

ADSORPTION OF URANIUM BY NATURAL SORBENTS: ZEOLITE AND CLAY

Eva Viglašová¹, Adrián Krajňák¹, Michal Galamboš¹, Olga Rosskopfová¹

¹ *Comenius University in Bratislava, Faculty of Natural Sciences, Department of Nuclear Chemistry, Mlynská dolina, 842 15, Bratislava IV; ejka.viglasova@gmail.com*

Abstract

The removal and recovery of uranium from contaminated surface, environment and ground water, as result of nuclear industries, has attracted more and more attentions. Several methods are available for removing of uranium f.e. reverse osmosis, chemical precipitation, extraction or micellar ultrafiltration. The adsorption among these, is the most attractive. In case of management of radioactive waste, the adsorption of radionuclides plays significant role. Among the natural sorbents applied to the adsorption of uranium zeolites and bentonites offer a number of advantages. The main aims of this work are investigations of adsorption properties of Greek zeolite and bentonite during adsorption of uranium from water solutions, comparison of their adsorption characteristics, fitting with isotherms and its behaviour during kinetics process.

Key words: *uranium; adsorption; bentonite; zeolite*

Introduction and the formula of the main aim

The removal and recovery of uranium from contaminated surface, environment and ground water, as a result of nuclear industries, has attracted more and more attentions. Several methods are available for removing uranium from aqueous solution [1] among which, adsorption is the most attractive method due to its high efficiency, ease of handling, and availability of different adsorbents. Adsorption in the system adsorbent-solution plays significant role in everyday life, industry and environment protection. Also plays an important role in a large number of reactions of solids and biological mechanisms [2, 3]. Various kinds of new adsorbents for removing and recovering RN, include U have been reported, among which natural zeolites or bentonite are considered as particularly effective, low-cost, and chemical stability [4]. Zeolite is natural porous mineral described as crystalline hydrated aluminosilicates. Inside the framework structure of zeolite, alkali or alkaline-earth cations are reversibly fixed in the cavities and can easily be exchanged by surrounding positive ions [5]. Clinoptilolite belongs to the natural zeolite with high ion-exchange and sorption properties and it is known to have high CEC and removal efficiency for some cations. It is known, that zeolite containing rocks are used in wastewater purification to remove toxic and radioactive elements [6, 7]. Clay rocks- bentonites- have an extraordinary importance in the waste and environmental management. Bentonites consist of the mineral of the dioctaedric smectite group – montmorillonite and accompanying materials such as clay mineral [8]. The qualities of bentonites such as low permeability, large SS, high swelling ability, ability to interchange ions as well as their colloid - chemical properties are planned to be taken advantage of in form of bentonite barriers in the DGR for high-level RAO and SNF [9]. The chemistry of U(VI) in oxidizing aqueous environment is nearly exclusively dominated by the linear dioxo cation UO_2^{2+} and an array of mononuclear and polynuclear hydrolysis species [10, 11,]. The main aims of this work are investigations of adsorption properties of Greek zeolite Metaxades and bentonite Kimolos during adsorption of UO_2^{2+} cation ($\text{pH}_{\text{init}}= 2.5$; C_{init} : 10 to 1000 mg U/L) from water solutions, comparison of their adsorption characteristics, fitting with isotherms and its behaviour during kinetics (C_{init} : 500 mg U/L; $\text{pH} = 2.5$), influenced by T.

Materials and methods

The natural zeolite – Metaxades and bentonite – Kimolos were selected for experimental work, after grinding were sieved to obtain fraction $<50\ \mu\text{m}$ [12]. For the sorption experiments 0.05 g of the sorbent were contacted in tubes for 24 h. with 10 mL of U solutions at different C_{init} : 10; 50; 100; 250; 500; 750 and 1000 mg U/L, at $\text{pH}=2.5$, (adjusted with $0.1\ \text{mol}\cdot\text{L}^{-1}$ HCl and $0.1\ \text{mol}\cdot\text{L}^{-1}$ NaOH). After separation of the solid and liquid phases by centrifugation, the equilibrium pH_{equil} was measured and the U concentration in the supernatant solution was determined spectrophotometrically using the Arsenazo III method. The samples were measured with Shimadzu UV-160A spectrophotometer at 660 nm. The obtained data were used to calculate the uptake capacity in mg/g and construct the corresponding sorption isotherms. The experiments were performed under equilibrium conditions with atmospheric CO_2 . The kinetics of uranium sorption by the bentonite/zeolite was investigated using a batch technique in tempered apparatus. In experiments 0.5 g of the sorbent was suspended with 100 mL of U solution, in order to obtain the ration between solution and absorbent. The C_{init} of solution was 500 mg U/L, using $\text{pH}=2.5$. At pre-determined time intervals (2 – 300 min) a 2 mL sample was withdrawn and the amount of U was determined by means of the Arsenazo III. method as well as in the equilibrium experiments.

Results and discussion

The U adsorption equilibrium data obtained at $\text{pH}=2.5$ are plotted in Fig 1. For correlate the experimental data were used traditional Freundlich, Langmuir and D-R isotherms. In order to explain the controlling mechanism of adsorption processes, such as mass transfer and chemical reaction, pseudo-first-order, pseudo-second-order and intra-particle diffusion models are usually applied to describe the kinetic of metal removal [13, 14, 15]. Our attempt was made to fit the adsorption data with pseudo-second order. Kinetic data at $\text{pH}=2.5$ $C_{\text{init}}=500\ \text{mg U/L}$ at different temperature are showed on Fig 2 and pseudo-second order is on Fig 3.

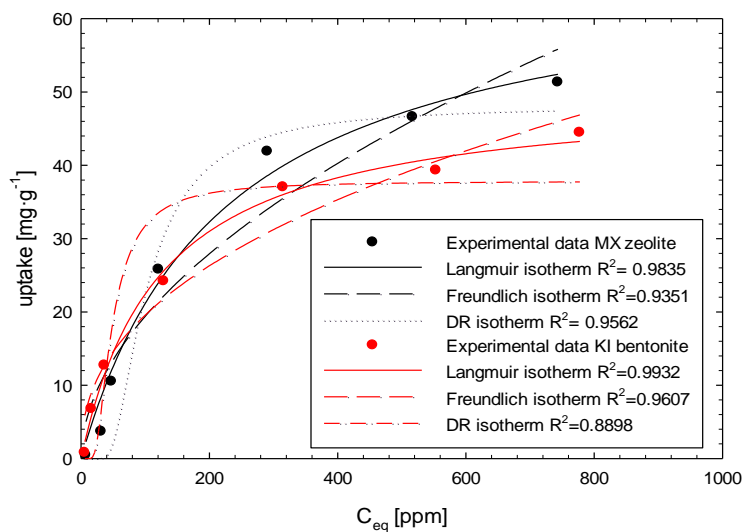


Fig. 1 Comparison of adsorption isotherm for KI bentonite and for MX zeolite at $\text{pH} 2.5$; C_{int} :10-1000 mg U/L; $T= 298.16\ \text{K}$

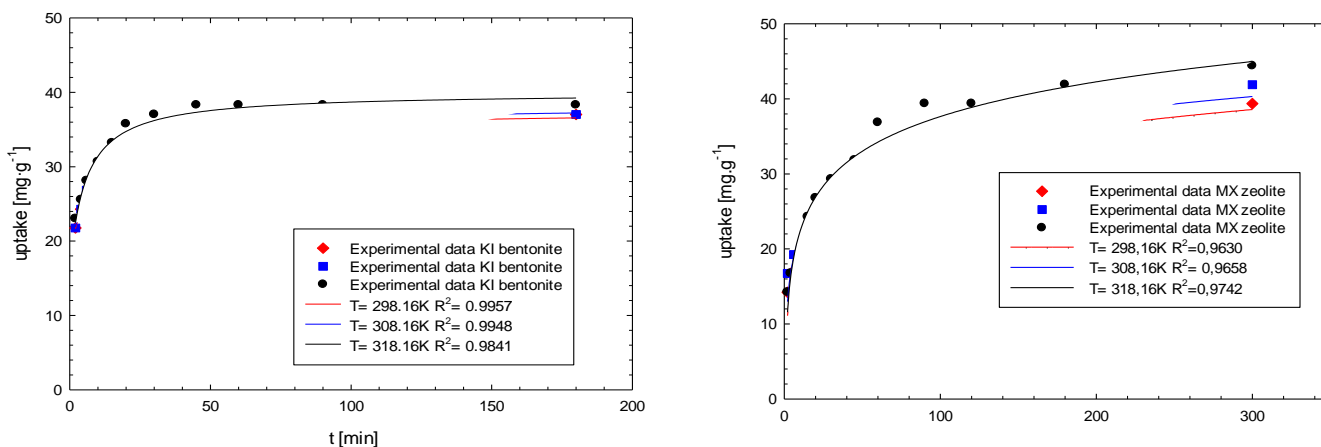


Fig. 2 Kinetic data for KI bentonite and for zeolite MX zeolite influenced by increase of T; pH = 2.5; $C_{init.} = 500$ mg U/L; T= 298.16K; 308.16K; 318.16K

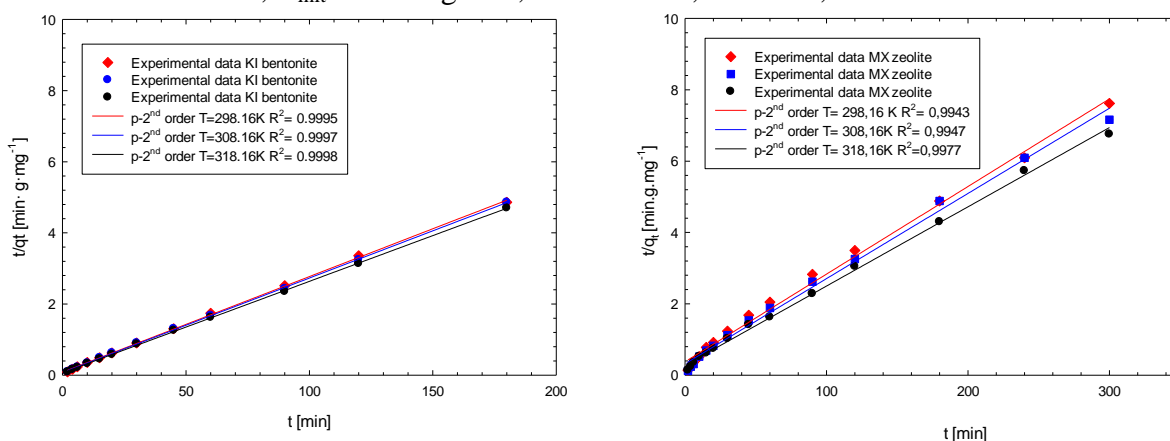


Fig. 3 Pseudo 2nd order for KI bentonite and for MX zeolite

Conclusion

A batch technique was employed to investigate the sorption behaviour of Greek zeolite and bentonite during adsorption of U. The value of R^2 showed that Langmuir isotherm model is better fitted with the experimental data than Freundlich or DR isotherm model in both case, for bentonite and for zeolite. The pseudo-second order equation fit very well our experimental data and increase of temperature caused increase of sorption ability of studied materials. In comparison adsorption properties zeolite vs. bentonite in our case, zeolite Metaxades showed little bit better removal of uranium from water media, improved with higher uptakes. Uranium uptake by the investigated sorbents was a little bit faster during kinetic experiments by bentonite. In the case of bentonite Kimolos in the first 2 min ca. 60 % of maximum uptake was observed, in compare with zeolite Metaxades, where it was just about 36 % of maximum uptake in the first 2 min. The equilibrium was established after 20 min. in the case of bentonite, in the case of zeolite it was around 60 min. In summary both materials Greek zeolite Metaxades and Greek bentonite Kimolos have good adsorption quality, but is necessary to do more extensive investigation with other conditions e. g. influence of pH, contact time, ratio solid/liquid phase etc.

Acknowledgment

This work was supported scholarship program N-SPP Hlavička 2011/2012; 203/Na-2002/689. At last but not at least I would like to say thank you to prof, Panagiotis Misaelides, Professor at Department of Chemistry from AUTH, Greece for opportunity to collaborate with him and for helpful advices during experimental work on AUTH, Greece.

References

- [1.] Environmental protection agency, [online]. [Washington D.C. (USA)], October 2012, [Cited: 18.03.2014] Dostupné na EPA WEB: <http://www.epa.gov/radiation/radionuclides/uranium.html>.
- [2.] MEUNIER A. *Clays*. Springer, Berlin, Germany, 2005, p. 58, ISBN 3-540-21667-7.
- [3.] SPARKS D.L. *Environmental Soil Chemistry*, Academic Press, London, UK, 2003, p. 133, ISBN 0-12-656446-9.
- [4.] CAMPOS V. *The sorption of toxic elements onto natural zeolite, synthetic goethite and modified powdered block carbon*. Environ Earth Sci, 2009, n. 59, p. 737.
- [5.] WEN D. *Comparative sorption kinetic studies of ammonium onto zeolite*. J Hazard Mater, 2005, n.133, p. 252.
- [6.] RAJEC P. *Thorium and uranium uptake by natural zeolitic materials*. Radioanal Nucl Chem, 2007, n. 275(3), p. 503.
- [7.] GALAMBOŠ M. *Sorption of anthropogenic radionuclides on natural and synthetic inorganic sorbents*. J Radioanal Nucl Chem, 2012, n. 293(2), p. 613.
- [8.] GALAMBOŠ M. *Utilization of Slovak bentonites in deposit of high-level radioactive waste and spent nuclear fuel*. J Radioanal Nucl Chem, 2011, n. 288, p. 765.
- [9.] GALAMBOŠ M. *Adsorption of cesium and strontium on natrified bentonite*. J Radioanal Nucl Chem, 2010, n. 283, p.803.
- [10.] WANG Y. Q. *Adsorption of U(IV) from aqueous solution*. J Radioanal Nucl Chem, 2012, n. 293, p.231.
- [11.] WARCHOL J. *Interaction of U(VI)aq with CHA-type zeolitic materials*. Microporous Mesoporous Mater, 2012, n. 153, p. 63.
- [12.] VIGLAŠOVA E. *Sorption of uranium species from aqueous solution by Greek zeolite Metaxades*. In Študentská vedecká konferencia, Bratislava: Prif UK, 2013.
- [13.] VIGLAŠOVÁ E. *Odstraňovanie uránových foriem z vodných roztokov prírodným a modifikovaným zeolitom*. In Prírodné a syntetické zeolity na Slovensku, Bratislava: FCHPT- STUBA, 2013.
- [14.] KRAJŇÁK A. *Slovak bentonites as engineering barriers in radioactive waste management*. In European Nuclear Conference, Manchester: YG- ENC, 2012.
- [15.] GALAMBOŠ M. *Adsorption equilibrium and kinetic studies of strontium on Mg-bentonite, Fe-bentonite and illite/smectite*. J Radioanal Nucl Chem, 2013, n. 298(2), p. 1031.

Abstrakt

Odstraňovanie uránu z kontaminovaného povrchu, prostredia a podzemných vôd v dôsledku jadrového priemyslu, priťahuje čoraz viac pozornosti. Vo výskume je dostupných viacero metód pre odstraňovanie uránu z vodných roztokov napr. chemické zrážanie, reverzná osmóza, extrakcia, micelárna ultrafiltrácia a adsorpcia, ktorá je jednou z najatraktívnejšou metódu. Adsorpcia v systéme adsorbent – roztok má veľký význam v každodennom živote, priemysle a pri ochrane životného prostredia. V manažmente ukladania RAO, hrá adsorpcia RN významnú úlohu. Z prírodných sorbentov aplikovaných pre adsorpciu uránu, zeolity a bentonity ponúkajú množstvo výhod. Hlavným cieľom práce sú výskum adsorpčných vlastností gréckeho bentonitu a zeolitu adsorpciou U z vodných roztokov, porovnanie ich adsorpčných charakteristík, namodelovanie adsorpčných izoterm a správanie počas procesu kinetiky.