

Some Aspects Concerning the Interaction between Uranium and ETS-10 Titanosilicate¹

CLAUDIU C. PAVEL¹, LUCIAN V. PAVEL², IGOR CRETESCU², KARIN POPA^{1,*}

¹ "Al.I. Cuza" University, Department of Chemistry, 11 - Carol I Blvd., 700506, Iași, Romania

² "Gh. Asachi" Technical University, Department of Environmental Engineering and Management, 71A - D. Mangeron Blvd., 700050, Iași, Romania

The present study reports the U(VI) uptake from solution on ETS-10 (Engelhard Titanium Silicate No. 10) and its modification achieved by post-synthesis treatment. The experiments were performed in the same conditions previously reported, in order to compare the influence of the mesoporosity in the large-size uranyl ion (UO₂²⁺) uptake. The results were evaluated using a Lagergren first order equation and the apparent thermodynamic parameters of the uranium uptake onto the considered materials were calculated.

Keywords: ETS-10, thermodynamic parameters, uranium(VI)

As an effort to reduce the heavy metal and radionuclide levels in water (waste water, drinking water or water for the agriculture) to the maximum permissible concentration, selective removal (by ionic exchange, adsorption, precipitation and membrane separation) is currently employed [1].

Some titanosilicates like ETS-10, ETAS-10, ETS-4, AM-4, and IONSIV were successfully used in model and real studies for Cu, Cd, Zn, Pb, Co, Ag, Hg, and Mn self sequestration [2-6]. Similarly, good results were obtained in the case of ⁶⁰Co, ^{110m}Ag, ^{115m}Cd, ¹²⁵Sb, ¹³⁴Cs, ¹³⁷Cs, and ²⁰³Hg radioisotopes [7-9], then the uptake can reach the ionic exchange capacity. On the contrary, the U(VI) is retained much less [10,11], and this phenomenon was explained taking into account the very big ionic radius of the hydrated uranyl ion. Consequently, it is not able to get into the pores and its uptake seems to be limited only to the external surface.

In drinking water, uranium is undesirable both as radioactive element (even naturally occurring) and as toxin to the kidney. Naturally occurring uranium contains 99.8% ²³⁸U, 0.72% ²³⁵U and 5.8·10⁻³ % ²³⁴U, all being radioactive nuclides. However, until the beginning of the 20th century, its concentration was extremely low in biosphere. Since the beginning of the nuclear era, uranium started to be mined, milled and enriched in its fissionable isotope. Therefore, in the areas of uranium facilities, its concentration increased to values exceeding the maximum admissible ones (0.1 mg/L), both in surface and groundwater.

In aquatic environment, uranium usually occurs in the U(VI) hexavalent form as a mobile, hydrated uranyl UO₂²⁺ ion. Its partitioning between aqueous and particulate phases, which is in turn affected by aqueous speciation, controls the mobility of uranium in natural waters. Temperature and pH, redox conditions, colloid formation and availability of complexing ligands play a role in determining the chemical speciation of uranium, and, consequently, its concentration in natural waters. U(VI) is extremely mobile and once entered in the living bodies provokes the inner irradiation (especially due to the γ -active decay products), the target organs being the skeleton and the kidneys. At high enough levels, it can cause permanent kidney damage, mostly due to the relative high biological half-life (about 100 days).

Because of this special concern, we had focused on improving uranium retention on titanosilicates. For the present study, ETS-10 (Engelhard Titanium Silicate No. 10) was chosen as a result of some cumulative factors: high ionic exchange capacity, high thermal, radiation and chemical stabilities and unique selectivity for certain metal cations [12-14]. This was possible after porosity modification. The uptake experiment was performed in the same conditions as the ones applied in [10]. Those results and the thermodynamic aspects of the uptake process of U(VI) on (meso-)ETS-10 are further discussed.

Experimental part

The hydrothermal synthesis of ETS-10 titanosilicates (with a typical unit cell composition of the as-synthesized material Na_{1.5}K_{0.5}TiSi₅O₁₃) was carried out by hydrothermal crystallization according to previous procedure [13], starting from a gel with the following molar composition: 1.0Na₂O: 1.49SiO₂: 0.2TiO₂: 0.6KF: 1.28HCl: 39.5H₂O. The gel was prepared at ambient temperature by mixing an acid solution (A) containing TiCl₄ (Merck), KF (Panreac) and HCl (37 wt. %, Riedel-De-Haen) with a basic solution (B) containing sodium silicate (27 wt. % SiO₂, 8 wt. % Na₂O, Merck) and NaOH (Carlo Erba) under constant stirring at room temperature. The crystallization was carried out at 463 K for 3 days. The product recovered by filtration was washed with distilled water and dried at 378 K overnight.

In the coming step, the porosity as well as the external surface of the as-made material has been increased by post-synthesis treatment with H₂O₂ under microwave irradiation. Details of the working procedure are reported in [15,16].

The retention of uranium on as-synthesized and mesopores-containing ETS-10 samples has been studied by batch technique. 0.1 g of ETS-10 samples were added to 20 mL uranyl nitrate UO₂(NO₃)₂·6H₂O solution (c_i = 250 mg U/L), previously thermostated at 277, 295, 313 and 323 K. In order to maintain free uranyl ions, the pH of the solutions was kept at 1.5-2.0 using 1M HNO₃. After equilibration for a given period of time, the suspension was filtered. The experiment was conducted under intermittent shaking.

The retention capacity was calculated from the residual concentration of uranium in solution using arsenazo III [2,7-

* email: kpopa@uaic.ro; Tel: +40-232-272478

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Table 1
THE BATCH DISTRIBUTION COEFFICIENT (K_d) OF U(VI) ON (MESO-)ETS-10
AS A FUNCTION OF CONTACT TIME AND TEMPERATURE

Temp, K	Sorbent	K_d , mL/g								
		5 min	15 min	30 min	1 h	2 h	3 h	24 h	168 h	
277	ETS-10	494	606	662	709	800	936	963	990	
	meso-ETS-10	677	1082	1800	1927	2073	2181	2300	2300	
295	ETS-10	800	990	1466	1883	1883	1927	1974	1974	
	meso-ETS-10	911	1082	1800	2364	2432	2503	3133	3133	
313	ETS-10	864	1050	1524	2073	2078	2181	2300	2300	
	meso-ETS-10	1883	2072	2180	2239	2578	3133	3248	3371	
333	ETS-10	911	1082	1723	2181	2300	2364	2432	2432	
	meso-ETS-10	1974	2181	2364	2578	3133	3371	3508	3508	

bis(2-arsenophenylazo) chromotopic acid, $C_{22}H_{18}As_2N_4O_{14}S_2$, Merck] as complexation agent [17,18]. The absorbance of the U(VI)-arsenazo III coordination compound was measured using Cecil 1020 UV-VIS spectrophotometer at 665 nm. Each determination was repeated three times. The standard error of the measurement was calculated to be less than 5%.

The batch distribution coefficient (K_d) was calculated as follows [19]:

$$K_d = \frac{c_i - c_f}{c_f} \cdot \frac{V}{m}, \text{ mL/g} \quad (1)$$

where c_i and c_f represent the initial and equilibrium concentrations of various metal ions in aqueous phase, respectively, m and V denote the weight of dry (meso-)ETS-10 and the volume of aqueous phase used in the experiments.

Results and discussions

The obtained ETS-10 has 4.5 meq/g ion exchange capacity and pore size of about 0.8 nm. Supermicropores of about 2 nm and well-defined mesopores with an average size of 10 nm were created in the structure by post-synthesis treatment with H_2O_2 under microwave irradiation (samples denoted meso-ETS-10). The structural defects appeared as a result of partial removal of the structural Ti-atoms without a substantial degradation of the crystallinity. These defective sites were generated at relatively mild conditions (5 wt.% H_2O_2 for 5 min) and increase significantly with the H_2O_2 concentration and time [15].

It can be observed that the K_d is increasing when the porosity is increased (meso-ETS-10) (typically, with a factor of two) and with the temperature (table 1). In most of the cases the equilibrium is reached after a few hours of contact time.

The uptake kinetic at short time is quite different for meso-ETS-10 in comparison to the as-synthesized ETS-10, being mostly determined by their porosity (fig. 1). Two different retention stages are identified in case of meso-ETS-10 sample: the first part, identical to ETS-10 (solid line), is determined by microposity, as adsorption and/or ion exchange process, and the second one (dash line) by supermicro- and mesoporosity due to diffusion of uranyl into large pores. Another factor which influences the uranium uptake would be the external surface area of titanosilicate, with a factor of 2 higher for meso-ETS-10. Recently, by an EXASAF study, it was found a specific strong interaction, chemically bonding, between uranyl ions and $[SiO_4]$ tetrahedra present especially on the surface of titanosilicate [20]. The $[UO_2^{2+}]-[SiO_2]$ interaction would involve one or both of the mechanisms presented in figure 2.

However, in this study we focus mostly on the kinetic and thermodynamic aspects of uranium retention process.

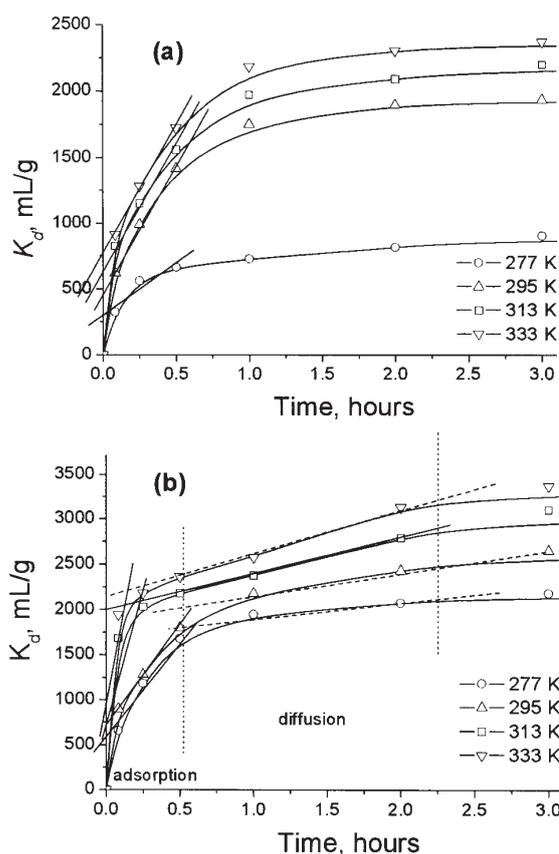


Fig. 1. Effect of short contact time on the retention of uranium on ETS-10 (a) and meso-ETS-10 (b)

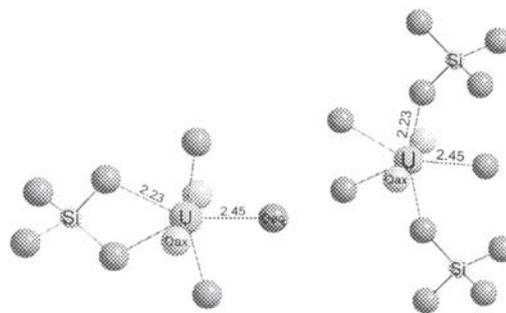


Fig. 2. Possible interactions between the uranyl ion and one or two sylanol groups

The rate of U(VI) uptake by (meso-)ETS-10 titanosilicate at 277, 295, 313 and 333 K trends to follow the Lagergren's first order equation [19]:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_s}{2.303} \cdot t \quad (2)$$

where q_t and q_e are the amount of U(VI) sorbed at the time t and, respectively, at the equilibrium, k_s is the uptake rate constant. As shown in figure 3 linear plots were obtained by representing $\lg(q_e - q_t)$ function on time (indicating the applicability of the first order kinetics). Only the points corresponding to a temperature where the equilibrium was established were used for the calculation.

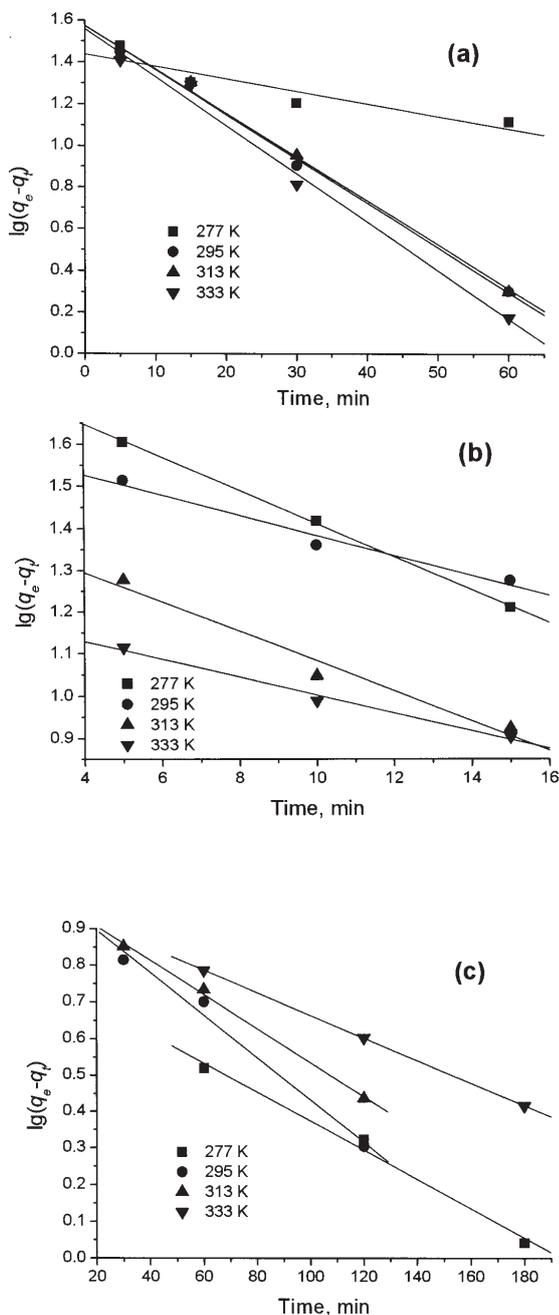


Fig. 3. Plot of $\lg(q_e - q_t)$ vs. time for ETS-10 (a) and meso-ETS-10 on adsorption (b) and diffusion (c) segments

The rate constants, k_s , calculated from the slopes of the plots, were used further to calculate the activation energy as derived from the Arrhenius equation:

$$k_s = k_0 \cdot e^{-E_a/RT} \quad (3)$$

where k_s is the sorption rate constant, k_0 - Arrhenius constant, E_a - activation energy, R - gas constant and T - absolute temperature. The best fit of $\ln(k_s) = f(1/T)$ was obtained without the consideration of the value a low temperature (277 K). The results show an activation energy, E_a , of 1.83 kJ/mol for ETS-10, much higher compared to $8.56 \cdot 10^{-6}$ kJ/mol corresponding for meso-ETS-10 calculated for the same contact times. For the diffusion part of meso-ETS-10, a value of $E_a = 13.47$ kJ/mol was found. However, due to the strong interaction between uranyl ions and titanosilicates surface, the contribution of external surface diffusion is not negligible as in the case of sorption of other radiocations of Cd^{2+} , Hg^{2+} , Co^{2+} and Cs^+ on ETS-10, previously investigated [8]. Therefore, the Lagergren equation will not be fully applicable at higher contact times for meso-ETS-10 sample.

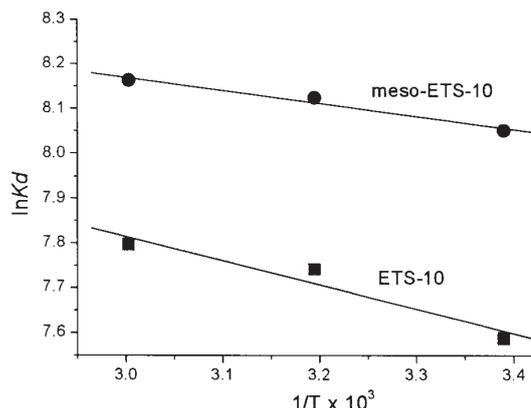


Fig. 4. Variation of $\ln K_d$ vs. $1/T$ for ETS-10 and meso-ETS-10

By increasing the uranium uptake with temperature, one could observe the endothermic effect of the sorption. The thermodynamic constants ΔH° and ΔS° were calculated from the slopes and intercepts, respectively, of the linear dependence of $\ln K_d$ vs. $1/T$ (fig. 4), expressed as

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where K_d is the distribution coefficient (mL/g), ΔS° the standard entropy, ΔH° the standard enthalpy, T the absolute temperature (K) and R the gas constant (kJ/K · mol). Only the sorption temperatures of 295, 313 and 333 K have been taken into consideration.

The standard free energy values, ΔG° , were calculated using the equation:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (5)$$

The values of ΔH° , ΔS° and ΔG° are given in table 2.

The thermodynamic results show a positive behaviour of both ETS-10 materials in the uptake of uranium from aqueous solution. Nevertheless, some differences could be noticed. The sorption of uranium on meso-ETS-10 is characterized by a low endothermic heat (1.1 kJ/mol), thus the process taking place easily at lower temperatures compared to ETS-10 (fig. 1). The increase of the absolute value of ΔG° with increasing of temperatures shows that higher temperatures favor the uptake process on both materials.

Table 2
THERMODYNAMIC PARAMETERS FOR THE SORPTION OF URANIUM BY (MESO-)ETS-10
TITANOSILICATES

Titanosilicate	ΔH° , kJ/mol	ΔS° , kJ/K·mol	ΔG° , kJ/mol		
			295 K	313 K	333 K
ETS-10	4.48	2.43	-25.52	-27.36	-29.40
meso-ETS-10	1.10	0.07	-19.75	-21.11	-22.61

Conclusions

The uptake capacity of ETS-10 titanosilicate for uranium present in aqueous solution was improved after a post-synthesis treatment, when an additional intracrystalline porosity was generated. In the sorption model we have used, ETS-10 would be preferred thermodynamically. However, meso-ETS-10 has given better results in the uranium retention, mainly because of the higher total surface. This was explained by the formation of extended silica-rich surface area for meso-ETS-10 and the strong interaction between uranyl ions and silica.

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CHIMIE ORGANICĂ MODERNĂ (O INTRODUCERE PE ÎNȚELESUL TUTUROR)

vol. 1 și 2

AUTORI: FLAVIAN CUIBAN, ION BOLOCAN ȘI EUGEN BARBU

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După câțiva ani de la apariția primului volum, volumul al doilea completează cursul universitar de chimie organică scris de colegul și prietenul de o viață, profesorul Flavian Cuiban, și colaboratorii săi. Am citit cu atenție ambele volume și consider că merită atât epitetul "modern" cât și cel de a fi fost scris "pe înțelesul tuturor".

Pornind de la concepte simple, expuse clar, autorii prezintă proprietățile și reacțiile compușilor organici pe baza mecanismelor de reacție, așa cum fac cursurile universitare folosite în prezent în toate țările avansate. De altfel, chimia românească a avut privilegiul de a crește împreună cu edițiile succesive ale tratatelor de chimie organică și de chimie generală concepute și elaborate magistral de Costin D. Nenițescu. La fel ca în chimia organică scrisă de Nenițescu (și spre deosebire de majoritatea cursurilor universitare străine), în cursul analizat aici nu se expun separat compușii aromatici de cei nearomatici, ceea ce prezintă anumite avantaje. Probabil că, textul analizat aici a reușit ca, folosind doar a zecea parte din amploarea informațională (adică din numărul de biți) din cele două volume ale cursului lui Nenițescu să transmită noțiunile esențiale ale chimiei organice. Pe de altă parte, la fel ca în majoritatea cursurilor universitare străine, aici fiecare capitol este însoțit de o serie de întrebări și probleme, iar soluțiile lor sunt prezentate la finele fiecărui volum.

Familiaritatea autorilor cu chimia biomedicală a făcut ca textul să fie însoțit de informații actuale privind activitatea biologică și aplicațiile farmacologice ale numeroaselor clase de compuși organici. De-a lungul cursului, autorii aplică consecvent raționamente logice pentru a reduce încărcarea memoriei; astfel numeroase reacții sunt arătate a fi guvernate de regula formării perechii "acid slab-bază slabă" din perechea conjugată "acid tare-bază tare".

Am apreciat respectarea nomenclurii internaționale care este destul de complicată, dar logică și consecventă (cu puține excepții, din păcate adoptate prin uzanța largă - de exemplu MTBE pentru denumirea care ar trebui să fie ordonată alfabetic și anume terț-butil metil eter). Spre deosebire de cursul lui Nenițescu, unde prefixele halogenilor nu conțin vocala finală o, ca în vechea nomenclură germană, aici este folosită aproape totdeauna denumirea internațională corectă - ca de exemplu bromometan și clorobenzen. În legătură cu denumirile adaptate chimiei românești, am apreciat faptul că autorii au căutat și găsit termeni mai potriviți decât "grupa fugace"; mi-a plăcut ideea de a scrie "sarcina parțial pozitivă" să fie *adăpostită* cât mai bine - când majoritatea textelor românești, chiar scrise de colaboratori din școala Nenițescu (Margareta Avram, Mircea Bănciu) foloseau neologisme ca "ecranată".

Ca să nu se rămână cu impresia că această recenzie este doar o înlănțuire de elogii, trebuie adăugat că acest curs are și o deficiență: probabil din cauza limitării de spațiu grafic, lipsește un capitol despre o clasă importantă de compuși organici, și anume heterocicurile aromatice. De aceea cred că studenții nu-și vor putea explica de ce elicea dublă de ADN conține trei punți de hidrogen între bazele nucleotidice citozina și guanina (C-G), în timp ce cealaltă împerechere de baze (A-T sau A-U) dă naștere doar la două asemenea punți - pentru aceasta ar fi fost nevoie de a explica diferența între aminopiridine și piridone (tautomerii stabili) față de iminopiridone și respectiv, hidroxipiridine.

Cu această unică rezervă, cred că acest curs universitar va permite studenților să descopere farmecul și frumusețea chimiei organice, învingând prejudecata care o situează printre cele mai dificile materii.

Prof. Alexandru T. BALABAN
Texas A&M University at Galveston