Removal of uranium from water media by bentonite and zeolite

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Abstrakt

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, but adsorption among the others, 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 Metaxades and Greek bentonite Kimolos during adsorption of uranium from water solutions, comparison of their adsorption characteristics, fitting with isotherms (Freundlich, Langmuir and DR isotherm) and its behaviour during kinetics process influenced by temperature.

Key words: *adsorption, uranium, 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, such as chemical precipitation, reverse osmosis, solvent extraction, micellar ultrafiltration and adsorption [1].

Among these, adsorption is an 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. It allows characterizing the surface and structural properties of new materials or adsorbents [2, 3].

Various kinds of new adsorbents for removing and recovering radionuclides, include uranium have been reported, among which natural zeolites or bentonite and their composites 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 exchange capacity 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. Their properties are subject to their chemical and mineralogical composition. Bentonites consist of the mineral of the dioctaedric smectite group- montmorillonite (50-58%) and accompanying materials such as clay mineral. Quartz diatomite, calcite, organic materials and others [8]. The qualities of bentonites such as low permeability, large specific surface, 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 deep geological repositories for high-level radioactive waste and spent nuclear fuel [9]. The study of adsorption properties of bentonites is a step inevitable for working out a migration model for different eco-toxically significant radionuclides such as Cs, Sr, Co, Tc, I, Rb, Pu, Am, U and others [8-13].

The main aims of this work are investigations of adsorption properties of Greek zeolite Metaxades and Greek bentonite Kimolos during adsorption of uranium (pH_{init}= 2.5; C_{init}: 10 to 1000 mg U/L) from water solutions, comparison of their adsorption characteristics, fitting with isotherms (Freundlich, Langmuir and DR) and its behaviour during kinetics process (C_{init}: 500 mg U/L; pH = 2.5), influenced by temperature (T = 25 °C, 35 °C, 45 °C).

Materials and methods

The natural materials zeolite- Metaxades and bentonite- Kimolos were selected for experimental work, after grinding was sieved to obtain fraction <50 µm [10]. The main characteristic of materials is in table 1, 2 and composition of material in (%) is in table 2, 3

Tab. 1 The main characteristic of material (Kimolos-Greece)

Origin of the material	CEC (mol/kg)	Exchangeable cation	Bentonite type	Bentonite content (%)
Kimolos/ Greece		Na, Ca	Montmorilonite	>90

Tab. 2 The main characteristic of material (Metaxades-Greece)

Origin of the material	CEC (mol/kg)	Exchangeable cations	Zeolite type	Zeolite content (%)
Metaxades/ Greece	1.16	Ca, K	HEU-type Clinoptilolite	>58

Tab. 3 The composition of material (Kimolos- Greece)

Material	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO	MnO	TiO_2	P_2O5	Cr_2O_3
Kimolos/Greece	35.94	12.78	0.02	0.01	17.47	1.05	2.12	0.01	0.09	0.04	0.002

Tab. 4 The composition of material (Metaxades- Greece)

Material	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	Fe_2O_3	MgO	MnO	TiO_2	H_2O	Si/Al
Metaxades/Greece	66.47	13.47	3.25	2.6	2.09	1.05	0.65	0.02	0.15	10	4.93

For the sorption experiments 0.05 g of the sorbent were contacted in tubes for 24 hours with 10 mL of uranium solutions at different concentration C_{init}: 10; 50; 100; 250; 500; 750 and 1000 mg U/L, at different pH, (adjusted with 0.1 mol·L^{-1} HCl and 0.1 mol·L^{-1} NaOH at room temperature) The uranium solutions were prepared by dilution of a stock $UO_2(NO_3)_2$.6 H_2O solution with concentration 1000 mg U/L with bi-distilled water.

After separation of the solid and liquid phases by centrifugation (3000rpm), the equilibrium pH (pH_{equil}) was measured and the uranium concentration in the supernatant solution was determined spectro-photometrically using the Arsenazo III method.

After 24 hours aliquot volume from tubes was diluted with a specific ratio pertaining to initial concentration, the next added 0.5 mL of 0.1 % solution of Arsenazo III, 4 mL of concentrated HCl and filled with the water to the volume 10 mL. 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 uranium solution, in order to obtain the ration between solution and absorbent. The C_{init} of solution was 500 mg U/L, using different initial pH depends on experiment condition, experiments of cation or anionic species. 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 uranium adsorption equilibrium data obtained at pH= 2.5 and initial solution concentration from 10 mgU/L to 1000 mgU/L 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, and pseudo-second-order kinetics equations were applied to describe the kinetic characteristic of U(VI) on selected material [11]

Kinetic data at pH=2.5 C_{init}= 500mgU/L at different temperature are showed on Fig 2, the pseudo-first order of this kinetic data is on Fig. 3 and pseudo-second order is on Fig 4.

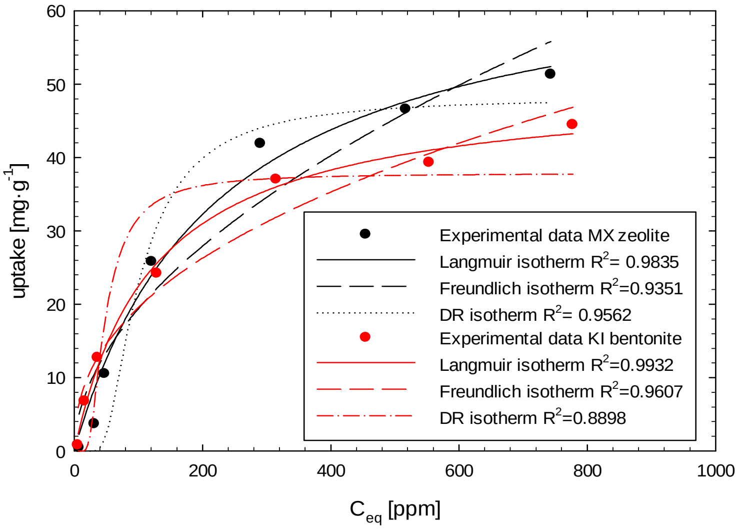

Fig. 1 Comparison of adsorption isotherm for bentonite Kimolos (KI bentonite) and for zeolite Metaxades (MX zeolite) at pH 2.5; C_{int} :10- 1000mgU/L; T= 298.16K

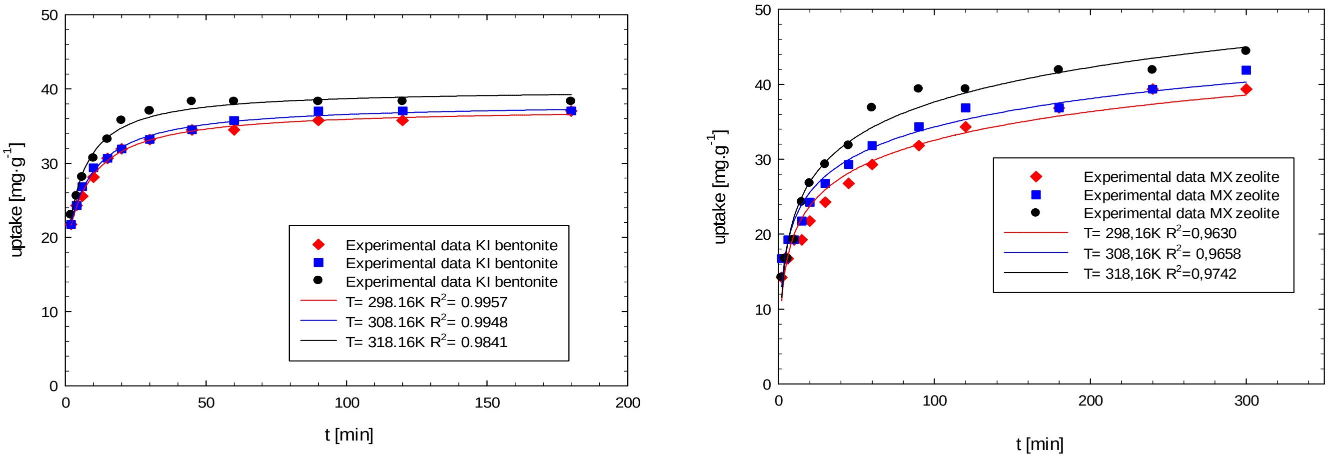

Fig. 2 Kinetic data for bentonite Kimolos (KI bentonite) and for zeolite Metaxades (MX zeolite) influenced by increase of temperature at pH=2.5; C_{init}.= 500 mgU/L; T= 298.16K; 308.16K; 318.16K

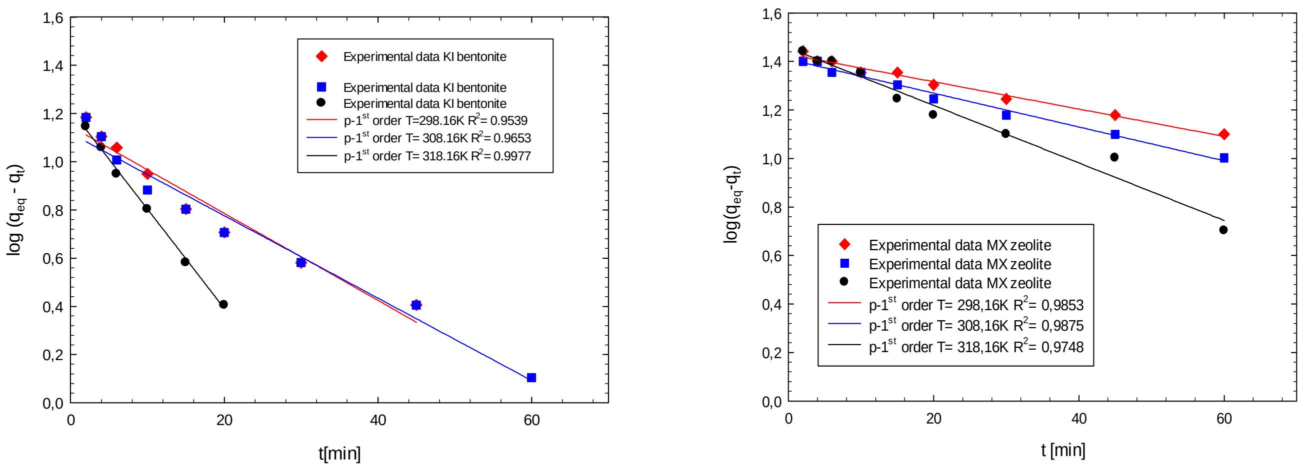

Fig. 3 Pseudo 1st order for bentonite Kimolos (KI bentonite) and for zeolite Metaxades (MX zeolite)

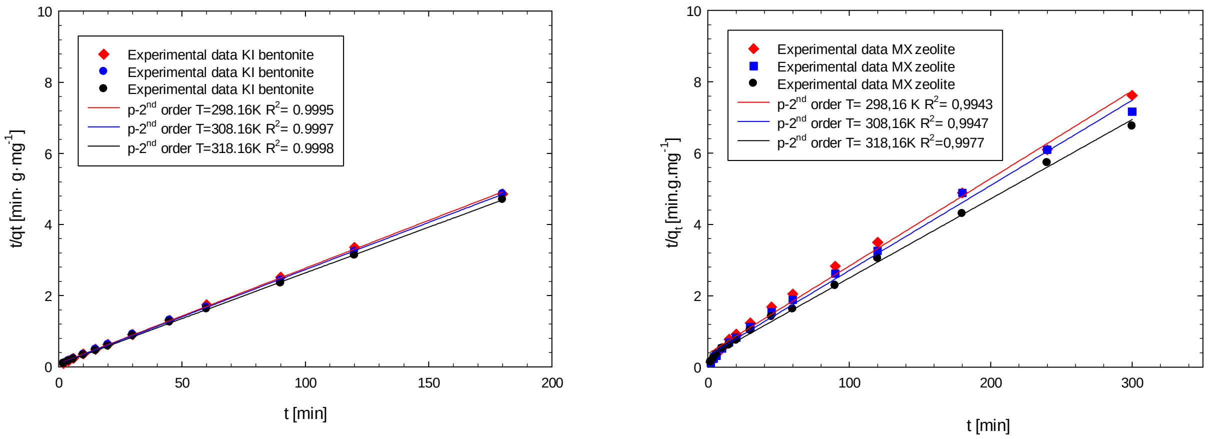

Fig. 4 Pseudo 2nd order for bentonite Kimolos (KI bentonite) and for zeolite Metaxades (MX zeolite)

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 to fitted with the experimental data than Freundlich or DR isotherm model in both case, for bentonite and for zeolite. The pseudo-second order equation was better than the value of the pseudo-first order 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.

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