



Removal of UO_2^{2+} from Aqueous Solutions by Maleic Anhydride-Styrene-vinyl acetate Terpolymer Modified with Ethylenediamine and Diethylenetriamine

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(Received: 4 January 2013;

Accepted: 3 August 2013)

AJC-13879

Maleic anhydride-styrene-vinyl acetate (MA-S-VA) terpolymer was prepared. It was modified by ethylenediamine (EDA) and diethylenetriamine (DETA) in order to get cross-linked polymers bearing carboxyl and amine groups. They were shown as MA-S-VA-EDA and MA-S-VA-DETA, and used as an adsorbent for the removal of UO_2^{2+} from water. The characterizations of structures of all the polymers were performed by Fourier transform infrared. The adsorptive features of adsorbents were then investigated for UO_2^{2+} in view of dependency on ion concentration, temperature and kinetics. Experimentally obtained isotherms were evaluated with reference to Langmuir, Freundlich and Dubinin-Radushkevich models. The maximum monolayer adsorption capacity for UO_2^{2+} was found to be 0.58 and 2.56 mol kg^{-1} for MA-S-VA-EDA and MA-S-VA-DETA, respectively. It is suggested that the new modified polymers prepared in our laboratory as new adsorbents for uranyl ions.

Key Words: Adsorption, Uranyl, Terpolymers, Amin.

INTRODUCTION

Uranium is amongst the longest-lived radio nuclides and possesses health risks to humans, particularly at relatively high concentrations because of its chemical toxicity and radioactivity. Therefore, the recovery of uranium from aqueous solutions is essential in view of nuclear fuel resource and human health. The general methods developed for the recovery or removal of uranium ions from aqueous solutions are extraction¹, precipitation², ion exchange³ and adsorption⁴. Amongst these approaches, adsorption is commonly used for the recovery of uranium ions at relatively low concentration. Additionally, adsorption is a more economic process, simple to design and easy to operate. It is reported that some minerals⁵, phosphates⁶, poly-resins⁷, polymers^{8,9}, composites¹⁰ and microorganisms¹¹ have been used as adsorbents for the recovery of UO_2^{2+} from wastewater.

Many types of polymer adsorbents have been developed and studied for the recovery and removal of uranyl ions from aqueous media^{12,13}. Chelate-forming polymeric ligands have been extensively studied by several authors and many reviews are already available in the field^{14,15}. Polymeric adsorbents containing an chelate-forming group have shown a growing interest because of the high uptake of uranyl, the rapid adsorption rate, the high selectivity for uranyl, and the safety of the environment.

In this study, uranium ion adsorption to synthetic polymer consisting of maleic anhydride-styrene-vinyl acetate (MA-S-VA) has been investigated. Firstly, MA-S-VA terpolymer was synthesized and the modified structure of polymer with ethylenediamine (EDA) and diethylenetriamine (DETA) was formed. The characterization of the modified polymer structures was done FTIR. The capacities of uranyl ion adsorption of the polymers used as adsorbent were investigated in terms of pH to adsorption, the impacts of temperature and the times of interaction.

EXPERIMENTAL

Maleic anhydride (MA), styrene (S), vinyl acetate (VA) monomers, 4-(2-pyridylazo) resorcinol (PAR) and azobisisobutyronitrile (AIBN) were purchased from Sigma. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and all other chemicals were obtained from Merck (Germany). All chemicals used were of analytical reagent grade. Distilled water was used in overall investigation. All experiments were always performed in duplicates. $\pm 5\%$ was the limit of experimental error of each duplicates, any experiment resulted in higher than this limit was repeated.

Preparation of the terpolymer: Maleic anhydride monomer was purified by recrystallization from anhydrous benzene solution and sublimation in vacuum. Styrene was freshly distilled before use. Vinyl acetate was purified by distillation. The initiator (azobisisobutyronitrile), was purified by

crystallization from methanol. The terpolymer was produced by using monomers maleic anhydride, styrene and vinyl acetate taking the mole proportions of 2:1:1. In a schlenk tube all the monomers were dissolved in 150 mL methyl ethyl ketone in the presence of azobisisobutyronitrile as initiator. The reaction mixture is allowed to react for 1 h at 70 °C. The polymer was isolated from reaction mixture by precipitation with diethyl ether and washed with ethyl alcohol twice then dried under 40 °C vacuum¹⁶.

Reaction of the terpolymer by amines: The prepared terpolymer was dissolved in acetone. It has been gelled by adding of ethylenediamine and diethylenetriamine solutions. This gel bathed several times in ethyl alcohol and water. It was mixed in pH 2 HCl solution for 4 h. After washing with distilled water, it was dried.

FT-IR spectrometric (Mattson 1000, UK) analysis was used to characterise the chemical structure of MA-S-VA, MA-S-VA-EDA and MA-S-VA-DETA. Pellets of samples were prepared by mixing with KBr and spectra were obtained at a resolution of 4 cm⁻¹.

Uranium adsorption: Adsorptive features of the adsorbent were investigated for UO₂²⁺. 0.1 g of the adsorbent in the studied solutions was equilibrated with 10 mL UO₂²⁺ at concentrations within range from 3.7 × 10⁻⁴–1.1 × 10⁻² mol L⁻¹. The adsorbent-solution systems were equilibrated for 24 h at 298 K in a thermostatic water bath and suspensions were then centrifuged at 2500 rpm for 5 min. The initial and final pH values 4–6 for UO₂²⁺.

4-(2-Pyridylazo)resorcinol was used complex forming reagent for determination of UO₂²⁺ in the supernatants¹⁷. A solution of 3.5 × 10⁻³ mol L⁻¹ of PAR in 0.7 mol L⁻¹ of Tris/HCl at pH 8–9 was prepared. A 50 µL fraction of supernatant was added onto 3 mL of the reagent and the absorbance of the formed metal complex was measured at 530 nm for UO₂²⁺.

Effect of temperature on adsorption of UO₂²⁺: Temperature effect on adsorption for determination of thermodynamic parameters was studied for three temperatures; 283, 298 and 313 K. Duplicates (0.1 g each) of the materials were equilibrated with solutions at 3.7 × 10⁻³ mol L⁻¹ for UO₂²⁺ and at the chosen temperatures for 24 h. The samples were subjected to the same procedure described above and equilibrium concentrations were determined.

Adsorption kinetics: 40 mL of solution of each ion was added on to 0.4 g of adsorbents. 50 µL fractions of solution were withdrawn for 12 h, starting immediately after the solution-solid contact and continued with time intervals. UO₂²⁺ contents of the fractions were determined.

Reusability and storage ability: The effectiveness of the same effluent was also tested for the modified polymer introduced in this study with a reusability study for UO₂²⁺.

To test of reusability, five duplicates of 0.1 g MA-S-VA-EDA and MA-S-VA-DETA samples in polypropylen tubes were equilibrated with 10 mL of 3.7 × 10⁻³ mol L⁻¹ for UO₂²⁺ at 24 h and the adsorbed amounts were derived from the ion contents of supernatants. The contents of columns were eluted with 5 mL fractions of 20 mL of 1 mol L⁻¹ HCl and the columns were then washed with distilled water until the effluents had a neutral pH. The UO₂²⁺ contents of the effluents (HCl) were determined.

The storage ability of the modified polymer was checked with reference to the repeatability of their adsorptive features for the ions of interest for one use for 2 months with a week interval.

Data evaluation: The amounts of adsorption of the ions (Q, mol kg⁻¹) were calculated from $Q = [(C_i - C_e)V/w]$, where C_i and C_e are the initial and equilibrium concentrations (mol L⁻¹), w is the mass of adsorbent (kg) and V is the solution volume (L). The Langmuir and Freundlich models defined with $Q = (K_L X_L C_e)/(1 + K_L C_e)$ and $Q = X_F C_e^\beta$ fit to the isotherms experimentally obtained, where X_L is the monolayer sorption capacity (mol kg⁻¹), K_L is the adsorption equilibrium constant (L mol⁻¹) related to the adsorption energy. X_F and 'β' are empirical Freundlich constants associated with the capacity and intensity of adsorption (β represents the heterogeneity of the adsorptive surface). The isotherms were also evaluated with reference to Dubinin-Radushkevich (DR) model to find out the constant (K_{DR}; mol² K J⁻²) related to the sorption energy from $Q = X_{DR} e^{K_{DR} \epsilon^2}$ where X_{DR} is sorption capacity (mol kg⁻¹) and ε is polanyi potential given with $\epsilon = RT \ln(1 + 1/C_e)$ in which R and T represent the ideal gas constant (8.314 J mol⁻¹ K⁻¹) and absolute temperature (298 K). Free energy change (E; J mol⁻¹) required to transfer one mole of ion from the infinity in the solution to the solid surface was then derived from $E = (-2K_{DR})^{1/2}$.

The distribution coefficients (K_d) were derived from $K_d = Q/C_e$ for each temperature and 'ln K_d' was depicted against 1/T to provide adsorption enthalpy (ΔH, J mol⁻¹) and entropy (ΔS, J mol⁻¹ K⁻¹) from the slopes (ΔH/R) and intercepts (ΔS/R) of the depictions with reference to $\ln K_d = \Delta S/R - \Delta H/(RT)$. Having had ΔH and ΔS, ΔG values were calculated from $\Delta G = \Delta H - T\Delta S$.

Equations related to the pseudo second order kinetic and intra particle diffusion were $t/Q_t = 1/(kQ_e^2) + t/Q_e$ and $Q_t = k_i t^{1/2}$ (Weber and Morris model) where Q_t and Q_e are the adsorbed amounts (mol kg⁻¹) at time t and equilibrium, k and k_i are the rate constants were applied to the results of kinetic studies to be able to envisage the controlling mechanism of the adsorption process. Initial adsorption rate (H) was also calculated from $H = kQ_e^{2.18,19}$.

RESULTS AND DISCUSSION

Structural evaluation: The FT-IR spectra of MA-S-VA, MA-S-VA-EDA and MA-S-VA-DETA were compared in Fig. 1.

The peaks observed at 1804 and 1840 cm⁻¹ in MA-S-VA spectra belong to C=O stretching vibrations and peaks at 1224 and 900 cm⁻¹ belong to C-O-C vibration of anhydride groups. The decrease or disappearance in the intense of peaks in 1804, 1840 and 1224 cm⁻¹ structures that take part in MA-S-VA-EDA and MA-S-VA-DETA shows the separation of anhydride groups. It was also evaluated as the evidence of inclusion of wide band amino groups in 3400–3000 cm⁻¹ into the structure^{20,21}.

Effect of pH on UO₂²⁺ adsorption: The change of the adsorption of UO₂²⁺ ion as a function of pH to the structures of MA-S-VA-EDA and MA-S-VA-DETA has been shown in Fig. 2. The level pH 7 has not been overpassed due to hydroxide

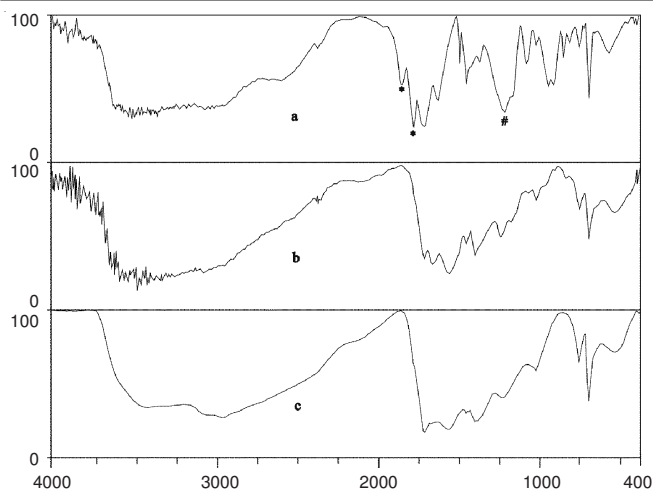


Fig. 1. FT-IR spectra of MA-S-VA (a), MA-S-VA-EDA (b) and MA-S-VA-DETA (c). (*defines carbonyl groups and # defines anhydride groups disappears its conversion to amine groups)

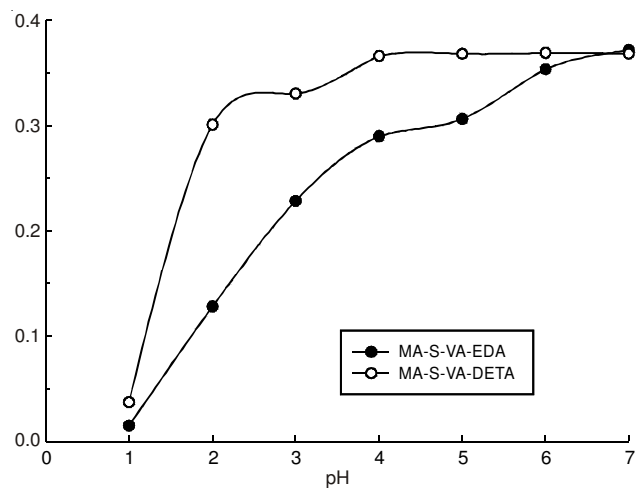


Fig. 2. pH dependence of the adsorption

precipitates of the UO_2^{2+} ion²². An increase is observed in the adsorption with the increase of pH (1-7).

The adsorption of UO_2^{2+} ions from the solution depends on pH because pH affects the surface weight, ion variations and the ionization of the functional group. The reduction of the adsorption in the low level pHs is explained by the metal ions which cannot approach to the active centres because of the pushing force caused by the protonation of the carboxylate and amine competition between ion and H_3O^+ with lowering of pH^{23,24}. pH on which the adsorption study has been carried out is between 4-6 and it is the natural range of the UO_2^{2+} ion.

Adsorptive features for UO_2^{2+} : The adsorption isotherms of UO_2^{2+} and their compatibility to the Langmuir, Freundlich and DR models are compared for each adsorbent (MA-S-VA-

EDA and MA-S-VA-DETA) Fig. 3. The parameters derived from the models were tabulated in Table-1. The profiles of isotherms correspond to L type class of the Giles classification, *i.e.*, the adsorption has a chemical character for all. The results obtained from adsorption isotherms for uranyl ions according to the Langmuir model are given in Table-1. It shows good correlation coefficients with the experimental data from adsorption equilibrium of uranyl ions, suggesting homogeneous adsorption, which means a monolayer. The adsorption hyperbolically increases with increasing concentration. The steep rise at the beginning lowers gradually and reaches a plateau defining the completion of filling the monolayer adsorption capacity (X_L).

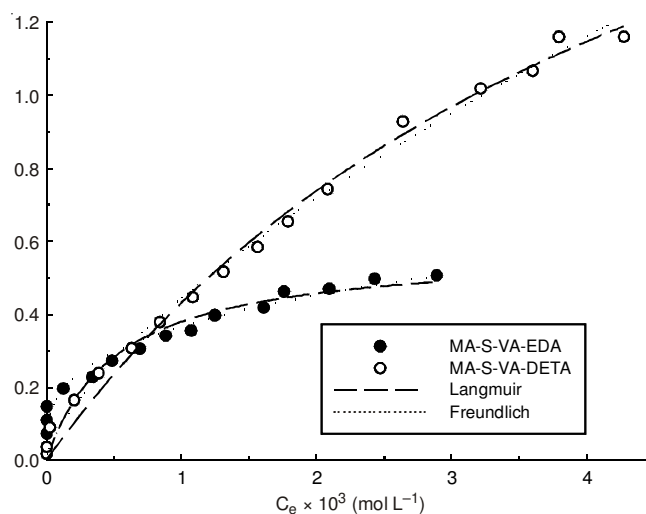


Fig. 3. Experimentally obtained adsorption isotherms UO_2^{2+} and their compatibility to Langmuir and Freundlich models

The adsorption capacities (X_L , X_F and X_{DR}) obtained from the models were in order of MA-S-VA-DETA > MA-S-VA-EDA.

K_L value, as a measure of adsorption affinity was cleared superior affinity of UO_2^{2+} for MA-S-VA-EDA. However, the sequence of K_{DR} value was MA-S-VA-DETA > MA-S-VA-EDA for UO_2^{2+} .

When Langmuir parameters are compared with Freundlich and DR parameters, existence of a systematic relationship of adsorbent and ion is observed either. The one who has higher X_L value also has higher X_F , β and X_{DR} values.

In amine modified structures, metal ion can move on the mechanism of chelate formation and ion change²³. Ion changing mechanism is effective on the adsorption because of nitrogen atoms including unshared electron pair besides chelate formation. The difference of adsorption capacity between MA-S-VA-EDA and MA-S-VA-DETA can be explained as the increase of the number of negative active groups in the structure

TABLE-1
LANGMUIR AND FREUNDLICH PARAMETERS OBTAINED FOR AND UO_2^{2+}
ADSORPTION ONTO MA-S-VA-EDA AND MA-S-VA-DETA

	Langmuire			Freundlich			DR		
	* X_L	** K_L	R^2	X_F	β	R^2	X_{DR}	***-KDR $\times 10^9$	R^2
MA-S-VA-EDA	0.58	1937	0.885	2.95	0.30	0.961	1.34	4.5	0.988
MA-S-VA-DETA	2.56	202	0.991	53.60	0.69	0.994	6.27	9.1	0.991

*mol kg⁻¹, **L mol⁻¹, *** mol² KJ⁻².

formed by DETA modification and with UO_2^{2+} conducive to complex formation. The numbers of the groups with negative charge in MA-S-VA-DETA structure is more than that of amine groups. The capacity of adsorption has been found high due to the reason that the number of the amine groups which help the chelate formation resulting from electrostatic attraction is more. The reduction in adsorption of low pH also proves this.

Thermodynamic parameters for adsorption of UO_2^{2+} :

Thermodynamic parameters derived from the depictions of ' $\ln K_d$ versus $1/T$ ' (Fig. 4) and by using related equations and free energy change (E_{DR}) derived from DR model are provided in Table-2. The ΔH° , ΔS° and ΔG° values show that the adsorption is endothermic, increased entropy, and as expected spontaneity ($\Delta G^\circ < 0$) features for all the studied adsorbents.

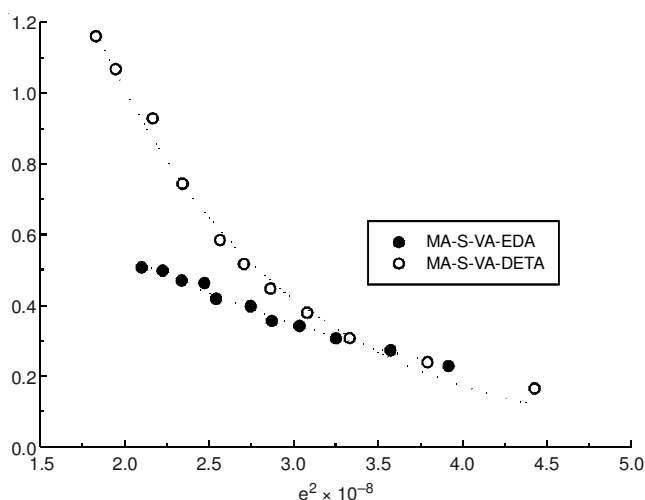


Fig. 4. Compatibility of experimentally obtained adsorption isotherms to DR models

The ΔH values are a measure of the energy barrier that must be overcome by reacting molecules²⁵. The values for ΔH suggest that these reactions are endothermic, meaning they consume energy.

The value of ΔS is an indication of whether or not the adsorption reaction is by associative or dissociative mechanism. The entropy measures the width of the saddle point of the potential energy surface over which reactant molecule must pass as activated complexes²⁵. Entropy change $> 10 \text{ J K}^{-1} \text{ mol}^{-1}$ generally implies dissociative mechanism²⁶. These results show that uranyl ions adsorption on both modified polymers is occurred through the dissociative mechanism. This abnormality may not necessarily mean that the adsorption of uranyl ions onto modified polymers adsorbent is dissociative in nature but that there could be some structural changes in the adsorbate and adsorbent during the adsorption reaction²⁷.

The value of DR constant is related to the adsorption free energy E_{DR} . Evaluation of E_{DR} and ΔG values together indicated that the sorption process is chemical. $E_{\text{DR}} \cong 8 \text{ kJ mol}^{-1}$ has

been assumed as a threshold for definition of the nature of adsorption; the physical forces such as diffusion process are effective on sorption if $E_{\text{DR}} < 8 \text{ kJ mol}^{-1}$, the nature of process is chemical (the complex formation/ion exchange) otherwise^{28,29}. Temperature dependence curves of the adsorption is given in Fig. 5.

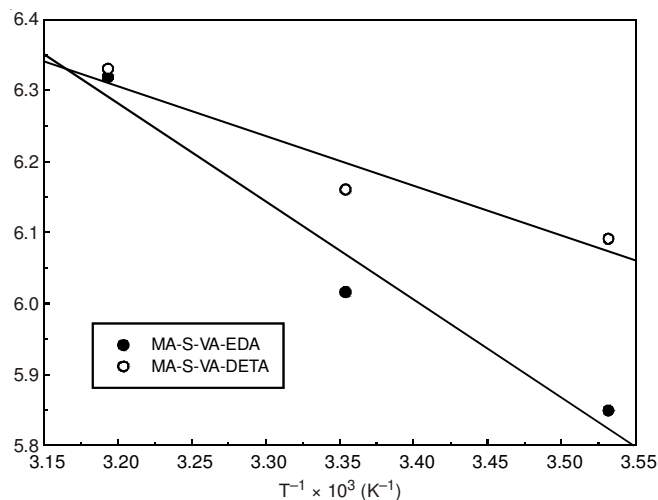


Fig. 5. Temperature dependence of the adsorption

Kinetics parameters for adsorption of UO_2^{2+} : The compatibility of experimental data to the second order kinetics and intraparticle diffusion models were evaluated with reference to the statistical significance of linearity obtained from ' $t - t/Q_t$ ' and ' $t^{0.5} - Q_t$ ' plots (Fig. 6).

The rate controlling mechanism is chemical processes if the second order model provides a statistically meaningful regression coefficient¹⁸. In addition, the values of adsorbed amounts at equilibrium obtained from the model (Q_M) should also be close to that obtained from the experiment (Q_e). The results of adsorption both ions to all adsorbents were well compatible to the second-order model ($p < 0.01$) and provided Q_M close to Q_e values. These findings (Table-3) eventually confirmed that nature of adsorption was concentration dependent so that the rate controlling-step is chemical sorption via complex formation and/or ion exchange³⁰. The values obtained from experiment for UO_2^{2+} were statistically meaningful results ($p < 0.01$).

The plot of Q_t versus $t^{0.5}$ (Weber and Morris model) showed that two types of mechanisms take place in the adsorption process; the initial rapid uptake under the boundary layer effects and the slow intraparticle diffusion after the completion of external coverage. The experiment results of UO_2^{2+} adsorption were statistical significant to Weber Morris model ($p < 0.01$).

The rate constants and evaluated initial adsorption rate from these were MA-S-VA-DETA $>$ MA-S-VA-EDA for UO_2^{2+} .

TABLE-2
THERMODYNAMIC PARAMETERS FOR UO_2^{2+} ADSORPTION ONTO MA-S-VA-EDA AND MA-S-VA-DETA

	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)	*R ²	E_{DR} (kJ mol ⁻¹)
MA-S-VA-EDA	11.5	89	-14.9	0.963	10.6
MA-S-VA-DETA	5.8	71	-15.7	0.931	7.4

*Coefficients of variations for the linearity of $\ln K$ vs. $1/T$ depictions used in obtaining ΔH° and ΔS° are significant at $p < 0.01$.

TABLE-3
KINETIC PARAMETERS FOR UO_2^{2+} ADSORPTION ONTO MA-S-VA-EDA AND MA-S-VA-DETA

	Pseudo-second order kinetic					Intraparticle diffusion	
	$^1k \times 10^2$	2Q_M	2Q_e	$^3H \times 10^3$	$^4t_{1/2}$	$^5k_i \times 10^3$	$^6R^2$
MA-S-VA-EDA	1.15	0.35	0.33	1.42	247	5.6	0.944
MA-S-VA-DETA	12.26	0.37	0.36	16.2	22.4	1.4	0.783

*Significant at $p < 0.01$ for coefficient of correlation, $^1(\text{mol}^{-1} \text{kg} \text{min}^{-1})$, $^2(\text{mol} \text{kg}^{-1})$, $^3(\text{mol} \text{kg}^{-1} \text{min})$, ^4dk , $^5(\text{mol} \text{kg}^{-1} \text{min}^{0.5})$.

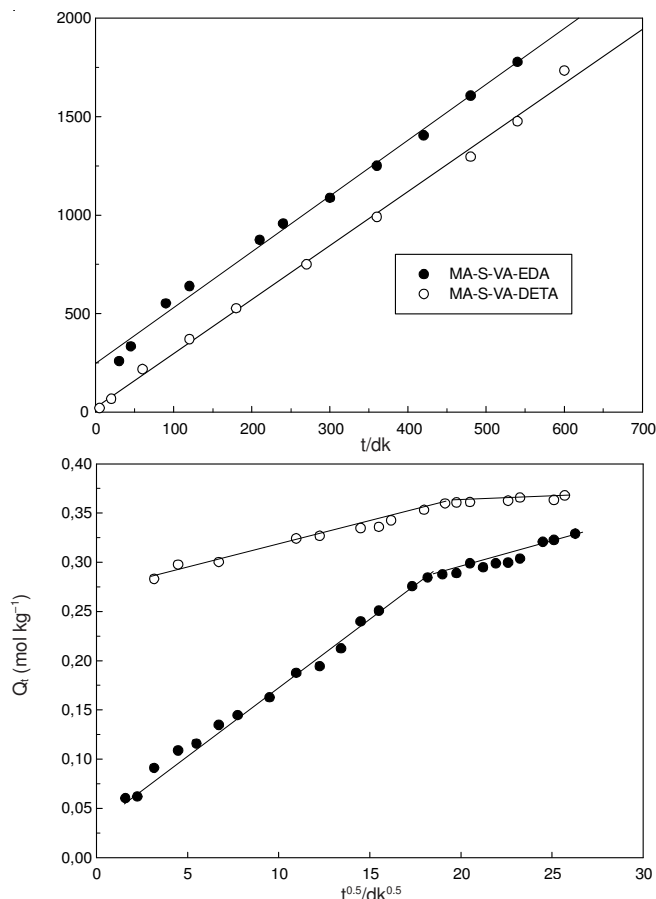


Fig. 6. Compatibility of UO_2^{2+} adsorption kinetics to pseudo-second-order (t/Q_t vs. t) and intraparticle diffusion (Q_t vs. $t^{0.5}$) models

This is a result of MA-S-VA-DETA's more interest to UO_2^{2+} than MA-S-VA-EDA.

Reusability and storage ability: The recovery of the adsorbed UO_2^{2+} was tested with 1 M HCl and it was observed that the total absorbed amount had been recovered. During the second usage, reducing was observed in the adsorbed amount. The reason of this decrease is impress with 1 M HCl of the amine groups.

The storage ability tests for one use of the all adsorbents performed for the ions of interest for 4 weeks with 1 week interval indicated that the fractional adsorptions remained unchanged, for which the unchanged IR spectra of the structures obtained with the intervals were the evidence.

After emphasizing the above mentioned adsorptive features, the sorption capacity of MA-S-VA-EDA and MA-S-VA-DETA for UO_2^{2+} of interest were compared with those extracted from literature in Table-4. The comparison obviously showed that these modified polymers synthesized in our laboratory should be considered amongst the favourite adsorbents.

TABLE-4
COMPARISON OF UO_2^{2+} ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS EXTRACTED FROM LITERATURE

Adsorbent	X ($\text{mol} \text{kg}^{-1}$)
Glycidyl methacrylate chelating resins ¹³	0.82
Sulfonated phenol-formaldehyde ³¹	0.31
2-Acrylamido-2-methylpropane sulfonic acid ³²	2.31
Amidoximated pine bark ³³	0.80
Poly(AAc/AAm)-cl-N,N-MBAAm ³⁴	0.87
Chitosan/PVA hydrogel ³⁵	0.58
Poly(acrylamidoxime-co-(1-(2-pirydylo)-2-naphthyl-2-methacrylate)-co-methacrylic acid) ^{36,37}	0.10
This study	
MA-S-VA-EDA	0.58
MA-S-VA-DETA	2.56

Conclusion

The cross-linked polymer adsorbents formed with the modification of MA-S-VA terpolymer by EDA and DETA can be easily used effectively and practically as a potential adsorptive in the recovery of UO_2^{2+} . When it is compared with the adsorbents in the literature, it will be seen that the functional groups of MA-S-VA-EDA and MA-S-VA-DETA synthesized in our laboratory are having a paramount adsorption capacity toward UO_2^{2+} ion.

ACKNOWLEDGEMENTS

This work was supported by The Research Fund of Cumhuriyet University (Project No. F290).

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