VI) ions on the crosslinked polyester resin containing acrylic acid functional groups

C_0 (mol/L)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol K)	$-\Delta G°$ (kJ/mol)			
			293 K	313 K	323 K	R
1×10^{-2}	15.055	8.37×10^{-2}	9.47	11.15	11.99	0.821
5×10^{-3}	15.500	8.74×10^{-2}	10.02	11.86	12.73	0.941
1×10^{-3}	13.787	8.39×10^{-2}	10.70	12.46	13.30	0.958
5×10^{-4}	9.278	6.72×10^{-2}	10.33	11.74	12.41	0.976

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

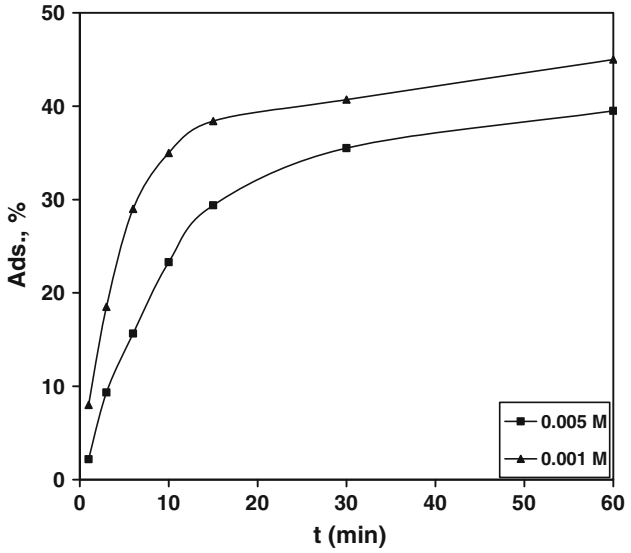


Fig. 8 The effect of contact time on the percentage of U(VI) adsorption for initial U(VI) concentration of 1×10^{-3} mol/L (*filled triangle*) and 5×10^{-3} mol/L (*filled square*) at 293 K

The Elovich kinetic model

The Elovich or Rodinky-Zeldovich kinetic equation is generally expressed as follows [7, 27, 44, 50, 52]:

$$\frac{dq_t}{dt} = A \exp(-Bq_t) \tag{16}$$

where q_t is the amount of U(VI) adsorbed by the crosslinked polyester resin functionalized with acrylic acid at time, t. A is the initial U(VI) adsorption rate (mmol/g min) and B is the adsorption constant (g/mol). The linearized form of the Elovich equation 16 can be given as follows.

$$q_t = B \ln(AB) + B \ln t \tag{17}$$

When the linear plot of q_t versus ln t is performed, the constants of A and B can be obtained from slope and intercept. In this case, a linear relationship was obtained between the adsorbed U(VI) (q_t) on the crosslinked copolymer and ln t with minimum correlation coefficient ($R = 0.984$) for the lines given in Fig. 10.

The A and B values have 1.364×10^4 and 2.262×10^{-5} for initial U(VI) concentration of 5×10^{-3} mol/L and 1.250×10^5 and 1.248×10^{-5} for initial U(VI) concentration of 1×10^{-3} mol/L, respectively. The quality of A in the Elovich equation is the equivalent to the initial gradient which varied with different U(VI) concentrations.

The Pesudo-first order kinetic model

The pseudo-first order kinetic model describes a reversible equilibrium between the ions in solution and those adsorbed on solid phase [7, 27, 50, 52–55]. In order to investigate the sorption rate of U(VI) on the crosslinked polyester resin functionalized with acrylic acid, the following pseudo-first order equation was used (18):

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{18}$$

where q_e and q_t are the amounts of uranium ions adsorbed by the crosslinked polyester resin at equilibrium and at

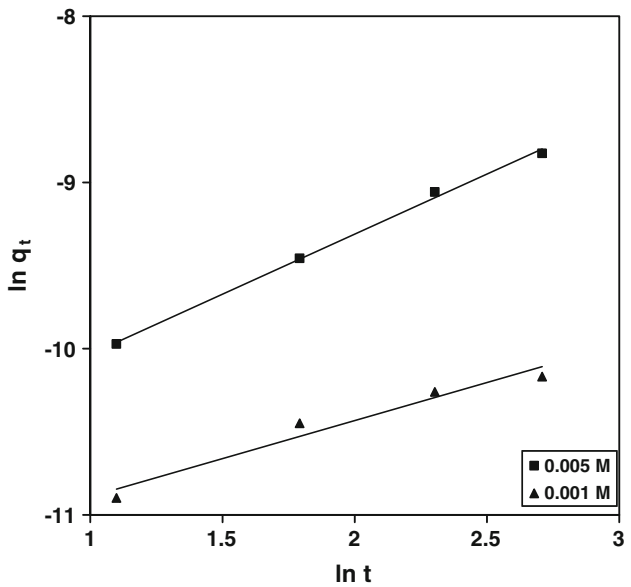


Fig. 9 The fitting of adsorption data on the modified Freundlich adsorption model for initial U(VI) concentration of 1×10^{-3} mol/L (*filled triangle*) and 5×10^{-3} mol/L (*filled square*) at 293 K

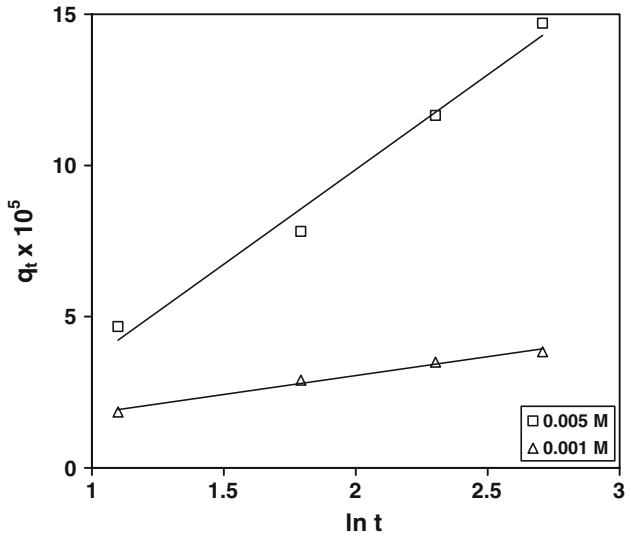


Fig. 10 The relation between q_t and ln t in the linearized Elovich adsorption equation for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid at 293 K. The initial U(VI) concentrations are 1×10^{-3} mol/L (*open triangle*) and 5×10^{-3} mol/L (*open square*)

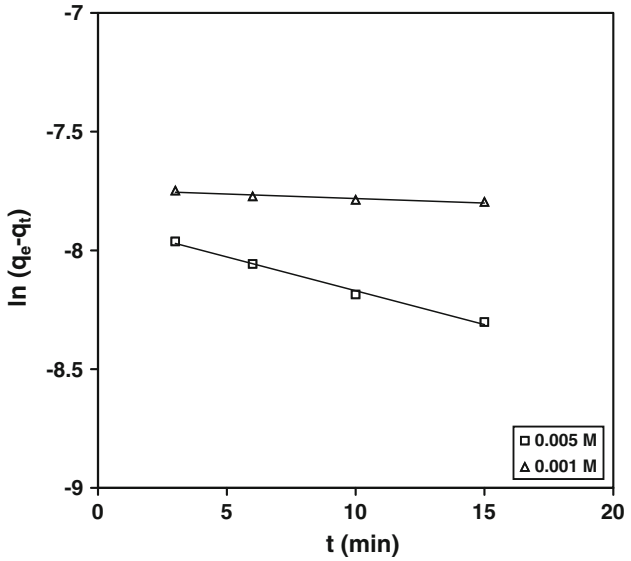


Fig. 11 The dependence of adsorption data $\ln(q_e - q_t)$ to time, using pseudo-first order kinetic model as a function of initial uranium concentrations of 1×10^{-3} mol/L (*open triangle*) and 5×10^{-3} mol/L (*open square*) at 293 K

time, t, respectively. The k (1/min) is the rate constant for pseudo-first order kinetic equation. The linearized form of the pseudo-first order kinetic equation can be given below.

$$\ln(q_e - q_t) = \ln q_e - kt \tag{19}$$

The results of the U(VI) adsorption on the crosslinked polyester resin containing acrylic acid functional groups were given in Fig. 11 for initial U(VI) concentrations of 5×10^{-3} and 1×10^{-3} mol/L. A linear relationship between $\ln(q_e - q_t)$ and t has been established with a fairly low correlation coefficient (R values = 0.993 and 0.887) (Table 2). The adsorption rate constants were determined as 2.85×10^{-2} and 0.38×10^{-2} min^{-1} for initial U(VI) concentration of 5×10^{-3} and 1×10^{-3} mol/L, respectively.

The Pseudo-second order kinetic model

The pseudo-second order kinetic model defines that the rate controlling mechanism formed by chemical reaction for the sorption of metal ions on adsorbents [7, 27, 52, 53, 56–59]. In order to describe U(VI) sorption on the crosslinked polyester resin for the initial U(VI) concentrations of 5×10^{-3} and 1×10^{-3} mol/L at constant temperature (293 K), the kinetic data obtained from batch adsorption experiments have been analyzed using the pseudo-second order kinetic equation given below.

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{20}$$

where q_e and q_t are the amounts of uranium ions adsorbed by the crosslinked polyester resin functionalized with acrylic acid at equilibrium and at time, t, respectively. The k (L/mol s) is the rate constant for pseudo-second order kinetic equation. By separating variables and integrating the equation for initial limit, $t = 0$, $q_t = 0$, the following Eq. 21 is obtained which is the integrated rate law of pseudo-second order reaction.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{21}$$

This Eq. 21 can be rearranged to obtain the following linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{22}$$

The kinetic plots of t/q_t versus t for U(VI) adsorption on the crosslinked polyester resin bearing acrylic acid functional groups are represented in Fig. 12. The figure exhibits a linear relationship between t/q_t and t for U(VI) adsorption on the crosslinked copolymer bearing acrylic acid functional groups. The results given in Table 6 indicated the adsorption rate constant (k), initial adsorption rate ($h = kq_e^2$) and equilibrium adsorption capacity (q_e) as a function of initial U(VI) concentrations As can be seen from Fig. 12 and Table 6, the data-fits have revealed high correlation coefficient ($0.991 \leq R \leq 0.996$), when the pseudo-second order kinetic model was employed to the experimental results. The goodness of the fit to the pseudo-second order kinetic model indicates that U(VI) adsorption on the crosslinked polyester resin occurred by chemisorption mechanism [27, 28, 52]. With increasing the

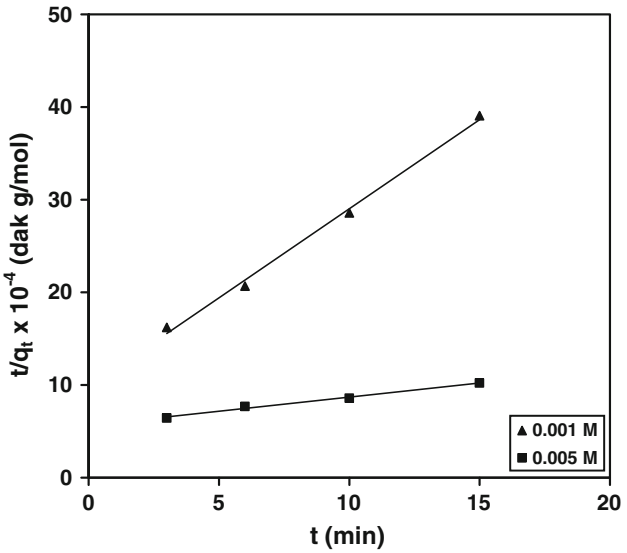


Fig. 12 The fitting of adsorption data on the pseudo-second order kinetic equation for the U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid at 293 K. The initial U(VI) concentrations are 1×10^{-3} mol/L (*filled triangle*) and 5×10^{-3} mol/L (*filled square*)

Table 6 The kinetic constants obtained from the pseudo-first order and pseudo-second order kinetic equation for the U(VI) adsorption on crosslinked polyester resin functionalized with acrylic acid from aqueous solutions at 293 K

C_0 (mol/L)	Pseudo-first order kinetic model		Pseudo-second order kinetic model			
	k (min^{-1})	R	q_e (mol/g)	k (g/min mol)	h (mol/min g)	R
5×10^{-3}	2.850×10^{-2}	0.993	3.245×10^{-4}	2.815	1.776×10^{-5}	0.991
1×10^{-3}	0.380×10^{-2}	0.887	0.519×10^{-4}	6.314	1.022×10^{-5}	0.996

initial U(VI) concentration from 1×10^{-3} to 5×10^{-3} mol/L, the adsorption capacity (q_e) and the initial adsorption rate (h) increased from 0.519×10^{-4} to 3.245×10^{-4} mol/g and from 1.022×10^{-5} to 1.776×10^{-5} mol/(min g) whereas the adsorption rate constant decreased from 6.314 to 2.815 g/(min mol), respectively. The result indicated that the kinetic data obtained from experimental results fitted better to the pseudo-second order kinetic model than other kinetic models.

The effect of pH

It is known that the pH of medium has an influence upon the adsorption of metal ions onto adsorbent [5, 27–29, 39, 44, 50]. The initial pH of solution (1×10^{-3} mol/L and 5 mL) containing 0.05 g of adsorbent was determined as 3.75. The pH values of the mixtures were adjusted by adding 2 N HCl and 0.1 N NaOH solutions. The pH values were varied from 0.6 to 6.2 keeping other parameters constant as adsorption temperature of 293 K and initial U(VI) concentration of 1×10^{-3} mol/L. The dependence of adsorption percentage of U(VI) ions on the pH of solution was given in Fig. 13. The adsorption percentage of the U(VI) ions adsorbed on the crosslinked polyester resin functionalized with acrylic acid indicated a marked influence with increasing pH of solution from 0.6 to 3.2 then started to decrease slightly with further increase in the pH of solution. Considering uranyl adsorption by amideoxime functional polymers [24, 60] and iron oxide based matrix sorbent [61, 62] operating in neutral or in alkaline medium, uranyl adsorption by the crosslinked polyester resin functionalized with acrylic acid under highly acidic condition (pH 0.6–3.2) was significant achievement. Since the ideal pH for the adsorption of common metal ions by chelating polymers was in neutral or weakly alkaline. Uranyl sorption ability of crosslinked polyester resin functionalized with acrylic acid made it superior in comparison of other sorbent materials. Since most other ions can not be adsorbed in the range of pH 0.6–3.2, the capacity of crosslinked polyester resin with acrylic acid has enhanced virtually. According to pH results our observations for U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid, the binding mechanism of

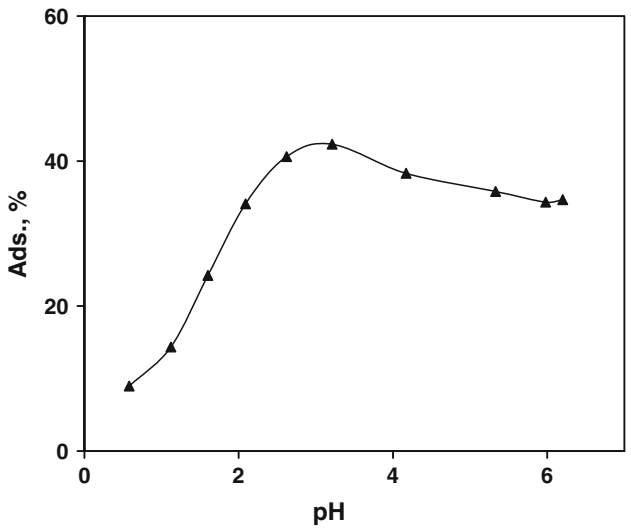


Fig. 13 The effect of the solution pH on the adsorption percentage of U(VI) ions. Initial pH of the mixture of 1×10^{-3} mol/L U(VI) solution (5 mL) and 0.05 g of adsorbent is 3.75. $T = 293$ K; $t = 60$ min

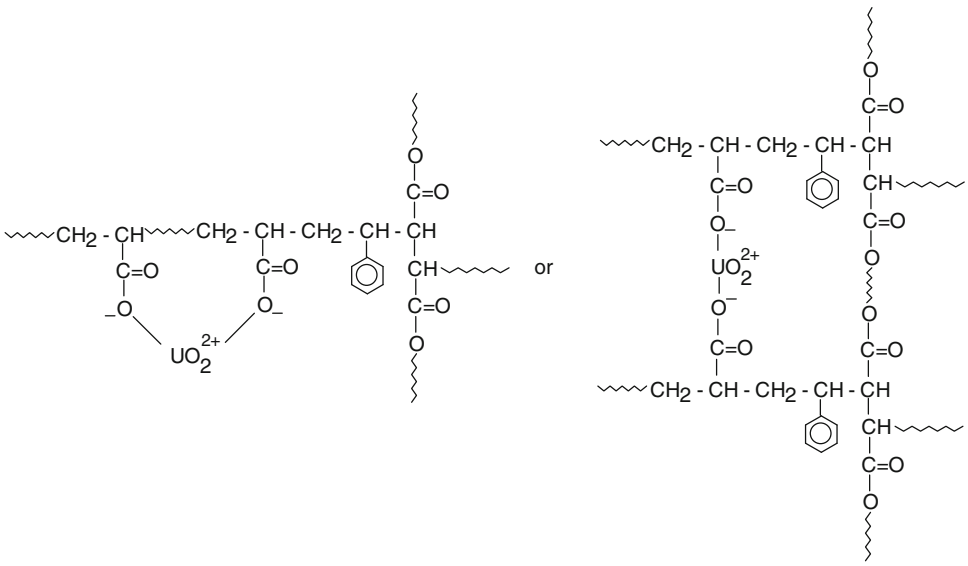
U(VI) ions by the carboxyl groups of crosslinked polyester resin can be shown in Scheme 2.

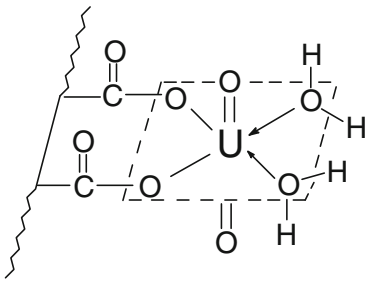
Since uranyl was four coordinating ion [21, 28, 63], additional two water molecules were expected to involve in the coordination to form a planar geometry as illustrated in Scheme 3.

Conclusion

A crosslinked copolymer of unsaturated polyester resin dissolved in styrene (80% as weight percentage) and acrylic acid (20% as weight percentage) was synthesized to use it for the adsorption of U(VI) ions from aqueous solutions. The effects of the parameters of the initial U(VI) concentration, contact time, pH and temperature on the U(VI) adsorption were examined. Experimental results indicated that with increasing initial uranium concentration from 1×10^{-3} mol/L to 5×10^{-3} mol/L at constant adsorption temperature ($T = 293$ K) and time ($t = 60$ min), the percentage of U(VI) adsorption observed at 0.05 g of adsorbent decreased from 50.33 to 34.00% however the amount of U(VI)

Scheme 2 Chemical structure of U(VI) bonding mechanism of the crosslinked polyester resin functionalized with acrylic acid





Scheme 3 The geometric structure of U(VI) bonding of the crosslinked polyester resin functionalized with acrylic acid

adsorbed on the crosslinked polyester resin functionalized with acrylic acid increased from 6.00 mg/g copolymer to 80.90 mg/g copolymer. When temperature in the adsorption measurement increased from 293 to 323 K at constant initial U(VI) concentration of 1×10^{-2} mol/L, the percentage and amount of U(VI) adsorbed on the crosslinked polyester resin bearing acrylic acid functional groups increased from 34.00 to 49.10% and from 80.90 mg U(VI)/g copolymer to 116.87 mg U(VI)/g copolymer, respectively due to diffusibility of U(VI) ions on the polymer matrix or more ionization of carboxyl groups by increase in the temperature. The obtained adsorption data depending on initial U(VI) concentration were analyzed by the Freundlich, Langmuir and D–R isotherms. The n_F value obtained from the Freundlich equation was determined to be lower than 1. This meant that the surface of adsorbent was heterogeneous. The average free energy change (E) was calculated by applying the D–R isotherm to the obtained adsorption data was found to be 7.33 kJ/mol. It was reported that an energy adsorption based on ion exchange mechanism was around 8–16 kJ/mol. The adsorption free energy of 7.33 kJ/mol found in this study was close to the energy range of ion-exchange. Therefore the adsorption by the crosslinked polyester resin functionalized with acrylic acid has been ion-exchange type. Enthalpy ($\Delta H°$), entropy ($\Delta S°$) and free energy change ($\Delta G°$) were calculated for the uranium adsorption on the crosslinked polyester resin containing acrylic acid functional groups. The enthalpy value found to be positive shows the nature endothermic adsorption process. The value of free energy ($\Delta G°$) has been negative and it was observed that a decrease in $\Delta G°$ values with increase in temperature. Positive entropy ($\Delta S°$) found in the experiments reflects the affinity of the crosslinked polyester resin functionalized with acrylic acid as adsorbent towards uranium ions in solution and the results indicate that contribution of enthalpy term makes the free energy change negative. The fitting of adsorption data obtained from experimental results depending on contact time was analyzed by the fractional power, the Elovich, the pseudo-first order and the pseudo-second order kinetic models. Experimental results indicate that the obtained adsorption data depending on contact time provided much better fitting for the pseudo-second order kinetic equation with high correlation coefficient ($0.991 \leq R \leq 0.996$). The goodness of the fit of adsorption data to the pseudo-second order kinetic model indicates that U(VI) adsorption on the crosslinked polyester resin functionalized with acrylic acid occurred by chemisorption mechanism. When the pseudo second order kinetic model was applied to the obtained experimental results depending on contact time, it was observed that with increasing the initial U(VI) concentration from 1×10^{-3} to 5×10^{-3} mol/L, the adsorption capacity (q_e) and initial adsorption rate (h) increased 0.519×10^{-4} to 3.245×10^{-4} mol/g and from 1.022×10^{-5} to 1.776×10^{-5} mol/(min g) whereas the adsorption rate constant (k) decreased from 6.314 to 2.815 g/(min mol) respectively. When the dependence of

adsorption percentage of U(VI) ions on the pH of solution was examined, It was observed that the adsorption percentage of U(VI) adsorbed on the crosslinked polyester resin bearing acrylic acid functional groups indicated a marked influence with increasing the pH of solution ranging from 0.6 to 3.2 then started to decrease slightly with further increase in the pH of solution.

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