

## Sorption of uranium anionic species from aqueous solutions on HDTMA-bentonite Jelšovský potok

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### Abstract

Bentonite deposit Jelšovský potok in Slovakia has great potential for use as an engineering barrier in the multibarrier system of deep geological repository. In this paper, HDTMA-modified bentonite J15m from Slovak bentonite Jelšovský potok was prepared and its sorption properties (sorption isotherms, kinetics) towards anionic uranium species was investigated. The removal of uranium anionic species from aqueous solutions (initial concentration: 10–1,000 mg/L) by J15m was studied in the absence of background electrolytes at initial pH range ( $\text{pH}_{\text{init}}$ ) 8.5; 9.5; 10.5. The amount of the sorbed U was determined spectrophotometrically using the Arsenazo III method. The maximum uptake capacity observed was 31.35 (mg/g) at 298 K. Experimental results were analysed by the Langmuir, Freundlich, Dubinin–Redushkevich and Tempkin isotherm. The kinetics of adsorption of U(VI) ions was also discussed using the pseudo-first-order and the pseudo-second-order at three different temperatures. The activation energy of the sorption for J15m was calculated as 23.534 kJ.mol<sup>-1</sup>.

**Key words:** adsorption, HDTMA-bentonite, uranium, equilibrium, isotherm, kinetic

### Introduction and formulation of objective

The  $\text{UO}_2^{+2}$  ion represents the uranium (VI) state and is known to form compounds such as uranyl carbonate, uranyl chloride and uranyl sulfate.  $\text{UO}_2^{2+}$  also forms complexes with various organic chelating agents, the most commonly encountered of which is uranyl acetate. Unlike the uranyl salts of uranium and polyatomic ion uranium-oxide cationic forms, the uranates, salts containing a polyatomic uranium-oxide anion, are generally not water-soluble. The interactions of carbonate anions with uranium (VI) cause the Pourbaix diagram to change greatly when the medium is changed from water to a carbonate containing solution. While the vast majority of carbonates are insoluble in water, uranium carbonates are often soluble. This is because a U(VI) cation is able to bind two terminal oxygen atoms (uranyl-cation) and three or more carbonates to form anionic complexes [1, 2].

The uranium fraction diagrams in the presence of carbonate illustrate this further: when the pH of a uranium (VI) solution increases, the uranium is converted to a hydrated uranium oxy hydroxide and at high pHs it becomes an anionic hydroxide complex. When carbonate is added, uranium is converted to a series of carbonate complexes if the pH is increased. One effect of these reactions is increased solubility of uranium in the pH range 6.0 to 8.0, a fact which has a direct bearing on the long term stability of spent uranium dioxide nuclear fuels [1].

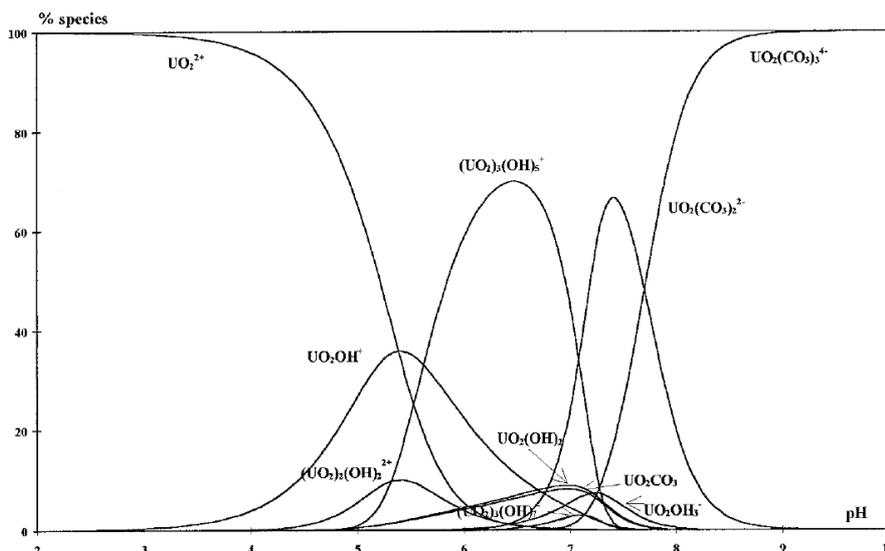


Fig. 1 Speciation diagram of uranium form in aqueous solution [2]

Bentonites are useful as engineering barriers in multi-barrier system of deep geological repository (DGR) for high level radioactive waste (HLRW) and spent nuclear fuel (SNF) from nuclear power facilities. In Slovakia is several bentonite deposits of Central European importance, which might find use for storing HLRW and SNF in DGR. There is the most popular and long mined bentonite deposit located in the Slovak upland in the locality Stará Kremnička: Jelšovský potok. It is mainly compose of Al-Mg montmorillonite and its overall presence of bentonite in the range 45 to 85 % [3 - 5].

Various kinds of new adsorbents for removing and recovering uranium have been reported [6, 7], among which natural clays and their composites are considered as particularly effective, low-cost, and chemical stability. Bentonite is a well-defined naturally occurring 2:1 aluminosilicate mineral consisting of one alumina octahedral layer sandwiched between two silica tetrahedral layers.

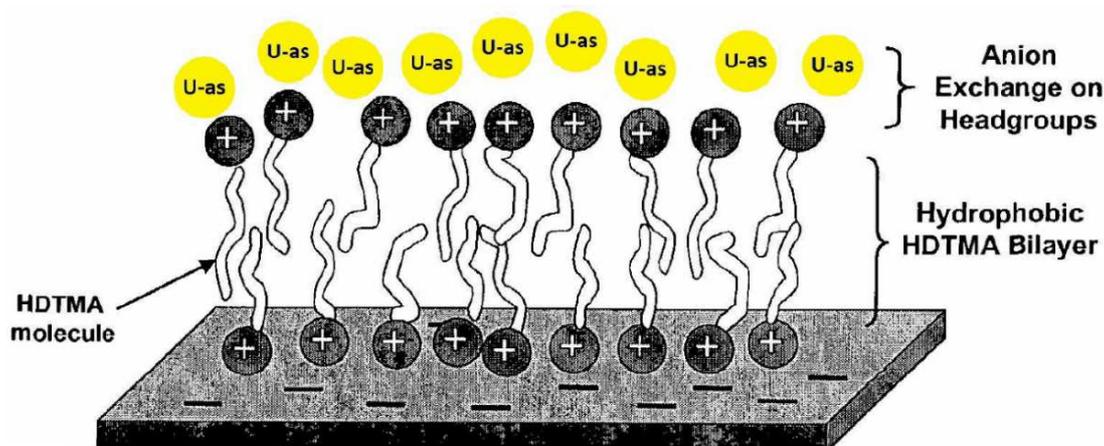


Fig. 2 Structure of HDTMA-modified bentonite

The potential adsorption sites for metal ions on bentonite include silanol ( $\equiv\text{SiOH}$ ) and aluminol ( $\equiv\text{AlOH}$ ), hydroxyl groups on the mineral edges and the permanently charged ( $\equiv\text{X}^-$ ) on the basal surfaces. The adsorption properties of bentonite can be improved by surface modification, such as the pillaring of certain metal oxides and polymeric species into interlayers, results in an increase in basal spacing, surface area and pore volume, which produces a structure with 2D micropores [8].

Several models can be used to express the mechanism of solute sorption onto a sorbent [9]. The kinetics of adsorption of uranium and its fission and activation products is needed to clarify their migration in the environment and is essential to a comprehensive characterization of the adsorption properties of engineering barriers [10-14].

Objective of this work is to study the adsorption of uranium anionic from aqueous solutions on HDTMA-modified bentonite Jelšovský potok.

## Materials and methods

As the adsorbent studied organo-bentonite HDTMA-modified form (the label J15m) from smectited bentonite Jelšovský potok [12] with a grain size below 15 microns, (the label J15). Five grams of J15 was mixed with 25 mL  $60 \text{ mmol}\cdot\text{L}^{-1}$  HDTMAB solution and these bentonite suspension followed by stirring at  $60 \text{ }^\circ\text{C}$  for 24 h. The suspension was filtered and was washed with deionized water until a negative bromide test had been obtained with  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{AgNO}_3$ , and then dried at  $60 \text{ }^\circ\text{C}$  for 24 h. All samples were ground and sieved to 15 microns.

For the sorption experiments using batch technique, 50 mg of the J15m were contacted in polypropylene tubes for 24 h with 10 mL of uranium solutions ( $c_{\text{init}}$ : 10 – 1,000 mg U/L,  $\text{pH}_{\text{init}}$  8.5 adjusted using NaOH at room temperature). The uranium solutions were prepared by dilution of a stock  $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  solution (Merck pro analysis) with bi-distilled water. Uranium carbonate complexes were prepared by adjusting the stock uranium solution at alkaline pH and the natural uptake of  $\text{CO}_2$  from the air, while mechanical stirring for 90 minutes. After separation of the solid and liquid phases by centrifugation, the equilibrium pH ( $\text{pH}_{\text{eq}}$ ) was measured and the uranium concentration determined spectrophotometrically by means of the Arsenazo III method at 660 nm [15]. The obtained data were used to calculate the uptake capacity in mg/g and construct the corresponding sorption isotherms. The uranium uptake data were modeled using number of 2-parametric non-linear isotherm equations.

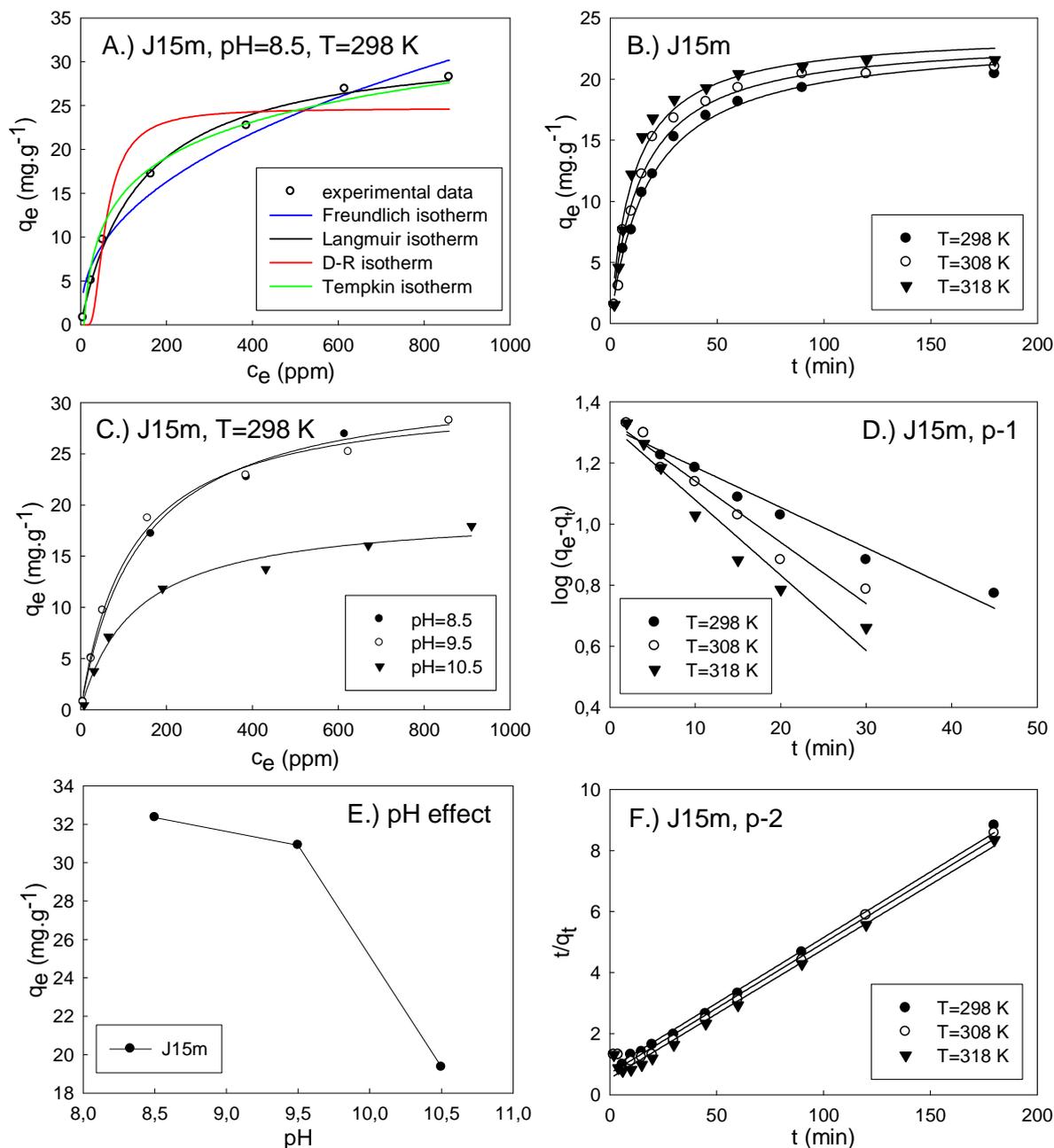
The sorption kinetics was also investigated and modelled using the pseudo-first and pseudo-second order equations. The kinetics model parameters were determined by linear regression. The kinetics of uranium sorption by the J15m was investigated using a batch technique. The 500 mg of the J15 came in contact with 100 mL of uranium solution of  $c_{\text{init}}$  500 mg U/L and  $\text{pH}_{\text{init}}$  8.5 at room temperature, 35 and 45 °C. At pre-determined time intervals (2 – 180 min) a 2 mL sample was withdrawn and the amount of U was determined by means of the Arsenazo III method.

## Results and discussion

The experimental results demonstrated that HDTMA-bentonite J15m can remove uranium anionic species from aqueous solutions at pH 8.5 and the highest rate of metal ions uptake was observed  $31.35 \text{ mg}\cdot\text{g}^{-1}$ . The analysis of the isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. Figure 3 A.) shows the plots of  $q_e$  versus of  $C_e$  for the adsorption isotherms of U(VI) on J15m at  $\text{pH} = 8.5$  and  $T = 298 \text{ K}$ , C.) the plots of  $q_e$  versus of  $C_e$  for the adsorption isotherms of U(VI) on J15m at various pH. The experimental data were reproduced very well and were analysed by the Langmuir, Freundlich, Dubinin–Redushkevich and Temkin adsorption isotherm. They were also compared their linear and non-linear forms. Based on the correlation coefficient of the determination ( $R^2$ ), the best approximation was obtained for the Langmuir model.

Kinetic models can be helpful to understand the mechanism of adsorption and evaluate performance of the adsorbents for species removal. For J15m in the first 2 min of the experiment only ca. 10 % of maximum uptake of uranium could be observed, the equilibrium was established in <60 min (Fig. 3 B.)). The kinetic data of the U-sorption by HDTMA-modified J15m under investigation could be very well fitted by the pseudo-second order equation. Figure 3 D.) illustrates pseudo-first order and F.) pseudo-second order sorption kinetics of adsorption of U(VI) on J15m at various temperatures. The values of  $R^2$ , obtained from the plots of pseudo-second order kinetics given are greater ( $R^2 > 0.99$ ) than that of the pseudo-first order. It also showed a good agreement between the experimental and the calculated  $q_e$  values (Tab. 1).

Activation energy of the sorption of U(VI) on J15m was estimated by Arrhenius equation and was calculated using the values of the rate constant from a pseudo-second order kinetic equation. The value of  $E_A$  from the Arrhenius plots is  $23.534 \text{ kJ}\cdot\text{mol}^{-1}$ .



**Fig. 3** Equilibrium and kinetic study of U(VI) on J15m

**Tab .1** Comparison of the pseudo-first order and pseudo-second order models for U(VI) on J15m

sample	T (K)	$q_{e,exp}$ ( $mg \cdot g^{-1}$ )	pseudo-first order			pseudo-second order		
			$R^2$	$q_{e,cal}$ ( $mg \cdot g^{-1}$ )	$k_1$ ( $min^{-1}$ )	$R^2$	$q_{e,cal}$ ( $mg \cdot g^{-1}$ )	$k_2$ ( $g \cdot mg^{-1} \cdot min^{-1}$ )
J15m	298	298	23.88	0.9698	20.83	0.0132	0.9977	21.46
	308	308	23.46	0.9636	21.98	0.0201	0.9977	21.38
	318	318	23.35	0.9484	21.17	0.0247	0.9976	23.04

## Conclusion

In this study, domestic bentonite rocks Jelšovský potok was modified by a quaternary ammonium cationic surfactant (1-hexadecyl)trimethylammonium bromide in order to produce a material suitable also for the removal of anionic species (e.g. uranium carbonate-complexes) from aqueous solutions. The result of study indicated that investigated HDTMA-modified bentonite J15m could effectively remove uranium anionic species from aqueous solutions.

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