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Removal of strontium ions by a crosslinked copolymer containing methacrylic acid functional groups

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A tail-made polymer matrix is proposed to remove strontium ions from aqueous solutions. The removal behavior of strontium ions on a crosslinked copolymer containing methacrylic acid as functional groups was investigated as a function of sorptive concentration, time, temperature and pH. It was observed that an increase of these parameters enhanced the removal of Sr(II) ions from aqueous solution. It is found that a maximum adsorption of Sr(II) ions can be obtained on the crosslinked copolymer after 30 minutes and at pH 8. The increase of Sr(II) ion concentration in the solution resulted in an increase in the amount of Sr(II) ions adsorbed on the crosslinked copolymer containing methacrylic acid as functional groups. However, after a maximum of Sr(II) concentration in the solution, the percentage of adsorbed Sr(II) ions decreased. The adsorption data are well represented by the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms. The adsorption capacity of the copolymer and the free energy change were calculated by using the D-R isotherm. For the adsorption of Sr(II) ions on the crosslinked copolymer the thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) were calculated.

Introduction

For the treatment of aqueous nuclear waste solution, the techniques of ion-exchange, solvent extraction and sorption on solids have been studied in previous papers.[1–8] In recent years, the use of polymeric adsorbents gives advantages for controlling the adsorption capacity.[9–14] The preconcentration and separation of Sr(II) ions from the waste solutions are important, therefore, it has found many applications in the nuclear industry and in the environmental waste disposal point of view.[4–6,15–17]

The present paper reports the adsorption behavior of Sr(II) ions on crosslinked copolymer containing methacrylic acid as functional groups. For this purpose, methacrylic acid and ethylene glycol dimethacrylate were copolymerized using the benzoyl peroxide-N,N-dimethyl aniline initiator system. Finally, a crosslinked copolymer containing methacrylic acid as functional groups was synthesized. The structure of the copolymer was examined by FT-IR and its carboxyl content was determined by titrimetry.

This copolymer was used for the investigation of the adsorption of Sr(II) ions from solution and here the batch method was applied. The effect of temperature, time, Sr(II) concentration and pH on the adsorption of Sr(II) ions from aqueous solutions was investigated. Freundlich, Langmuir and Dubinin-Radushkevich(D-R) adsorption isotherms were used for fitting the adsorption data. Loading experiments were performed in the function of strontium concentration. The thermodynamic parameters of $\Delta H°$, $\Delta S°$ and $\Delta G°$ were calculated for the adsorption of Sr(II) on the crosslinked copolymer.

Experimental

Reagent

Ethylene glycol dimethacrylate (Merck), methacrylic acid (Merck), N,N-dimethyl aniline (Fluka), dibenzoyl peroxide paste in dibutyl phthalate (Lucidol BT-50, Akzo Nobel), strontium chloride (Merck) were used without further treatment and noted as EGDM, MA, DMA, BPO and Sr(II), respectively.

Synthesis of crosslinked copolymer

In previous studies, polymers bearing carboxylate functional groups such as methacrylic acid or imino acetic acid were synthesized for metal uptakes from solutions, using different initiator system.[18–20] Peroxide and hydroperoxide can be employed for free radical polymerization or copolymerization reactions. Decomposition of an organic peroxide or hydroperoxide can be accomplished either thermally or by addition of chemical reducing agents. Tertiary amines are commonly used as promoters or co-promotors of polymerization reactions especially for systems using benzoyl peroxide or methyl ethyl ketone peroxide–cobalt octoate initiator systems, respectively.[21–23] From this point, of view we purposed to synthesize an insoluble copolymer bearing carboxylate groups for the investigation of the absorption of metal ions from solutions.

Dibenzoyl peroxide-N,N-dimethylaniline (DMA) initiator system was used to initiate the copolymerization of methacrylic acid (MA) and ethylene glycol dimethacrylate (EGDM) at room temperature.

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For this purpose, 75 g EGDM and 25 g MA were mixed together in a 250-ml beaker and 2.2 g benzoyl peroxide (BPO) paste was added, and the mixture was stirred. During stirring, 0.2 ml DMA was added to start the copolymerization of EGDM and MA at room temperature. Finally a crosslinked copolymer having the following structure was synthesized (Scheme 1).

The structure of the crosslinked copolymer was examined by FT-IR and the carboxyl content was determined by titrimetry.

The FT-IR spectrum of the crosslinked copolymer is given in Fig. 1. A broad absorption band due to the O–H bond present in the –COOH group can be observed in the range of 3200–3500 cm^{-1}. The C=O of carboxylic acid or ester group shown in the chemical formula in Scheme 1 is observed at 1730 cm^{-1}. The bands at 1400 cm^{-1} and 1460 cm^{-1} indicate O–H bending and the existence of C–O stretching in the plane C–O–H bending. The CH_3 bending of the methacrylic acid group also appears at 1400 cm^{-1}. The C–O–C asymmetric stretching in the ester groups is observed at 1280 cm^{-1} and 1170 cm^{-1}.

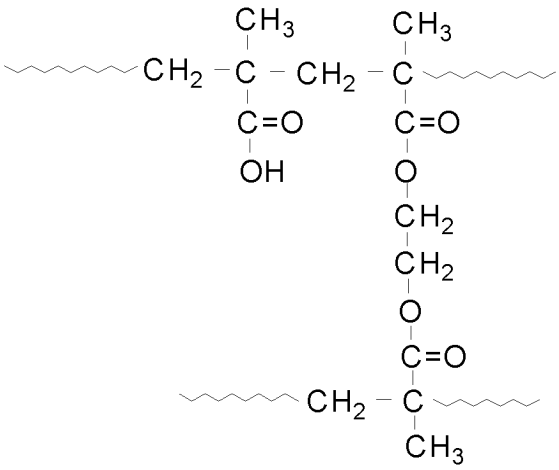
For the titrimetric determination of carboxyl groups in the copolymer, 1 g of copolymer sample was treated by 20 ml of 2M NaOH solution for 4 hours. Then, it was filtered and washed carefully three times with 20 ml distillated water to remove the excess of NaOH over the stoichiometric amount bound by carboxylate groups. Then, 0.5 g dried copolymer sample in 10 ml distillated water was titrated with 0.105M HCl solution. The volume of consumed HCl solution at the neutralization point was 5.85 ml and the titration was completed in 30 minutes. The amount of carboxyl groups was found as 1.53 mmol/g copolymer.

Adsorption measurements

The obtained crosslinked copolymer was in solid form. For the adsorption experiments it was ground to powder and the particles having a grain size under 160 μm of diameter were used. The batch method was used for the adsorption of strontium ions on the copolymer sample (0.02 g copolymer/5 ml strontium ion solution). Sr(II) uptake experiments were performed under non-buffered conditions at pH 4.5–4.6. The dependence of adsorption on the strontium concentration ($1\cdot10^{-2}$, $1\cdot10^{-3}$, $1\cdot10^{-4}$, $1\cdot10^{-5}$ and $1\cdot10^{-6}$ mol/l), temperature (283, 293 and 303 K), time (1, 5, 15, 30 and 60 minutes) and pH (between 2 and 8) was investigated.

A 0.02 g copolymer sample was immersed in 5 ml of Sr(II) solution. After shaking the mixture for 60 minutes, two phases were separated by centrifugation at 3500 rpm for 20 minutes.

The β-activities of the solutions can be measured by a Geiger-Müller (GM) counter.



Scheme 1. Synthesized crosslinked copolymer

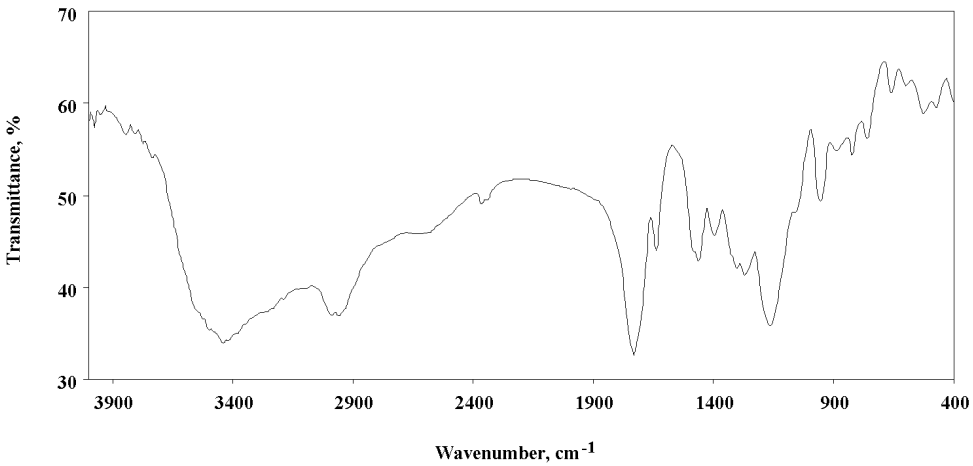


Fig. 1. FT IR spectrum of copolymer synthesized from EGDM and MA using the BPO-DMA initiator system at room temperature

In the radiometric method, the decay of radioactive isotope is described by:

$$N_t = N_0 e^{-\lambda t} \tag{1}$$

where N_0 represents the number of atoms at $t=0$, N_t is the number of atoms at time t, and λ is the decay constant. For a sample of N_t nuclei at a given time, having a decay constant λ, the expected number of nuclei decaying per time unite is:

$$A_t = \lambda N_t \tag{2}$$

where A_t is the activity of the sample at time t. The term specific activity of gases or liquids is given as activity/volume (Bq/m^3 or Ci/m^3). During the measurement of the Sr(II) adsorption on the copolymer, the change in the β-activity of the solution was determined with ERG Mullard G-M tube type MX123. The adsorption percentage (Ads.%) and the distribution coefficient (K_D) were calculated by:

$$\text{Ads.}\% = \frac{A_i - A_f}{A_i} \times 100 \tag{3}$$

$$K_D = \frac{A_i - A_f}{A_i} \cdot \frac{V}{m} \tag{4}$$

where A_i and A_f are the initial and final activities (Bq/cm^3) of the solution, respectively, V is the volume of solution (ml) and m is the amount of the adsorbent (g).

Result and disscusion

Effect of concentration

The adsorption of Sr(II) on the crosslinked copolymer containing methacrylic acid as functional groups has been studied as a function of strontium concentration from $1\cdot10^{-6}$ mol/l to $1\cdot10^{-2}$ mol/l at various temperatures ($T=283$, 293 and 303 K) (Fig. 2). As seen, a decrease of strontium concentration indicated an increase in the percentage of strontium adsorption on the crosslinked copolymer. Due to previous studies the reason for the increase in adsorption might be the creation of new adsorption sites, acceleration of some originally slow adsorption steps or transport against the concentration gradient and/or diffusion controlled transport across the energy barrier.[1,24–25]

Table 1 represents the concentration dependence of the adsorption ability of the material at various temperatures ($T=283$, 293 and 303 K). The table indicates that when the Sr(II) content of the solution ($1\cdot10^{-2}$M) exceeds the capacity, the molar ratio of the absorbed Sr(II) to the carboxyl content becomes 0.408 at 293 K. It seems likely that approximately two and half carboxyl functions are utilized for binding one Sr(II) ion. However, almost all carboxyl functions can not be involved in metal binding, in such a tightly crosslinked polymer matrix. Indeed, at 303 K, this ratio rises up to 0.622 and goes down to 0.255 at 283 K. As a result, this assumption is not true and each Sr(II) ion may be anchored less then all the carboxyl functions. Due to our opinion, the temperature increase have increased the diffusibility of the ions into the polymer matrix, or might be due to the increased ionization of carboxyl groups by increasing temperature. The low binding capacity of the crosslinked copolymer seems to be common for extremely low concentrations. This is largely due to the equilibrium of the adsorption–desorption process, because in this case, there is a competition between the hydrogen ions (produced by dissociation) and the Sr(II) ions.

Adsorption isotherms

The modeling of the equilibriums of the uptake processes were carried out using the Freundlich, the Langmuir and the D-R isotherms.

The fitting of adsorption data by the Freundlich adsorption isotherm was studied at a constant temperature of 293 K using the following equation:

$$q_e = K_F \cdot C_e^{n_F} \tag{5}$$

where q_e is the amount of Sr(II) adsorbed at equilibrium (mol/g) and C_e is the equilibrium solution concentration in mol/l, n_F and K_F are the Freundlich adsorption constants. Figure 3 shows that the log q_e versus log C_e plot is a straight line for the adsorption of Sr(II) ions on the crosslinked copolymer. The concentration of Sr(II) ions was between $1.0\cdot10^{-2}$ and $1.0\cdot10^{-6}$ mol/l. The values of n_F and K_F which are Freundlich constants were calculated from the slope and intercept of this line and found to be 0.866 and 0.287, respectively. The correlation coefficient (R) of the straight line was found as 0.997. The intercept value of $n_F=0.886$ is lower than 1. This indicates that a heterogeneous adsorption reaction occurs. The value of n ($0<n<1$) indicates that the surface of adsorbent is heterogeneous.[1,8]

According to the empirical Freundlich constants the adsorption of Sr(II) ions is a heterogeneous reaction. This means that a chemical adsorption reaction takes place on the copolymer in case of the adsorption of Sr(II) ions.

The strontium adsorption process studied is a heterogeneous process being the adsorbent a solid phase and the Sr(II) ions are in the liquid phase. The exponent in the Freundlich isotherm, n means somewhat different. In the case where $n<1$, the adsorption process is referred to as heterogeneous in which the adsorbed entities accumulate heterogeneously on the adsorbent phase.

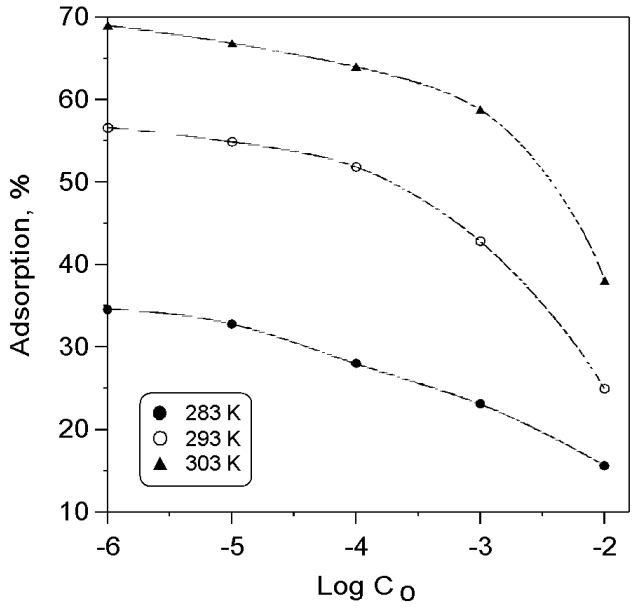


Fig. 2. Relation between initial strontium concentration and the percentage of Sr(II) adsorbed on crosslinked copolymer containing methacrylic acid functional groups at various temperatures; ● T = 283 K, ○ 293 K and ▲ 303 K. Contact time: t = 60 minutes

Table 1. Adsorption characteristics of Sr(II) on the copolymer at various temperatures

Temperature, K	C_0, mol/l	Adsorption percentage, %	$n_{0,\,Sr(II)}/n_{COOH}$	$n_{A,\,Sr(II)}/n_{COOH}$
283	$1\cdot10^{-6}$	34.54	$16.34\cdot10^{-5}$	$5.64\cdot10^{-5}$
	$1\cdot10^{-5}$	32.80	$16.34\cdot10^{-4}$	$5.36\cdot10^{-4}$
	$1\cdot10^{-4}$	27.99	$16.34\cdot10^{-3}$	$4.57\cdot10^{-3}$
	$1\cdot10^{-3}$	23.06	$16.34\cdot10^{-2}$	$3.77\cdot10^{-2}$
	$1\cdot10^{-2}$	15.62	$16.34\cdot10^{-1}$	$2.55\cdot10^{-1}$
293	$1\cdot10^{-6}$	56.59	$16.34\cdot10^{-5}$	$9.24\cdot10^{-5}$
	$1\cdot10^{-5}$	54.88	$16.34\cdot10^{-4}$	$8.96\cdot10^{-4}$
	$1\cdot10^{-4}$	51.86	$16.34\cdot10^{-3}$	$8.47\cdot10^{-3}$
	$1\cdot10^{-3}$	42.86	$16.34\cdot10^{-2}$	$7.00\cdot10^{-2}$
	$1\cdot10^{-2}$	24.97	$16.34\cdot10^{-1}$	$4.08\cdot10^{-1}$
303	$1\cdot10^{-6}$	68.98	$16.34\cdot10^{-5}$	$11.27\cdot10^{-5}$
	$1\cdot10^{-5}$	66.82	$16.34\cdot10^{-4}$	$10.92\cdot10^{-4}$
	$1\cdot10^{-4}$	63.99	$16.34\cdot10^{-3}$	$10.45\cdot10^{-3}$
	$1\cdot10^{-3}$	58.80	$16.34\cdot10^{-2}$	$9.61\cdot10^{-2}$
	$1\cdot10^{-2}$	38.06	$16.34\cdot10^{-1}$	$6.22\cdot10^{-1}$

Contact time: t = 60 minutes.
C_0: Initial Sr(II) concentration.
$n_{0,\,Sr(II)}$: Number of Sr(II) ions (mmol) in solution at t=0.
$n_{A,\,Sr(II)}$: Number of adsorbed Sr(II) ions(mmol) at t=60 minutes.
n_{COOH}: Number of available carboxyl groups in 0.02 g crosslinked copolymer (n_{COOH} = 0.02 g×1.53 mmol/g = $3.06\cdot10^{-2}$ mmol).

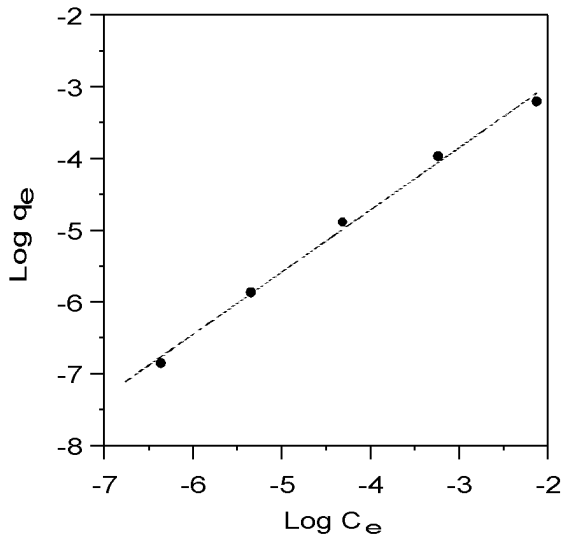


Fig. 3. Freundlich adsorption isotherm for the adsorption of Sr(II) on crosslinked copolymer containing methacrylic acid functional groups at 293 K

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

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

where q_e is the strontium concentration absorbed on the crosslinked copolymer at equilibrium (mol/g), C_e is the equilibrium solution concentration in mol/l, the constants of K_L and b are the characteristics of the Langmuir equation. Figure 4 indicates a plot of C_e/q_e versus C_e. The relationship between the C_e/q_e and C_e values is not linear. This indicates that the adsorption data do not fit to the Langmuir adsorption isotherm. The deviation from linearity could be due to the fact that these type of isotherms have originally been deviated from the adsorption of gases on adsorption surfaces and, therefore, there are limitations in the extrapolation for the interpretation of the adsorption of other compounds,[2,27] as in the present study.

The D-R isotherm model is applicable at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. The D-R isotherm model is represented by:

$$q_e = q_m \cdot \exp(-K\varepsilon^2) \quad (7)$$

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

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (8)$$

The value of q_m and K were determined by plotting $\ln q_e$ versus ε^2 as given in Fig. 5 and found to be $1.321 \cdot 10^{-3}$ and $-79.16 \cdot 10^{-4}$, respectively. The correlation coefficient (R) of the straight line was 0.997.

The value of K (mol/kJ)^2 is the constant related to the mean free energy of adsorption, E (kJ/mol) which is defined as the free energy change required to transfer one mole of ions from the infinity in the solution to the solid surface:

$$E = (-2K)^{-1/2} \quad (9)$$

For the adsorption of Sr(II) ions on the crosslinked copolymer E was found as 7.947 kJ/mol at 293 K. The magnitude of E can be used for estimating the type of adsorption reaction.[28] In our experiments, we found 7.947 kJ/mol which is near to the energy range of ion-exchange reactions, 8–16 kJ/mol.

Effect of contact time

Five ml-solutions with strontium(II) ion concentrations between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-2}$ mol/l were mixed with 20 mg copolymer containing methacrylic acid as functional groups at 293 K. It was observed that with increasing of time, the amount of Sr(II) ions adsorbed on crosslinked copolymer increased and reached an equilibrium after 30 minutes (Fig. 6). The further increase in Sr(II) concentration resulted in a decrease in the adsorption percentage of Sr(II) on the crosslinked copolymer.

There are three phases for the adsorption of Sr(II) ions on the copolymer: a rapid uptake (Phase I), a transition phase (Phase II) and an almost flat phase (Phase III). In Phase I the most readily available adsorbing sites will be occupied on the adsorbent surfaces (bulk diffusion). Also ion-exchange reaction could take place during this rapid uptake of Sr(II) ions on the copolymer. Phase II, exhibiting additional removal, can be attributed to the diffusion of the adsorbate from the surface into the macro-pores of the adsorbent (pore diffusion or intraparticle diffusion), stimulating a further migration of the adsorbate from the liquid phase onto the adsorbent surface. Phase III represents a state of equilibrium.[1,8,29]

Effect of loading and temperature

For the adsorption of Sr(II) ions on the croslinked copolymer, the loading curve was constructed by plotting K_D values versus log[Sr(II)] as illustrated in Fig. 7. The units of K_D and Sr(II) were given in l/g and mol/g, respectively. The loading curve at 293 K indicates a single adsorption layer.

Temperature dependence of the adsorption of Sr(II) ions on the crosslinked copolymer was studied at various strontium concentrations between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-2}$ mol/l in the temperature range of 283 to 303 K. The following equation was used to calculate $\Delta H°$ and $\Delta S°$:

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

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 8 shows the relation between $1/T$ and $\ln K_D$.

The standard free energy values were calculated by:

$$\Delta G° = \Delta H° - T\Delta S° \tag{11}$$

where $\Delta G°$ is the standard free energy. The calculated values of $\Delta H°$, $\Delta S°$ and $\Delta G°$ are given in Table 2. It was observed that $\Delta H°$ is positive for the adsorption reaction of Sr(II) on the crosslinked copolymer. This means that endothermic reaction takes place during the adsorption of Sr(II) ions on the copolymer. The values of free energy are negative and indicate a decrease in $\Delta G°$ with increase in temperature. This indicates that the reaction is fast and runs easier at high temperature.

Effect of pH

It is known that pH is an important factor in the adsorption of metal cations on adsorbents. The initial pH of each mixture of Sr(II) solution ($1 \cdot 10^{-3}$M, 5 ml) and 0.02 g copolymer was 4.55. The pH values of solutions were adjusted by 0.1N HCl and 0.1N NaOH solutions. The effect of pH on the adsorption of Sr(II) on the crosslinked copolymer containing methacrylic acid as functional groups is shown in Fig. 9. With increasing pH of the solution, the amount of Sr(II) adsorbed on the crosslinked copolymer increased up to pH 8 and reached an equilibrium after pH 8. Our results show that the Sr(II) ions are able to be bound chemically to the carboxyl groups in the copolymer. The metal bonding mechanism of the copolymer containing methacrylic acid groups can be seen in the formula given in Scheme 2.

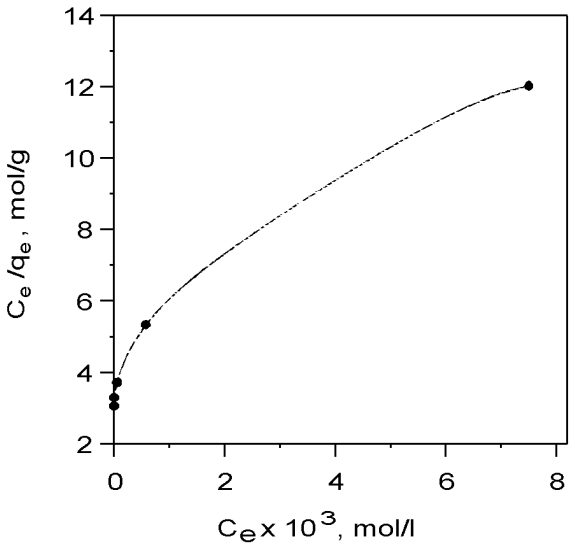


Fig. 4. Dependence of adsorption data on the Langmuir adsorption isotherm at 293 K

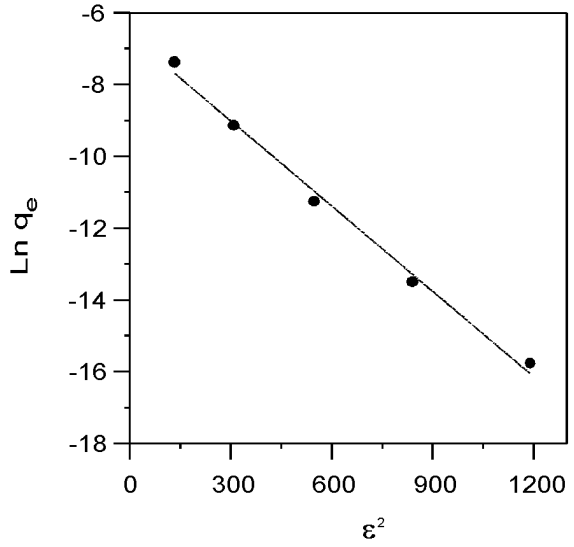


Fig. 5. D-R adsorption isotherm for the adsorption of Sr(II) on crosslinked copolymer containing methacrylic acid functional groups at 293 K

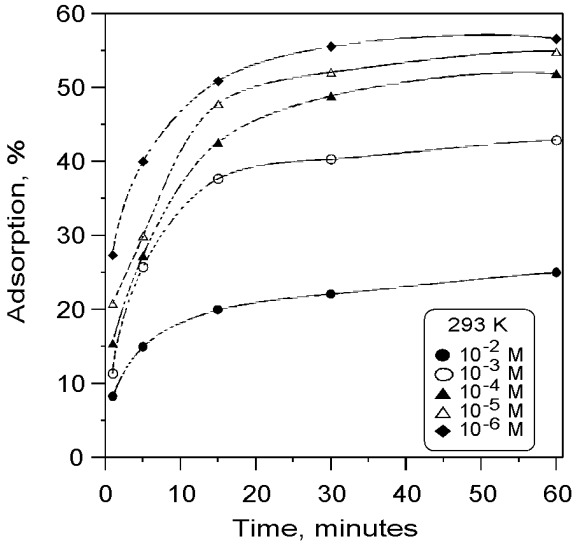


Fig. 6. Dependence of adsorption of Sr(II) ions on contact time. Initial concentrations of Sr(II): ♦ $1 \cdot 10^{-6}$, Δ $1 \cdot 10^{-5}$, ▲ $1 \cdot 10^{-4}$, ○ $1 \cdot 10^{-3}$ and ● $1 \cdot 10^{-2}$ mol/l

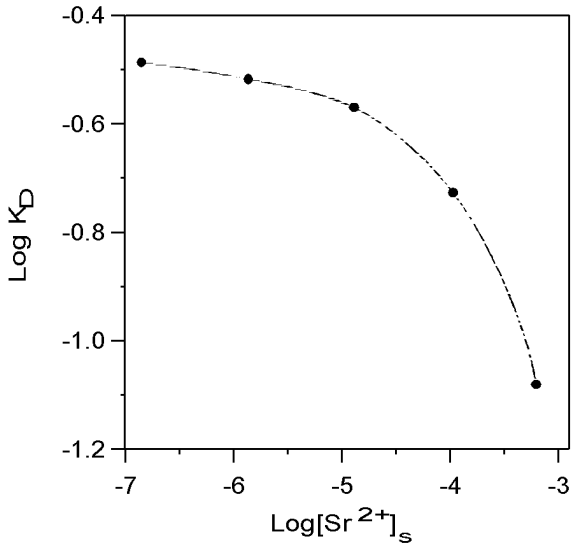
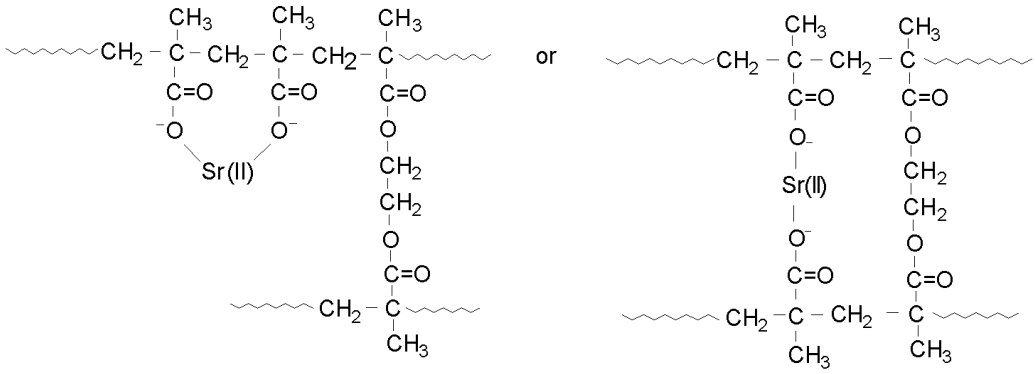


Fig. 7. Loading curves for the adsorption of Sr(II) on crosslinked copolymer at 293 K



Scheme 2. Metal bonding mechanism of the copolymer

Table 2. Calculated values of thermodynamic parameters for the adsorption of Sr(II) ions on crosslinked copolymer containing methacrylic acid functional groups

C_0, mol/l	$\Delta H°$, $\times 10^2$ kJ/mol	$\Delta S°$, kJ/mol·K	$\Delta G°$, kJ/mol			R
			283 K	293 K	303 K	
$1 \cdot 10^{-6}$	4.279	0.182	–51.7	–53.6	–55.4	0.999
$1 \cdot 10^{-5}$	5.577	0.233	–65.9	–68.3	–70.6	0.996
$1 \cdot 10^{-4}$	5.443	0.231	–65.3	–67.6	–69.9	0.984
$1 \cdot 10^{-3}$	5.074	0.220	–62.1	–64.3	–66.5	0.989
$1 \cdot 10^{-2}$	5.146	0.223	–63.0	–65.2	–67.5	0.992

C_0: Initial Sr(II) concentration.

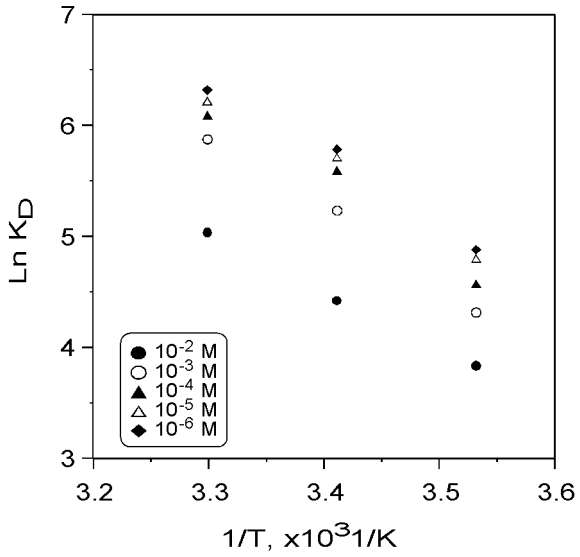


Fig. 8. Variation of log K_D versus $1/T$ for the adsorption Sr(II) on crosslinked copolymer containing methacrylic acid functional groups. Initial concentrations of Sr(II): ♦ $1 \cdot 10^{-6}$, Δ $1 \cdot 10^{-5}$, ▲ $1 \cdot 10^{-4}$, ○ $1 \cdot 10^{-3}$ and ● $1 \cdot 10^{-2}$ mol/l

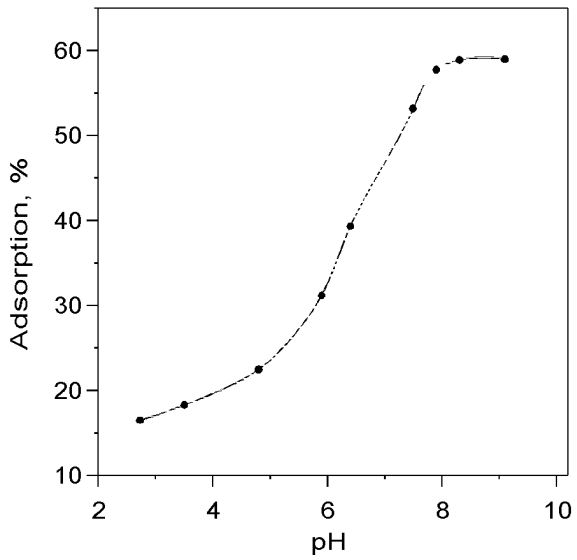


Fig. 9. Effect of pH on the adsorption of Sr(II) ions on crosslinked copolymer at 293 K. Initial concentration of Sr(II): $1 \cdot 10^{-3}$ mol/l; Contact time: $t = 60$ minutes. Initial pH of the mixture of Sr(II) solution ($1 \cdot 10^{-3}$M) and 0.02 g of crosslinked copolymer was 4.55

Conclusions

The effects of strontium concentration, time, temperature and pH on the adsorption of Sr(II) ions were studied by using a crosslinked copolymer containing methacrylic acid as functional groups as adsorbent. The fitting of adsorption data to the Freundlich, Langmuir and the D-R isotherms was investigated. The results indicate that this copolymer having methacrylic acid as functional groups can be used to remove Sr(II) ions from waste solution. The value of free energy was found to be negative which indicated a decrease in $\Delta G°$ values with the increase in temperature, i.e., the reaction takes place easier at higher temperatures. The increase of pH of the solution up to pH 8 leads to an increase of the amount of Sr(II) ions adsorbed on the copolymer. This indicates that the adsorption of Sr(II) ion on the copolymer bearing methacrylic acid functional groups can be a chemical process. Since this adsorbent can be produced from commercially available starting materials, the procedure described here might be a cost effective alternative for the removal of radioactive Sr(II) ions from wastes.

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