

Uranium(VI) adsorption on surfactant modified heulandite/clinoptilolite rich tuff

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Abstract: The adsorption of uranium(VI) on heulandite/clinoptilolite rich zeolitic tuff modified with different amounts (2, 5 and 10 meq/100 g) of hexadecyltrimethyl ammonium (HDTMA) ion was investigated. The organozeolites were prepared by ion exchange of inorganic cations at the zeolite surface with HDTMA ions, and the three prepared samples were denoted as OA-2, OA-5 and OA-10. The maximal amount of HDTMA in the organozeolite OA-10 (10 meq/100 g) was equal to the external cation exchange capacity of the starting material. The results showed that uranium(VI) adsorption on unmodified zeolitic tuff was low (0.34 mg uranium(VI)/g adsorbent), while for the organozeolites, the adsorption increased with increasing amount of HDTMA at the zeolitic surface. The highest adsorption indexes were achieved for the organozeolite OA-10, in which all the surface inorganic cations had been replaced with HDTMA. An investigation of the adsorption of uranium(VI) ions onto organozeolite OA-10 at different pH values (3, 6 and 8) showed that the adsorption index increased with increasing amount of adsorbent in the suspension. Since uranium(VI) speciation is highly dependent on pH, from the adsorption isotherms, it can be seen that uranium(VI) adsorption on organozeolite OA-10 at pH 6 and 8 is well described by a Langmuir type of isotherm, while at pH 3, it corresponds to a Type III isotherm.

Keywords: zeolite, clinoptilolite/heulandite, organozeolite, uranium(VI), adsorption.

INTRODUCTION

Uranium is the most important element for the nuclear industry. It has a long half life and has a coordination chemistry consisting of multiple stable oxidation states and stable solid and aqueous forms within the ecosystem. Under standard environmental conditions, uranium typically occurs in its hexavalent form as the mobile, aqueous uranyl (UO_2^{2+}) ion.¹

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Adsorption of uranium(VI) onto various solids is important from purification, environmental and radioactive waste disposal points of view. In the last decades, the adsorption of uranium(VI) onto activated carbon, metal oxides, as well as onto natural and modified aluminosilicate adsorbents has been the subject of many investigations.²⁻⁴

The heulandite group of zeolites (structure code HEU), including the minerals clinoptilolite and heulandite, are the most abundant zeolites in nature.^{5,6} HEU Zeolites are widely used in many applications, such as catalysis, soil amendment, contaminant remediation and as a barrier to radionuclide migration. The high selectivity of the natural zeolite – clinoptilolite for Cs and Sr, permits its application in the treatment of radioactive fallout from nuclear tests and accidents. Several zeolite processes have been developed to counteract the fallout from the Chernobyl disaster.⁷ Clinoptilolite and heulandite are a crystalline hydrated tectoaluminosilicates of alkaline or earth alkaline cations, consisting of three dimensional frameworks of SiO_4^{4-} or AlO_4^{5-} tetrahedra linked through the shared oxygen atoms. According to Mumpton,⁸ clinoptilolite is distinguished from heulandite based on the Si/Al ratio and thermal stability. Cationic surfactant-modified zeolites (organozeolites) have been investigated for the adsorption of a variety of compounds, such as hydrophobic organic molecules (benzene, toluene, xylenes, *etc.*), inorganic cations, anions and inorganic oxyanions.⁹ These materials demonstrated chemical and biological stability and were tested as permeable barriers for ground water remediation. Organozeolites were also tested for *in vitro* adsorption of large low polar mycotoxin molecules (aflatoxin B1, ochratoxin A and zearalenone). They showed high adsorption efficiency at different pH values.^{10,11}

In this work, the adsorption of uranium(VI) from aqueous solutions onto organozeolites obtained by modification of clinoptilolite/heulandite rich zeolite tuff with different amounts of hexadecyltrimethyl ammonium (HDTMA) ions was studied. The aim of these investigations was to determine if organozeolites are effective adsorbents for uranium(VI) removal at different solution pH values.

EXPERIMENTAL

The starting material used in these experiments was natural zeolite tuff from the Beočin deposit (Fruška Gora, Serbia).

The cation exchange capacity, CEC, of the clinoptilolite rich tuff was measured with 1 M NH_4Cl while its external exchange capacity, ECEC, was determined using the method of Ming and Dixon.¹²

The surfactant hexadecyltrimethyl ammonium (HDTMA), as the Cl^- salt, supplied by Hoechst AG, was used for the preparation of three organozeolites. In order to obtain organozeolites with different HDTMA loadings, the zeolite tuff was treated with three different amounts of surfactant (2 meq/100g, 5 meq/100 g and 10 meq/100 g). Zeolitic tuff (5g) was mixed with 100 ml of each of the three HDTMA solutions in a turbo mixer at 9000 r.p.m. for 3 min at 50 °C. After mixing, the suspensions were filtered and the concentrations of exchanged Ca^{2+} , Mg^{2+} , Na^+ and K^+ were measured in the supernatants using atomic absorption spectrophotometry (AAS). The amount of unreacted amine was also measured in supernatants.¹³ The organozeolites were rinsed with distilled water until Cl^- ions were no longer detected and then dried at 60 °C. These products were denoted as OA-2, OA-5 and OA-10.

Adsorption of uranium(VI) on natural zeolitic tuff as well as on three organozeolites was carried out by the batch technique. Uranium(VI) solutions were prepared using uranyl nitrate hexa-

hydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Sigma-Aldrich Co.). The preliminary batch studies were carried out by shaking of the known amounts of each adsorbent and uranium(VI) solution at room temperature for at least 24 h at pH 6. The organozeolite OA-10 was selected for further experiments. Since, at pH values higher than 8.5, precipitation of a yellow uranyl carbonate complex was noticed, all experiments were performed in pH range from 3 to 8. In order to investigate the influence of the amount of organozeolite in the suspension on the adsorption of uranium(VI) at different pH values (3, 6 and 8), the following experiments were performed: the volume of the solution (50 ml) and concentration of uranium(VI) (50 mg/l) were kept constant while the amount of adsorbent was varied from 0.025 to 1 g. The pH was adjusted with HNO_3 and NaOH . The suspensions were shaken for 2 h, at room temperature, after which the solids were separated by centrifugation and the concentration of uranium(VI) remaining in the supernatants was determined.

In order to investigate the uranium(VI) adsorption isotherms on organozeolite OA-10, 50 ml of uranium(VI) solution of varying concentration, 10, 20, 25, 30, 40, 50 mg/l, was added to 0.125 g of adsorbent. The adsorption of uranium(VI) ions onto the organozeolite was studied in duplicate at different pH values. The samples were shaken for 2 h, centrifuged at 10,000 rpm for 10 min and the uranium(VI) concentration in the supernatants was measured using a fluorometric method based on the fluorescence of U in a fused mixture of NaF , Na_2CO_3 and K_2CO_3 .¹⁴ The amount of uranium(VI) adsorbed on the natural zeolite and organozeolites was calculated from the differences between the initial uranium(VI) concentration and the uranium(VI) concentration in solution after equilibration.

RESULTS AND DISCUSSION

The natural zeolitic tuff from the Beočin deposit had the following chemical composition: SiO_2 – 56.00 %, Al_2O_3 – 14.40 %, Fe_2O_3 – 1.86 %, CaO – 6.20 %, MgO – 2.64 %, Na_2O – 0.52 %, K_2O – 2.67 %, I.L. – 15.50 %.

Based on qualitative mineralogical analysis, the content of clinoptilolite/heulandite was over 80 %, while the minor minerals were quartz, feldspar, mica, calcite and clay minerals.

Based on the thermal behavior of clinoptilolite/heulandite zeolites, the zeolitic tuff from Beočin deposit may be recognized as Type II, because the heating of this zeolitic tuff at temperature above 550 °C resulted in the collapse of the structure.^{15–17}

The cation exchange capacity (CEC) of the zeolitic tuff was 168 meq/100 g and the external cation exchange capacity (ECEC) was 10.5 meq/100 g.

The organozeolites for the uranium(VI) sorption experiments were obtained by ion exchange of inorganic cations at external zeolitic surface with HDTMA. Three dimensional framework zeolites retain high molecular weight cationic surfactants on their external surface, where at sufficient surfactant loading a bilayer is formed. The bilayer formation results in charge reversal on the external surface, providing sites where anions will be retained and cations repelled.¹⁸ As uranium(VI) is present in solution at the investigated pH values in a cationic form (see below), for the preparation of organozeolites, HDTMA was added in amounts \leq ECEC of the zeolitic tuff (10.5 meq/100 g), *i.e.*, in amounts of 2 meq/100 g, 5 meq/100 g and 10 meq/100 g. It is well known that when a long chain organic cation is added in amounts \leq ECEC, quantitative ion exchange is observed.¹⁹ The content of inorganic cations released from the zeolitic surface during the ion exchange, as well as the amount of unreacted HDTMA in the supernatants are presented in Table I.

TABLE I. The content of HDTMA at the zeolitic surface, the content of inorganic cations in the supernatants and content of unreacted HDTMA in the supernatants, calculated in meq/100 g

HDTMA at zeolitic surface	meq/100 g				HDTMA unreacted	
	Ca ²⁺	Mg ²⁺	Na ²⁺	K ⁺		
	In supernatant					
OA-2	2	1.2	0.4	2.1	0.1	0.01
OA-5	5	3.5	0.6	2.3	0.1	0.01
OA-10	10	5.4	2.3	2.7	0.3	0.21

Comparing the amount of HDTMA added in meq/100 g for the preparation of all three organozeolites with the amount of inorganic cations released into the supernatants from the zeolitic surface during the ion exchange (calculated in meq/100 g of zeolitic sample) (Table I), it can be concluded that quantitative ion exchange had occurred. Also, from the contents of the inorganic cations released from the zeolitic surface, it may be seen that main cation at the surface was calcium, up to about 50 % of the exchanged cations in meq/100g. Furthermore, for each organozeolite, measurement of the content of unreacted HDTMA in the supernatants after ion exchange confirmed that when HDTMA was added in amounts \leq ECEC of the zeolitic tuff, no free amine was detected in the supernatants.

Preliminary uranium(VI) ion adsorption experiments at pH 6 on natural unmodified zeolitic mineral at a mass ratio adsorbent: uranium(VI) ion of 1000: 1 showed that the uranium(VI) adsorption index was 35 % (0.34 mg uranium(VI)/g adsorbent), while the uranium(VI) adsorption on the three organozeolites at pH 6 at a mass ratio adsorbent: uranium(VI) ion of 200: 1 increased in following order: 26.8 % (1.28 mg/g) for OA-2 < 50.5 % (2.41 mg/g) for OA-5 < 97.7 % (4.66 mg/g) for OA-10. The results demonstrated that the presence of organic cations on the organozeolite improve the adsorption of uranium(VI) ions and that the adsorption increases with increasing amount of organic cations at the zeolitic surface. The organozeolite OA-10, with an HDTMA content equal to the ECEC capacity of the starting zeolitic tuff (10 meq/100 g), showed the highest uranium(VI) adsorption index and this adsorbent was selected for further investigations.

In order to determine the equilibrium time for uranium(VI) adsorption on the selected organozeolite, the kinetics of the adsorption was investigated. It was found that at the beginning the adsorption was very fast and that most of the uranium(VI) ions were adsorbed in less than 2 h (> 95 %). Practically, there were no changes in the adsorption within the next 48 h. Based on these results, the subsequent experiments were conducted with an adsorption time of 2 h.

It is well known that uranium(VI) speciation is highly dependent on pH;²⁰ in low pH solutions, U(VI) exists as the uranyl cation, UO_2^{2+} , while at high pH values mononuclear (*e.g.*, $[\text{UO}_2(\text{OH})]^+$) as well as polynuclear (*e.g.*, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$,

$[(\text{UO}_2)_3(\text{OH})_5]^+$ etc.) hydrolysis products are formed. The occurrence of species such as $\text{U}_2\text{O}_5^{2+}$, $\text{U}_3\text{O}_8^{2+}$ has also been suggested.²¹ Uranium(VI) carbonate anionic complexes may be formed at pH values higher than 9.²² Thus, the characteristics of uranium(VI) adsorption may be different at different pH values. The results of uranium(VI) ion adsorption with different amounts of organozeolite OA-10 at pH values of 3, 6 and 8 are presented in Fig. 1. The initial uranium(VI) concentration was 50 mg/l.

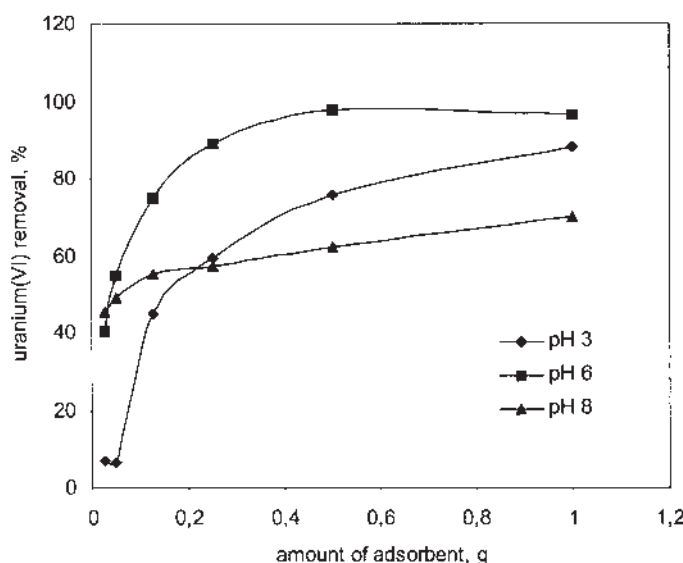


Fig. 1. Effect of the adsorbent concentration on the removal of uranium(VI) ions, at pH 3, 6 and 8.

From results presented in Fig. 1, it can be seen that with increasing amount of adsorbent OA-10, the uranium(VI) adsorption increases at all the investigated pH values. These results were expected because increasing the number of adsorbent particles in the solution results in more uranium(VI) ions interacting with these particles.²³ It can be noticed that the highest adsorption was achieved at pH 6. Comparing the adsorption of uranium(VI) ions onto organozeolite OA-10 at pH 3 with the adsorption at pH 6 and 8, it can be concluded that even with lower amounts of organozeolite in the suspension (0.025 and 0.05 g), the uranium(VI) adsorption at pH 6 and 8 is still high. Also, the adsorption results at pH 6 and 8 with lower amounts of solid phase show that the adsorption of uranium(VI) ions was less pH dependent.

Adsorption isotherms for the adsorption of uranium(VI) ions on organozeolite OA-10 at three different pH values are presented in Fig. 2. These isotherms were obtained by plotting the concentration of uranium(VI) ions in solution after equilibrium against the amount of uranium(VI) ions adsorbed per unit weight of each adsorbent. As can be seen from Fig. 2, the uranium(VI) adsorption on organozeolite OA-10 at pH 6 and 8, according to the IUPAC classification, is well described

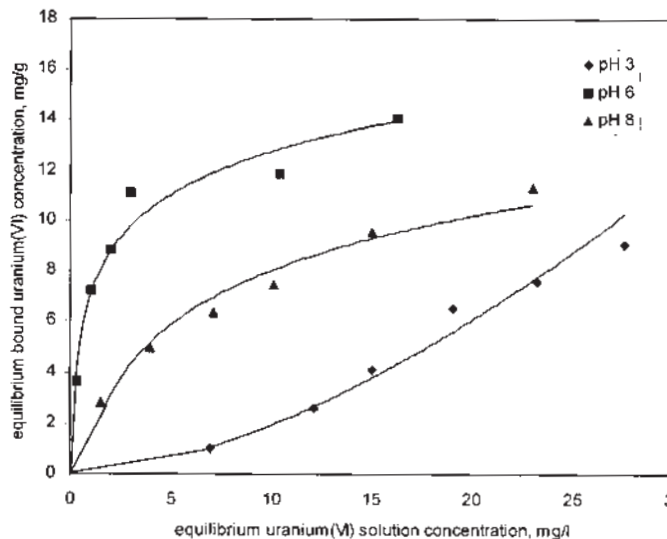


Fig. 2. Uranium(VI) adsorption on organozeolite OA-10, at pH 3, 6 and 8.

by a Langmuir type of isotherm (Type I).²⁴ The parameters of the isotherm were calculated from the well-known Langmuir equation:²⁵

$$c_{\text{ads}} = \alpha\beta c_{\text{eq}} / (1 + \alpha c_{\text{eq}})$$

where c_{ads} and c_{eq} denote the equilibrium concentration of uranium(VI) in the organozeolite and aqueous phase, α is a constant related with the binding energy and β is the maximum amount of solute that can be adsorbed by the solid.

The linearized form of the Langmuir isotherm:

$$c_{\text{eq}} / c_{\text{ads}} = \beta^{-1} c_{\text{eq}} + \alpha^{-1} \beta^{-1}$$

is presented in Fig. 3. As mentioned above, the adsorption data for both pH values were well-described by Langmuir isotherms, with calculated coefficients of determination (r^2) of 0.9911 for pH 6 and 0.9732 for pH 8. The adsorption maxima calculated from the linear Langmuir plots give estimates of the adsorption capacity of organozeolite OA-10 for uranium(VI) ions. The calculated maxima (β) are 14.49 mg/g at pH 6 and 14.90 mg/g at pH 8.

Misaelides *et al.*²¹ reported that uranium(VI) removal from aqueous solutions by zeoliferous rock samples at different pH values is related both to the aqueous chemistry of uranium(VI) as well as to the surface properties of the applied materials. The adsorption of uranium(VI) ions on organozeolite OA-10 at pH 3 corresponds to Type III isotherms. A Type III isotherm for gas adsorption describes adsorption on a macroporous adsorbent with weak adsorbate–adsorbent interactions (IUPAC classification).²⁴ Brunauer *et al.*²⁶ concluded that conformity of adsorption data to this type of isotherm indicates that the forces between the adsorbate molecules and the adsorbent are considerably weaker than the forces existing

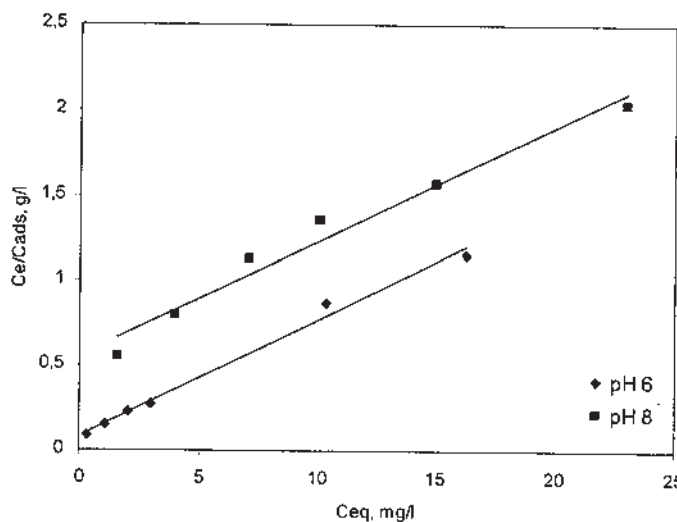


Fig. 3. Linearized form of the Langmuir isotherm for the adsorption of uranium(VI) ions on organozeolite OA-10, at pH 6 and 8.

between the adsorbate molecules in the liquid phases. The type of isotherm obtained at pH 3 indicates that this adsorption of uranium(VI) ions on the organozeolite involves only weak interactions and may be a physical phenomenon. As is already mentioned above, the hydrolysis of uranium(VI) begins practically at pH 3 and is more intense for pH values higher than 5. In the literature, it is indicated that uranium(VI) hydrolysis products can be exchanged or adsorbed on zeoliferous rock samples.²¹ In a previous study, the results of IR spectroscopy and thermal analysis of organozeolites after electrolyte treatment at pH 1, 7 and 10 confirmed that organozeolites are completely stable over the pH region from 1 to 10.¹¹ The fact that the isotherms obtained for uranium(VI) adsorption on OA-10 at pH 6 and 8 are the same may be an indication that uranium(VI) is adsorbed on the same surface sites.

CONCLUSIONS

The results reported in this paper demonstrate that organozeolites obtained by modification of clinoptilolite/ heulandite rich zeolitic tuff is effective for the removal of uranium(VI) from aqueous solutions. The availability of clinoptilolite/heulandite tuffs, their low cost and the simple procedure for the preparation of organozeolites are the main advantages for the production of large quantities of these materials. Organozeolites as adsorbents are also promising materials for the removal of uranium(VI) from contaminated soils and ground water systems.

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ИЗВОД

АДСОРПЦИЈА УРАНИЈУМ(VI)-ЈОНА НА МОДИФИКОВАНОМ
ХЕЈЛАНДИТСКО/КЛИНОПТИЛОЛИТСКОМ ЗЕОЛИТСКОМ ТУФУСРЂАН МАТИЈАШЕВИЋ, АЛЕКСАНДРА ДАКОВИЋ, МАГДАЛЕНА ТОМАШЕВИЋ-ЧАНОВИЋ,
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У раду је испитивана адсорпција уранијум(VI)-јона на површински модификованом хејландитско/клиноптилолитском зеолитском туфу (органозеолиту). Органозеолити су добијени јонском изменом неорганичких катјона са површине зеолита са хексадецил триметил амонијум (НДТМА) јонима. Добијени резултати су показали да је адсорпција уранијум(VI)-јона на немодификованом зеолитском туфу ниска (индекс адсорпције 35% односно 0,34 mg уранијум(VI)-јона/g адсорбента), док код органозеолита, адсорпција уранијум(VI)-јона расте са порастом садржаја НДТМА на површини хејландита/клиноптилолита. Највиши индекси адсорпције су добијени на органозеолиту од којег су сви катјони са спољашње површине замењени са НДТМА (ОА.-10). Испитивања адсорпције уранијум(VI)-јона на органозеолиту ОА.-10, на различитим рН су показала да адсорпција расте са порастом садржаја адсорбента у суспензији. Како облик уранијум(VI)-јона у раствору, зависи од рН средине, исти облик адсорпционих изотерми на рН 6 и 8 (Langmuir-ов тип изотерме), указује да се уранијум(VI)-јон у истом облику адсорбује на површини зеолитског туфа. Адсорпција уранијум(VI)-јона при рН 3 одговара Типу III адсорпционе изотерме.

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