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Investigation of Cs(I) adsorption on densely crosslinked poly(sodium methacrylate) from aqueous solutions

Cemal Özeroğlu · Emine Doğan · Gönül Keçeli

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Abstract In this study, a crosslinked copolymer bearing sodium methacrylate functional groups has been proposed to remove Cs(I) ions from aqueous solutions. For this purpose, the crosslinked copolymer of ethylene glycol dimethacrylate (EGDM) and methacrylic acid (MA) containing 25% MA as weight percentage was synthesized by using benzoyl peroxide (BPO)-*N*,*N*-dimethyl aniline initiator system. The available carboxyl groups in copolymer were converted to the groups of sodium methacrylate using 2 N NaOH. The adsorption behavior of cesium ions on the densely crosslinked poly(sodium methacrylate) from aqueous solutions were investigated by the technique of ICP-MS measurements of cesium ions in solutions. Batch adsorption method was used to analyze the Cs(I) adsorption as a function of parameters such as the amount of adsorbent, contact time, pH of solution, initial Cs(I) concentration and temperature. The adsorption data were evaluated by the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherms. The adsorption capacity and free energy change were calculated by using D–R isotherm. The adsorption data obtained from experimental results have been tested by the fractional power, the Elovich, the pseudo-first order and the pseudo-second order kinetic models.

Keywords Cs(I) adsorption · Poly(sodium methacrylate) · Kinetic equations · Isotherms

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Introduction

Toxic or radioactive metals cause progressive or irreversible renal injury and in acute cases, may lead to kidney failure and dead [1–9]. Nuclear technologies have provided a better quality of different fields of life. However, this leads to accumulation of substantial amounts of radioactive wastes or waste solutions and the radionuclide ^{137}Cs is produced in high yield during the fission processes. It is potentially very hazardous nuclide due to its long half-life ($t_{1/2} = 30.17$ years) and is a very radiocontaminant having high solubility in aqueous media [1, 10–13]. 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. A lot separation and preconcentration techniques such as chemical precipitation, ion-exchange, solvent extraction and sorption on the solid have developed to remove metal ion [14–22]. Nowadays, there is an increasing effort for removing toxic or radionuclide contaminants from aqueous waste solutions or wastes by using various polymeric adsorbents [23–29]. 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 phosphoric, methacrylic, itaconic, succinic, imminoacetic and hydroxamic acids for removal metal ion from waste solutions [30–36]. In this study, ethylene glycol dimethacrylate (EGDM) has been chosen deliberately due to reasonably high hydrolytic stability of their ester linkage and methacrylic acid (MA) has been chosen as chelating compound because of its well-known chelating ability with metal ions as mentioned previously [2, 27, 32].

Mechanism of adsorption involves chemical reaction between functional groups on the adsorbents and metal ions or mass-transport processes such as in bulk of liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in macropores or micropores. Adsorption isotherms and kinetics fitting to adsorption data have been examined to determine the constants of adsorption isotherms and of kinetic equation for adsorption of toxic or radioactive metal ions by using inorganic or polymeric adsorbents [1, 2, 22, 23, 37–39].

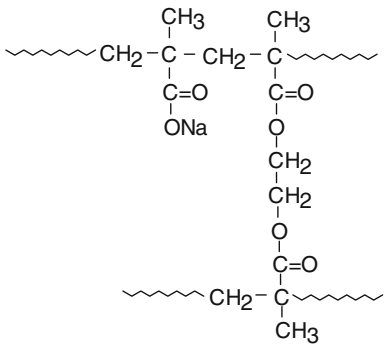
In this study, adsorption behavior of cesium ions on the densely crosslinked poly(sodium methacrylate) from aqueous solutions were investigated by the technique of ICP-MS measurements. Batch adsorption method was used to analyze the Cs(I) adsorption as a function of parameters such as the amount of adsorbent, contact time, pH of solution, initial Cs(I) concentration and temperature. Adsorption data obtained from experimental results have been tested for a number of kinetic and isotherm equations. The constants in adsorption isotherm and kinetic equations have been determined. The adsorption free energy has been calculated by using Dubinin–Radushkevich (D–R) isotherm to adsorption data.

Experimental

The synthesis and characterization of the solid crosslinked copolymer of EGDM and MA containing 25% MA were describe in detail in previous studies [2, 27, 32]. This solid polymer was ground into powder for adsorption experiments. The adsorption ability of Cs(I) on this crosslinked copolymer bearing MA functional groups from aqueous solution was very low due to low interaction between MA functional groups and Cs(I) in aqueous solution. For this reason, carboxylic acid groups in copolymer were converted to sodium methacrylates which are highly ionizable groups. For this purpose, in order to convert all suitable carboxylic acid groups to sodium methacrylates in copolymer, 1 g of polymer sample was treated with 20 mL of 2 N NaOH solution for 4 h. Then it was filtered and three times washed with 20 mL of distilled water to remove excess of NaOH from polymer particles and then it was dried in oven at 60 °C. The crosslinked copolymer having following chemical structure given in Scheme 1 was synthesized.

The particles under 160 μm of diameter was used in adsorption measurements of Cs(I) from aqueous solution and the batch method was used for adsorption of cesium ions on the samples (0.02 g copolymer/5 mL solution of cesium ions) of the crosslinked copolymer containing sodium methacrylate functional groups.

The dependence of adsorption on the amount of adsorbent ($m_{\text{Adsorbent}} = 0.005$, 0.010, 0.020, 0.040, 0.080 and 0.150 g for the constant initial Cs(I) concentration of $C_{\text{Cs(I)}} = 1 \times 10^{-3}$ mol/L, $t = 60$ min and $T = 293$ K), the Cs(I) concentration ($C_{\text{Cs(I)}} = 5 \times 10^{-3}$, 2×10^{-3}, 1×10^{-3}, 5×10^{-4}, 1×10^{-4} and 5×10^{-5} mol/L for $t = 60$ min, $T = 293$ K and $m = 0.02$ g), the temperature ($T = 283$, 293, 303 and 323 K for $t = 60$ min, $m = 0.02$ g and various Cs(I) concentrations), the contact time ($t = 1$, 2, 3, 5, 8, 12, 20, 30 and 60 min for 1×10^{-3} and 5×10^{-4} M initial Cs(I) concentrations at 293 K) and pH from 1 to 9 at 293 K was investigated. During Cs(I) uptake on the crosslinked copolymer containing sodium methacrylate functional groups, 0.02 g polymer sample was immersed in 5 mL Cs(I) solution to measure the effect of parameters of Cs(I) concentration, temperature, pH and contact time for Cs(I) sorption on the crosslinked copolymer from aqueous solutions.



Scheme 1 The chemical structure of crosslinked poly(sodium methacrylate)

Cs(I) sorption was assigned by determining the amount of Cs(I) in solution at beginning and after adsorption by IC-MS measurements. 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:

$$\text{Ads.}\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$K_D = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (2)$$

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

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

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

where C_0 is the initial Cs(I) concentration (mol/L); K_d is the batch distribution coefficient; C_t and C_e are the Cs(I) concentrations (mol/L) in solutions at time, t and at equilibrium at 60 min, respectively; q_t and q_e are the amount of adsorbed Cs(I) in terms of mmol/g on the crosslinked copolymer at time, t and at equilibrium

($t = 60$ min), respectively; V is the volume of Cs(I) solution (mL) in the adsorption experiment and m is the amount of adsorbent (g).

Results and discussion

The effect of the amount of adsorbent

Each of various amounts of crosslinked copolymer containing MA and sodium methacrylate functional groups was mixed with 5 mL of 1×10^{-3} M CsCl to remove Cs(I) from solutions (Fig. 1) at pH = 6.3–6.4. As can be seen from figure, it was observed that the adsorption ability of Cs(I) on the crosslinked copolymer bearing MA functional groups was very low due to low interaction between cesium ions in solution and the crosslinked copolymer containing MA functional groups (Fig. 1, curve 1). For this reason, the available groups of carboxylic acid in the crosslinked copolymer were converted to the groups of sodium methacrylate which are highly ionizable carboxylate groups and the crosslinked copolymer containing sodium methacrylate functional groups was used for the adsorption of Cs(I) from aqueous solution. The effects of mass of the densely poly(sodium methacrylate) as adsorbent on adsorption percentage of Cs(I) ions (Fig. 1, curve 2) and the amount (Fig. 1, curve 3) of its adsorption of 1×10^{-3} mol/L at 293 K have been summarized in Table 1. As can be seen from Fig. 1 and Table 1, at Cs(I) concentration of 1×10^{-3} mol/L, With increasing the amount of adsorbent from 0.005 to 0.150 g in adsorption measurements at 293 K, the adsorption percentage increased from 50.64 to 95.26%

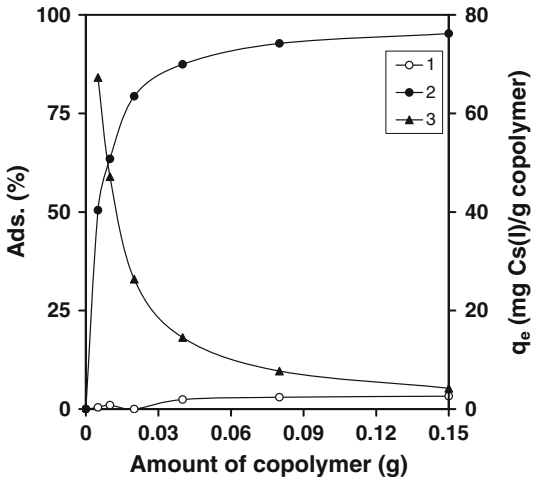


Fig. 1 The dependence of the percentage of Cs(I) adsorption on densely crosslinked poly(methacrylic acid) (*1*) and the effects of percentage (*2*) and the amount (*3*) of adsorbed Cs(I) on the densely crosslinked poly(sodium methacrylate) as adsorbent at constant Cs(I) concentration of 1×10^{-3} mol/L at 293 K. The initial pH of Cs(I) solution and contact time are 6.3 and 60 min, respectively

Table 1 The effects of percentage and the amount of adsorbed Cs(I) on densely crosslinked poly(sodium methacrylate) as adsorbent at constant Cs(I) concentration of 1×10^{-3} mol/L at 293 K

Adsorbent mass m (g)	K_D (mL/g)	Ads. (%)	q_e (mg Cs(I)/g copolymer)
0.005	1026.08	50.64	67.30
0.010	869.18	63.48	42.18
0.020	959.58	79.33	26.35
0.040	869.74	87.43	14.51
0.080	798.88	92.74	7.71
0.150	670.74	95.26	4.21

The initial pH of Cs(I) solution and contact time are 6.3 and 60 min, respectively

whereas the equilibrium adsorption capacity (q_e) of 1 g of adsorbent decreased from 67.30 to 4.21 mg Cs(I)/g copolymer. This indicate that more available sodium carboxylate groups occur and more cesium ions could be adsorbed at lower adsorbent mass in adsorption measurements as reported in previous study [40, 41]. With increasing the amount of adsorbent in the adsorption measurements, the adsorption percentage of Cs(I) ions on the crosslinked copolymer increased and reached an equilibrium at the range of the amounts of 0.02–0.03 g of copolymer (Fig. 1, curve 2). An equilibrium for Cs(I) adsorption was observed at the range of 0.02–0.03 g of copolymer. For this reason, 0.02 g of adsorbent which has an adsorption efficiency of 79.33% was used for further experiments. The ion exchange mechanism for the adsorption of Cs(I) on the crosslinked copolymer containing sodium methacrylate functional groups is shown in Scheme 2.

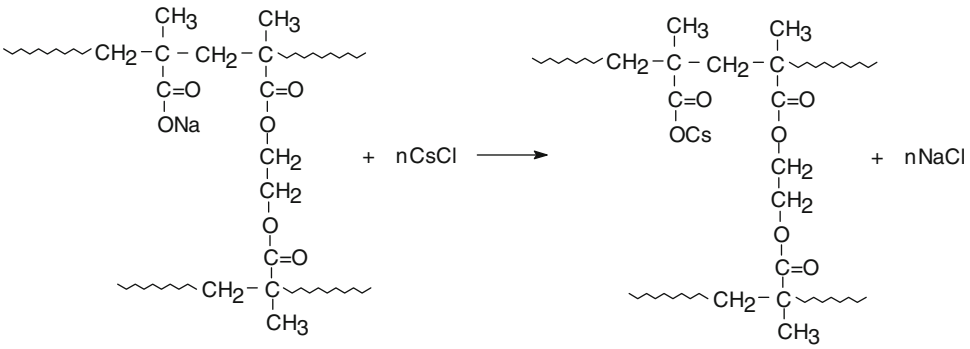
The effect of Cs(I) concentration

The adsorption of Cs(I) on the crosslinked copolymer containing sodium methacrylate functional groups has been analyzed as a function of Cs(I) concentration at 293 K and at constant contact time ($t = 60$ min) (Fig. 2). As can be seen from Fig. 2, an increase in the Cs(I) concentration in the adsorption experiments resulted in a decrease in the percentage of the adsorbed Cs(I) over the crosslinked copolymer (Fig. 2, curve 1). However, the amount of Cs(I) adsorbed on the crosslinked copolymer increased from 0.011 to 0.695 mmol/g, with increasing the initial Cs(I) concentration from 5×10^{-5} to 5×10^{-3} mol/L (Fig. 2, curve 2).

The adsorption isotherms

An adsorption isotherm is a functional expression for the variation of adsorption with concentration to adsorbate in bulk solution at constant temperature. The data obtained from adsorption experiments ranging the concentration

Scheme 2 The ion exchange mechanism for the adsorption of Cs(I) on the crosslinked copolymer



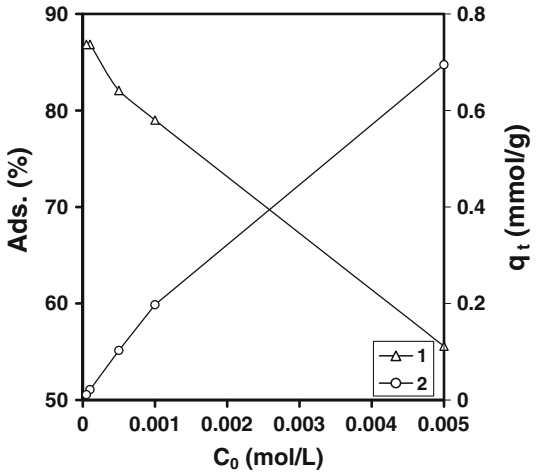


Fig. 2 The effect of the initial Cs(I) concentration on the percentage (*1*) and amount (*2*) of the adsorbed Cs(I) ions on the densely crosslinked poly(sodium methacrylate) at 293 K. The contact time is 60 min, the pH range of initial Cs(I) solutions is 6.3–6.4

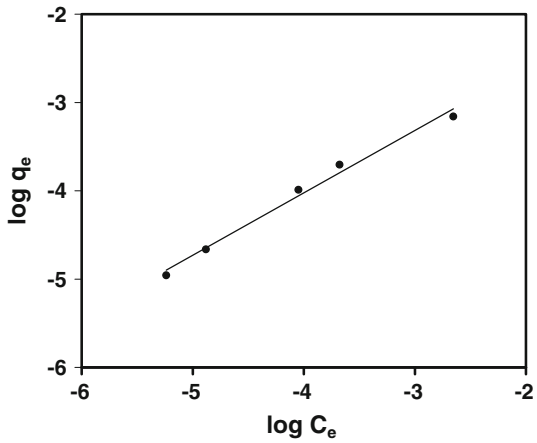


Fig. 3 Application of the Freundlich adsorption isotherm to the data of the adsorbed Cs(I) ions on the densely crosslinked poly(sodium methacrylate) from aqueous solutions at 293 K. $C_{Cs(I)} = 1 \times 10^{-3}$ mol/L, $t = 60$ min, the pH range of initial Cs(I) solutions is 6.3–6.4

from 5×10^{-5} to 5×10^{-3} mol/L for the adsorption of Cs(I) on the crosslinked copolymer bearing sodium methacrylate functional groups were analyzed in the model of the Freundlich, the Langmuir and the D–R isotherms.

The fitting of adsorption data on the Freundlich adsorption isotherm was studied at constant temperature of 293 K using Eq. 6:

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

where q_e is the amount of Cs(I) 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. Figure 3 indicates that the log q_e against log C_e plots shows a straight line given in Eq. 7 for the adsorption Cs(I) on the crosslinked copolymer.

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

For the range of initial Cs(I) concentrations from 5×10^{-3} to 5×10^{-5} mol/L at 293 K, the n_F and K_F values of Freundlich adsorption constants were calculated from the slope and intercept of this line and found to be 0.706 and 6.3×10^{-2}, respectively. The Correlation coefficient of straight line was determined to be 989. This indicates that the relationship between adsorption data and the Freundlich adsorption equation has been fairly good with this correlation coefficient. The slope value ($n_F = 0.706$) was lower than 1. This indicates that heterogeneous adsorption reaction has occurred and the higher n value has meant the higher heterogeneous of surfaces as describe in previous studies [2, 42–44].

Fitting of adsorption data on the Langmuir adsorption isotherm was studied and the following linearized form of Langmuir equation was used to describe 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 Cs(I) 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. Figure 4 shows the plot of C_e/q_e versus C_e indicating the relationship between the C_e/q_e and C_e values was not linear. The deviation from linearity of Langmuir isotherm could be due to the fact that these type of isotherms have originally been

deviated from the adsorption of gases on the adsorption surfaces and thus have been limitation in the extrapolation of adsorption of other compounds [2, 3] as in current study.

It has been reported that the D–R isotherm is popular adsorption model, applicable at low concentration ranges and could be used to describe the apparent free energy of adsorption [45]. The D–R isotherm model was represented by the following equation:

$$q_e = q_m \exp -\left(K\varepsilon^2\right) \quad (9)$$

where ε is the Polanyi 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

$$\ln\ q_e = \ln\ q_m - K\varepsilon^2 \quad (10)$$

The value of q_m and K were determined by plotting $\ln\ q_e$ versus ε^2 shown in Fig. 5 and found to be 3×10^{-3} mol/g and -6.5×10^{-3} (mol/kJ)^2 respectively. The correlation coefficient (R) of straight line was found to be 0.999.

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 (11):

$$E = (-2K)^{-1/2} \quad (11)$$

The apparent free energy change from D–R model parameter is 8.77 kJ/mol for Cs(I) adsorption on the crosslinked copolymer bearing sodium methacrylate groups. According to Kundu and Gupta [37] and Sari et al. [46], the adsorption energy could be employed to estimate the type of adsorption based on ion-exchange mechanism is around 8–16 kJ/mol. The adsorption energy

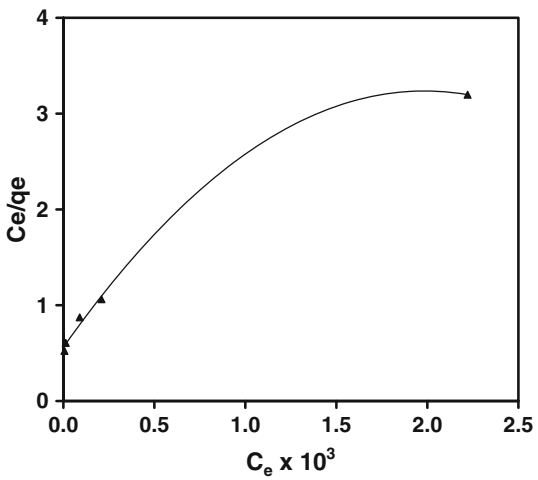


Fig. 4 Dependence of adsorption data on the Langmuir adsorption isotherm at 293 K. $C_{Cs(I)} = 1 \times 10^{-3}$ mol/L, $t = 60$ min, the pH range of initial Cs(I) solutions is 6.3–6.4

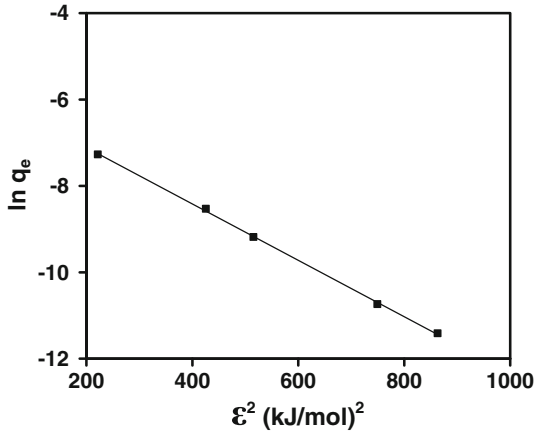


Fig. 5 The relation between $\ln\ q_e$ and ε^2 in the D–R adsorption isotherm for Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) at 293 K. $C_{Cs(I)} = 1 \times 10^{-3}$ mol/L, $t = 60$ min, the pH range of initial Cs(I) solutions is 6.3–6.4

($E = 8.77$ kJ/mol) determined in this study was between the above energy ranges of 8–16 kJ/mol. Therefore, the adsorption by crosslinked copolymer with sodium methacrylate functional groups has been of ion-exchange.

The effect of temperature

The effect of temperature on the adsorption of Cs(I) by crosslinked copolymer containing sodium methacrylate functional groups was examined for various initial Cs(I) concentrations and very little changes were observed upon changing temperature from 283 to 323 K (Fig. 6). As seen from Fig. 6, when temperature increased, the amount and percentage of adsorbed Cs(I) on the crosslinked copolymer did not change sufficiently. This might be due to that the change in the mobility of ionic species in solution and acceleration of some originally slow steps between low and high temperatures did not change in Cs(I) adsorption with increasing temperature.

The effect of pH

The adsorption of metal ion on the adsorbents as reported in previous investigations depends on pH of medium [2, 32]. The initial pH of solution (1×10^{-3} mol/L and 5 mL) containing 0.02 g copolymer was 6.3–6.4. The pH values of mixtures were adjusted by adding 1 N HCl and 1 N NaOH solutions. The pH values were varied between 1 and 9, keeping other parameters constant. Figure 7 shows the influence of pH for the adsorption of Cs(I) on the crosslinked copolymer with sodium methacrylate functional groups from aqueous solutions. The amount of Cs(I) adsorbed on the crosslinked copolymer showed a marked increase with increasing pH from 2 to 5 and reached an equilibrium after pH = 6. The amount of adsorbed

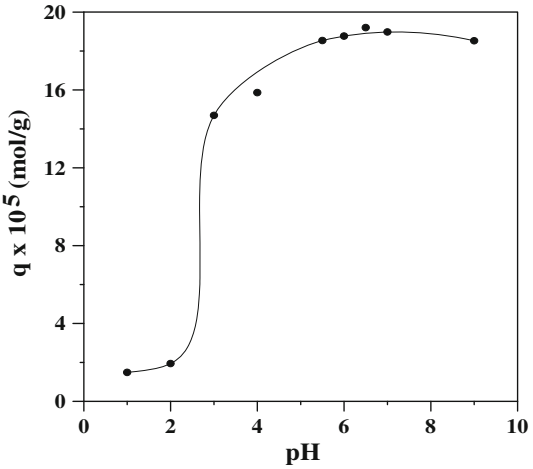


Fig. 6 The effect of pH on the Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) from aqueous solutions at 293 K. The contact time and initial Cs(I) concentration are 60 min and 1×10^{-3} mol/L respectively

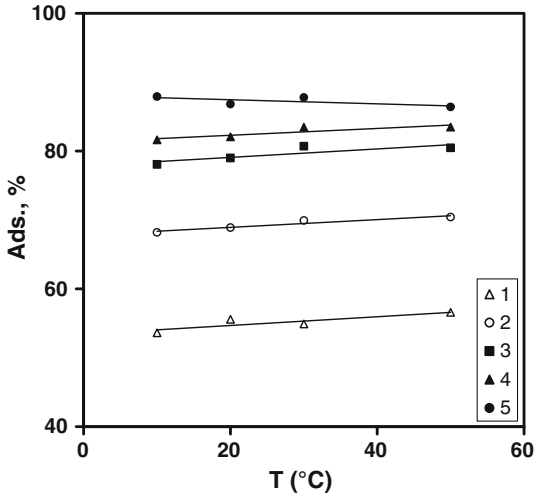


Fig. 7 The dependence of adsorption percentage on the temperature for the Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) from aqueous solutions. Initial Cs(I) concentrations are 5×10^{-3}(1), 2×10^{-3}(2), 1×10^{-3}(3), 5×10^{-4}(4) and 1×10^{-4}(5) mol/L, $t = 60$ min, the pH range of initial Cs(I) solutions is 6.3–6.4

Cs(I) on the crosslinked copolymer with sodium methacrylate functional groups had a maximum value at pH = 6.3 and found to be 0.198 mmom/g. Cs(I) adsorption ability of the crosslinked copolymer bearing sodium methacrylate functional groups made it better in comparison of other sorbent material. Since most of other radioactive ions can not be adsorb in the range of pH = 2–5 accept for uranyl ions reported in previous studies [2, 27, 32, 44, 45].

The effect of contact time

The effect of contact time for Cs(I) adsorption on the crosslinked copolymer bearing sodium methacrylate functional groups from aqueous solutions at pH = 6.3–6.4 was given in Fig. 8. With increasing contact time, the percentage of the adsorbed Cs(I) on the crosslinked copolymer increased and reached an equilibrium value after 30 min. As described in previous investigations, a rapid initial Cs(I) adsorption on the crosslinked copolymer 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. 12 given below [32, 39, 47]:

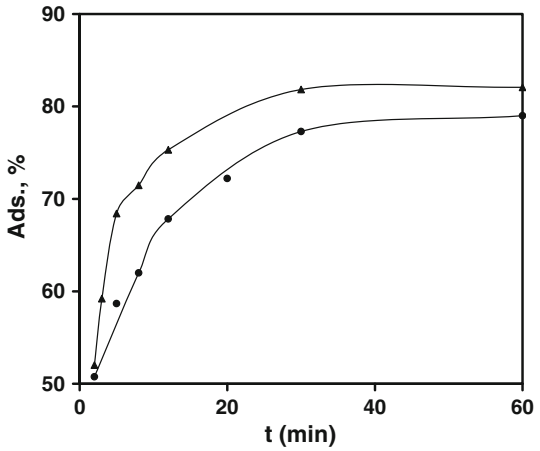


Fig. 8 The relation between adsorption percentage and the contact time for initial Cs(I) concentrations of 5×10^{-4} mol/L (*filled triangle*) and 1×10^{-3} mol/L (*filled circle*) at 293 K and $t = 60$ min

$$q_t = at^b \tag{12}$$

The linearized form of Eq. 12 can be written by following Eq. 13.

$$\ln q_t = \ln a + b \ln t \tag{13}$$

where q_t is the amount of Cs(I) adsorbed by crosslinked copolymer bearing sodium methacrylate 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 Cs(I) on the crosslinked copolymer at initial Cs(I) concentration of 5×10^{-4} and 5×10^{-3} mol/L at constant temperature (293 K). As seen

from Fig. 7, 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 5.85×10^{-5}, 0.203 and 0.945 for initial Cs(I) concentration of 5×10^{-4} mol/L and 11.26×10^{-5}, 0.160 and 0.988 for initial Cs(I) 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.

The Elovich kinetic model

The Elovich or Rodinky–Zeldovich kinetic equation is generally expressed as follows [2, 39, 47]:

$$\frac{dq_t}{dt} = A \exp(-Bq_t) \tag{14}$$

where q_t is the amount of Cs(I) adsorbed by the crosslinked copolymer at time, t; A is the initial Cs(I) adsorption rate (mmol/g min) and B is the adsorption constant (g/mol). The linearized form of the Elovich equation (14) can be given as follows.

$$q_t = B \ln(AB) + B \ln t \tag{15}$$

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 Cs(I) (q_t) on the crosslinked copolymer and ln t with minimum correlation coefficient ($R = 0.962$) for the lines given in Fig. 10.

The A and B values have 23.86×10^5 and 1.61×10^{-5} for initial Cs(I) concentration of 5×10^{-4} mol/L and 11.33×10^3 and 10.90×10^{-5} for initial Cs(I) 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 Cs(I) concentrations.

The pseudo-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 [2, 39, 47, 48]. In order to investigate the sorption rate of Cs(I) on the crosslinked copolymer containing sodium methacrylate functional groups, the following pseudo-second order equation was used (16):

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{16}$$

where q_e and q_t are the amounts of cesium ions adsorbed by the crosslinked copolymer at equilibrium and at 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.

$$\ln(q_e - q_t) = \ln q_e - kt \tag{17}$$

The results of the Cs(I) adsorption on the crosslinked copolymer containing sodium methacrylate functional groups were given in Fig. 11 for initial Cs(I) concentrations of 5×10^{-4} and 1×10^{-3} mol/L. A linear relationship between ln ($q_e - q_t$) and t has been established with a fairly good correlation coefficient (R values = 0.946 and 0.993) (Table 2). The adsorption rate constants were determined as 14.23×10^{-2} and 8.90×10^{-2} min^{-1} for initial Cs(I) concentration of 5×10^{-4} and 1×10^{-3} mol/L, respectively.

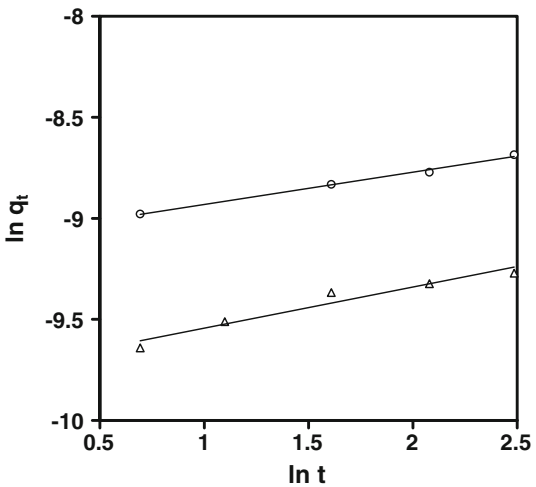


Fig. 9 The fitting of adsorption data on the fractional power adsorption model for Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) at 293 K. The initial Cs(I) concentrations are 5×10^{-4} (*open triangle*) and 1×10^{-3} (*open circle*) mol/L, the pH range of initial Cs(I) solutions is 6.3–6.4

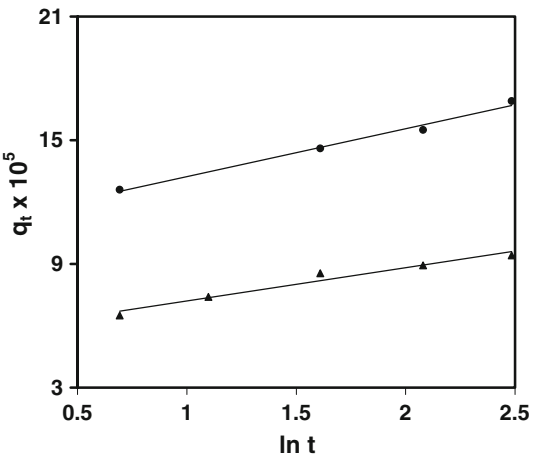


Fig. 10 The relationship between q_t and ln t in the Elovich adsorption equation for Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) at 293 K. The initial Cs(I) concentrations are of 5×10^{-4} mol/L (*filled triangle*) and 1×10^{-3} mol/L (*filled circle*), the pH range of initial Cs(I) solutions is 6.3–6.4

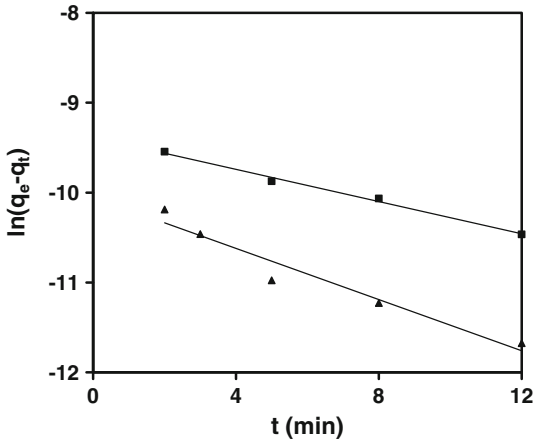


Fig. 11 The dependence of ln ($q_e - q_t$) on the time for the adsorption of initial Cs(I) concentrations of 5×10^{-4} mol/L (*filled triangle*) and 1×10^{-3} mol/L (*filled square*) on the densely crosslinked poly(sodium methacrylate) from aqueous solutions at 293 K. The pH range of initial Cs(I) solutions is 6.3–6.4

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 [2, 39, 42, 43, 47–52]. In order to describe Cs(I) sorption on the crosslinked copolymer for the initial Cs(I) concentrations of 5×10^{-4} 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.

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{18}$$

where q_e and q_t are the amounts of cesium ions adsorbed by the crosslinked copolymer at equilibrium and at time, t, respectively; the k (L/mol s) is the rate constant for pseudo-first order kinetic equation. By separating variables and integrating the equation for initial limit, $t = 0$, $q_t = 0$, the following Eq. 19 is obtained which is the integrated rate law of pseudo second order reaction.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{19}$$

This Eq. 19 can be rearranged to obtain the following linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{20}$$

The kinetic plots of t/q_t versus t for Cs(I) adsorption on the crosslinked copolymer bearing sodium methacrylate functional groups are represented in Fig. 12. The figure exhibits a linear relationship between t/q_t and t for Cs(I) adsorption on the crosslinked copolymer bearing sodium methacrylate functional groups. The results given in Table 2 indicated the adsorption rate constant (k), initial adsorption rate ($h = kq_e^2$) and equilibrium adsorption capacity (q_e) as a function of initial Cs(I) concentrations As can be seen from Fig. 12 and Table 2, the data-fits have revealed very high correlation coefficient ($0.997 \leq R \leq 0.999$), 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 Cs(I) adsorption on the crosslinked copolymer occurred by chemisorption mechanism [2, 39]. With increasing the initial Cs(I) concentration from 5×10^{-4} to 1×10^{-3} mol/L, the adsorption capacity (q_e) and the initial adsorption rate (h) increased from 1.02910^{-4} to 1.813×10^{-4} mol/g and 9.013×10^{-5} to 1.679×10^{-4} mol/(min g) whereas the adsorption rate constant decreased from 8,512 to 5,108 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.

Conclusion

The densely crosslinked poly(sodium methacrylate) was used as an adsorbent to remove Cs(I) ions from aqueous solutions as a function of parameters of the amount of adsorbent, contact time, pH of solution, initial Cs(I) concentration and temperature. The increase in the amount of adsorbent showed an increase in the percentage of the adsorbed Cs(I) ions and reached to 95.26% for 0.15 g of adsorbent and for 1×10^{-3} mol/L of initial Cs(I) concentration at 293 K and $t = 60$ min. The percentage of Cs(I) adsorption observed at 0.02 g of adsorbent was determined as 79.33%. This point was taken as equilibrium adsorption value and used in the adsorption experiments. It was observed that the adsorption capacity resulted in an increase from 0.010 mmol/g copolymer to 0.695 mmol/g copolymer, with increasing initial Cs(I) concentration from 5×10^{-5} to 5×10^{-3} mol/L at 293 K and $t = 60$ min. The result obtained various temperatures for the Cs(I) adsorption on the crosslinked copolymer bearing sodium methacrylate functional groups showed that the amount of the adsorbed Cs(I) did not change sufficiently, due to unchanging of the amounts of ionizable carboxyl groups at higher temperatures. The sorption data were evaluated by the Freundlich, the Langmuir and the D–R isotherms. The n_F value in the Freundlich equation was found lower than 1. This meant that the surface of adsorbent was heterogeneous. The free energy change (E) was calculated by the D–R isotherm and found to be 8.77 kJ/mol. It was reported that an energy adsorption based on ion-exchange mechanism was around 8–16 kJ/mol.

Table 2 The kinetic constants obtained from the pseudo-first order and pseudo-second order kinetic equation for the Cs(I) adsorption on densely crosslinked poly(sodium methacrylate) from aqueous solutions

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^{-4}	14.23×10^{-2}	0.946	1.029×10^{-4}	8,512	9.013×10^{-5}	0.999
1×10^{-3}	8.90×10^{-2}	0.993	1.813×10^{-4}	5,108	1.679×10^{-4}	0.997

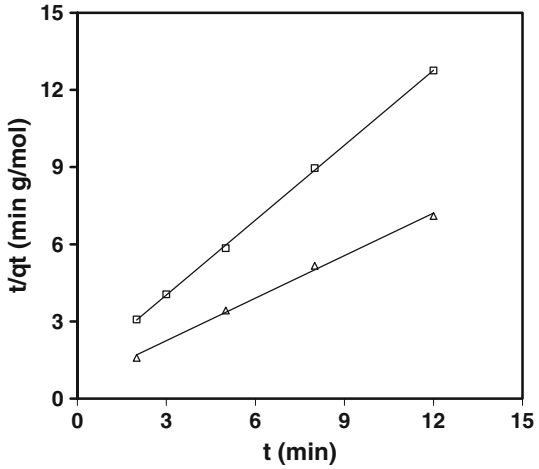


Fig. 12 The fitting of adsorption data to the pseudo-second order kinetic model for Cs(I) adsorption on the densely crosslinked poly(sodium methacrylate) at the initial Cs(I) concentrations of 5×10^{-4} mol/L (*open square*) and 1×10^{-3} mol/L (*open triangle*) at 293 K. The pH range of initial Cs(I) solutions is 6.3–6.4

8.77 kJ/mol of adsorption energy found in this study was in this range. Therefore the adsorption by densely crosslinked poly(sodium methacrylate) has been of ion-exchange type. The fitting of adsorption data to the fractional power, the Elovich, the pseudo-first order and pseudo-second order kinetic models indicated that the data values obtained from experimental results for the Cs(I) adsorption on densely crosslinked poly(sodium methacrylate) provided much better fitting for the pseudo-second order kinetic equation with high correlation coefficient ($0.997 \leq R \leq 0.999$). Adsorption rate constants (k), initial adsorption rates (h) and equilibrium adsorption capacities (q_e) were determined for 5×10^{-4} and 1×10^{-3} mol/L of initial Cs(I) concentrations. The adsorption rate constants, initial adsorption rates and equilibrium adsorption capacities were calculated as 8,512 g/(min mol), 9.013×10^{-5} mol/(min g) and 1.029×10^{-4} mol/g for 5×10^{-5} mol/L of the initial Cs(I) concentration and 5,108 g/(min mol), 1.679×10^{-4} mol/(min g) and 1.813×10^{-4} mol/g for 1×10^{-3} mol/L of initial Cs(I) concentration. As a result, the synthesized densely crosslinked poly(sodium methacrylate) could be used for removal of the Cs(I) ions from aqueous solution and since this adsorbent was produced from commercially available starting materials, the procedure describe here was cost alternative of removal of Cs(I) ions from waste solutions or wastes.

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