



## The separation of uranium ions by natural and modified diatomite from aqueous solution

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### ABSTRACT

In this work the natural and the surfactant modified diatomite has been tested for ability to remove uranium ions from aqueous solutions. Such controlling factors of the adsorption process as initial uranium concentration, pH, contact time and ionic strength have been investigated. Effect of ionic strength of solution has been examined using the solutions of NaCl, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub>. The pseudo-first order and the pseudo-second order models have been used to analyze the adsorption kinetic results, whereas the Langmuir and the Freundlich isotherms have been used to the equilibrium adsorption data. The effects of the adsorbent modification as well as uranium adsorption on the diatomite surface have been studied using X-ray powder diffraction, scanning electron microscopy and FTIR spectroscopy. The maximum adsorption capacities of the natural and the modified diatomite towards uranium were 25.63 μmol/g and 667.40 μmol/g, respectively. The desorptive solutions of HCl, NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, CaCO<sub>3</sub>, humic acid, cool and hot water have been tested to recover uranium from the adsorbent. The highest values of uranium desorption (86%) have been reached using 0.1 M HCl.

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### 1. Introduction

Uranium is one of the most hazardous heavy metals due to its high toxicity as well as its radioactivity. Uranium contamination poses a threat both to surface and ground waters. Purification of waste waters contaminated by uranium compounds is a topical problem in uranium production [1,2].

The development of effective methods of water purification requires understanding of nature of uranium compounds, their concentration and properties. Numerous researchers studied physicochemical state of uranium compounds in natural and waste waters [3–6]. In surface waters and top horizons of the soil uranium exists predominantly as a hexavalent element. In aqueous solutions corresponding to the aerobic condition of surface water bodies, uranium may be found primarily as uranyl-ion UO<sub>2</sub><sup>2+</sup> and as different complexes UO<sub>2</sub>OH<sup>+</sup>, (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>5</sub><sup>+</sup>, UO<sub>2</sub>(OH)<sub>2</sub>, UO<sub>2</sub>CO<sub>3</sub>, (UO<sub>2</sub>)<sub>2</sub>CO<sub>3</sub>(OH)<sub>3</sub><sup>-</sup>, etc. [1].

Among such traditional methods of water purification from uranium described in the published sources as adsorption [7–15], coagulation [2] and membrane separation [16] the first one is considered as the most effective. Such adsorbents as gibbsite [7], iron oxides [12], synthetic and natural zeolites [10,11], composite ion

exchangers [15], activated clay [13], chitosan [14], biological sorbents [8,9] are used in practice of water purification from uranium. Being a low-cost material diatomite seems to be one of the most perspective sorbents taking into account its ability of heavy metals removal from wastewater [17]. Adsorption of Th(IV) on the natural diatomite [18] as well as removal of uranium from aqueous solutions by diatomite [19] were studied. It is reported that OH groups and oxygen bridges of the diatomite surface act as adsorption sites forming hydrogen bonds with the adsorbate [20]. The silanol group is an active component tending to react with many polar organic compounds and various functional groups. Different methods of the diatomite modification allowing to increase its adsorption properties are described [21–23]. In particular, an organophilic surface and interlayer environment can be produced by replacing naturally occurring inorganic cations with various organic cations [24].

Generally the wide range of adsorption capacities of the different organic and inorganic adsorbents towards uranium ions has been reported. For example, Jung et al. [25] observed that the maximum uranium adsorption capacity of the nanoporous carbon was 151.5 mg U/g adsorbent and the experimental results of Mellah et al. [26] showed the maximum adsorption capacity of the carbon sorbent towards uranium as 28.3 mg/g. The very high adsorption capacity was exhibited for adsorption of uranyl ion by various microorganisms. The such bacteria as *Arlhrobacter nicoliana*, *Bacillus subtilis*, and *Micrococcus luteus*. *A. nicotiana* demonstrated the best performance adsorbing about 700 mg uranyl ions per gram dry wt. of microbial cells [8]. The maximum

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capacity of coir pith was determined as 250.0 mg/g [27]. Vidya et al. [10] found 9.5 wt.% of uranium loaded in MCM-41 and 12.5 wt.% in MCM-48 as a result of the study of uranium adsorption with mesoporous molecular sieves. Natural zeolite, clinoptilolite, was also tested for its ability to remove uranium from aqueous solutions. The maximum adsorption capacity of the natural clinoptilolite zeolite was found as 1.2 mg/g [28] and 0.34 mg/g [29]. At the same time the modified clinoptilolite tuff adsorbed 14.90 mg/g uranium [29]. The low amount adsorption of uranium (3.54 mg/g) was observed for hematite [30].

The aim of the study was to analyze kinetic and equilibrium adsorption of uranium ions from water solution onto the natural diatomite and the diatomite modified by hexadecyltrimethylammonium (HDTMA). Influence of pH value and ionic strength of uranium solutions on adsorption behavior of U (VI) has also been investigated.

## 2. Materials and Methods

### 2.1. Diatomite samples

The samples of the natural diatomite were obtained from Borownica deposit, Poland. The particle size of the diatomite used in these experiments was less than 0.25 mm. The modified diatomite samples were prepared by chemical treatment of 2% (w/w) solution of hexadecyltrimethylammonium bromide ( $C_{16}H_{33}N(CH_3)_3Br$ ) in the proportion 1 part diatomite to 10 parts solution (w/w). After 24 h the solid phases were separated from the solutions, washed by deionized water and dried at 60 °C. Washing of the modified diatomite samples (HDTMA–diatomite) was repeated to achieve the complete removal of Br-ions as indicated by the  $AgNO_3$  test of the supernatant solutions.

### 2.2. Kinetics and equilibrium study

The adsorption experiments were carried out at 21 °C. The reaction mixture (50 ml) containing 0.1 g adsorbent background electrolyte (0.01 M NaCl) to maintain an ionic strength and the desired amount of U(VI) ions from  $UO_2Ac_2$  solution were prepared. In equilibrium study pH value of the mixtures was adjusted to 6.2. Uranium concentration between 50 and 2000  $\mu mol/L$  were employed.

Kinetic experiments and study of pH value influence were carried out at the initial uranium concentration of 200  $\mu mol/L$ . Effects of ionic strength and inorganic anions concentration were tested at 0.1 M, 0.01 M and 0.001 M NaCl,  $Na_2CO_3$  and  $K_2SO_4$  solutions. The system was adjusted to the desired pH value by addition of negligible volumes of 0.01 or 0.1 M HCl, or 0.01 or 0.1 M NaOH. The pH value of the solution was controlled by pH meter PC 505. Ionic strength was 0.01 M in all experiments by adjusted to the desired values with 1.0 M NaCl solution. After stirring the suspensions for 1 h in an automatic shaker the solid and liquid phases were separated by use of centrifuge ROTINA 48 at 5000 rpm for 30 min.

The amount of U (VI) adsorbed on the diatomite was calculated as a difference between the initial concentration and the equilibrium concentrations. The equilibrium amount of metal adsorption from aqueous solution was determined using the formula:

$$q = (C_{init} - C_{equil})V/m \quad (1)$$

where  $q$  is the amount of metal ions sorbed at equilibrium expressed in  $\mu mol/g$  of sorbent;  $m$  is the adsorbent mass (g);  $C_{init}$  and  $C_{equil}$  are the initial and the equilibrium concentrations of metal ions respectively ( $\mu mol/L$ );  $V$  is the volume of solution (L).

In the desorption experiment 0.1 g of the modified diatomite loaded with 30.464  $\mu mol/g$  U was mixed with 50 ml of 0.1 M solution of HCl and NaOH (aggressive environment), 0.05 M  $Na_2CO_3$  and

0.05 M  $K_2SO_4$  solutions, 0.05 M suspension of  $CaCO_3$  (as the dominant ions in surface water), 0.1 g/L of humic acid solution (as the highest concentration in surface water in the spring season) and with cool (15 °C) or hot (100 °C) water (that corresponds to different process conditions). The rest of the procedure was the same as that in the adsorption batch experiment excepting pH adjustment. The efficiency of uranium desorption was calculated directly as an amount of uranium desorbed into the solution as follows:

$$E_{des} = (C_{des} * V * 100)/(q * m) \quad (2)$$

where  $E_{des}$  is the efficiency of uranium desorption in %, and  $C_{des}$  is the uranium concentration in the desorptive solution.

### 2.3. Analytical methods

Total organic carbon (TOC) in the diatomite samples was determined using a Total Organic Carbon Analyzer TOC-5000 Series combined with SSM-5000A (Shimadzu, Kyoto, Japan). Total carbon (TC) was detected in the samples with use of catalytically aided combustion oxidation at 900 °C, while inorganic carbon (IC) was analyzed in the samples after pre-acidification at an oven temperature of 250 °C. TOC was calculated as a difference between TC and IC and was used for calculation of the surfactant content in modified diatomite.

The chemical composition of the natural diatomite and the coating of the diatomite surface by the surfactant ions were examined using scanning electron microscopy (SEM LEO 1430VP) coupled with EDX spectrometer (detector XFlash 4010 Bruker AXS).

XRD patterns of the natural and the HDTMA-diatomite were obtained by X-ray diffraction analyses using X'Pert Pro diffractometer, Cu  $K\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ; 40 kV, 40 mA) and the samples were scanned from 0° to 80° ( $2\theta$ ) in step sizes of 0.04.

The infrared spectra of the natural and the HDTMA-diatomite were obtained using a Fourier Transform IR spectrophotometer Spectrum 2000 (Perkin Elmer) in order to determine the structure groups of the diatomite in question. The FTIR spectra in the wave number range from 400 to 4000/cm were obtained by using KBr pellet technique.

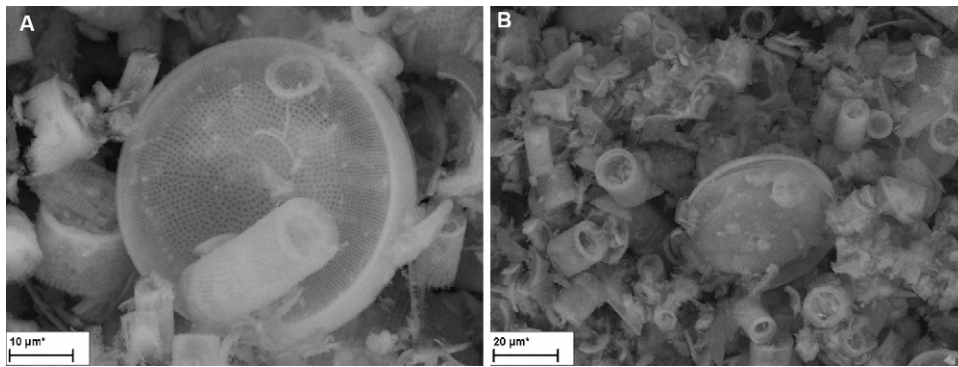
The concentration of uranium was determined by spectrophotometry on UNICAM HELIOS at 665 nm by using the U-arsenazo (III) complex. All chemicals of analytical grade used in this study were obtained from POCh, Gliwice, Poland. All experimental data are the averages of duplicate or triplicate experiments. The average standard deviation of the measurement was less than 0.5%. The standard reproducibility deviation was between 0.3–10%.

## 3. Results and discussion

### 3.1. Characteristics of natural and modified diatomite

Microphotographs of diatomaceous earth are presented in Fig. 1(A–B). The microphotographs show that the well preserved forms of diatoms generally have cylindrical and plate shapes with well-developed porous structure. There are also small broken particles of other kinds of diatoms (Fig. 1B). As one can see in Fig. 1A, the centric diatom is approximately 30  $\mu m$  in radius and 7  $\mu m$  in thickness. The body of this diatom is closely covered by clean pores of 300–500 nm in diameter. The diatomaceous particle of cylindrical shape is a 10–20  $\mu m$  in stretch and 5–10  $\mu m$  in external diameter. The thickness of diatomaceous cylinders is about 3  $\mu m$  and their surface is also covered by pores of 300–400 nm in diameter. Moreover, the walls of cylinders are folded by a few circular belts. The characteristics of the diatomite porosity point that this material may be successfully modified by surfactant phases.

The chemical composition of the natural diatomite obtained by SEM/EDS analyses at Quantax 200 (detector XFlash 4010 Bruker



**Figure 1.** Scanning electron microphotographs of the diatomite.

AXS) is as follows: 54.5% O, 35.4% Si, 7.8% Al, 1.1% Fe, 0.5% K, and 0.4% Na.

The cationic surfactant concentration on the diatomite was calculated from the organic carbon content. The results indicated that TOC (total organic carbon) content in the surfactant-modified diatomite was 5.56% (w/w) that corresponds to 6.67% (w/w) of the HDTMA-ions. As it is shown in Figure 2A, the diatomite surface is covered by cluster forms of the surfactant mainly. The clusters sizes range from one to several micrometers in size.

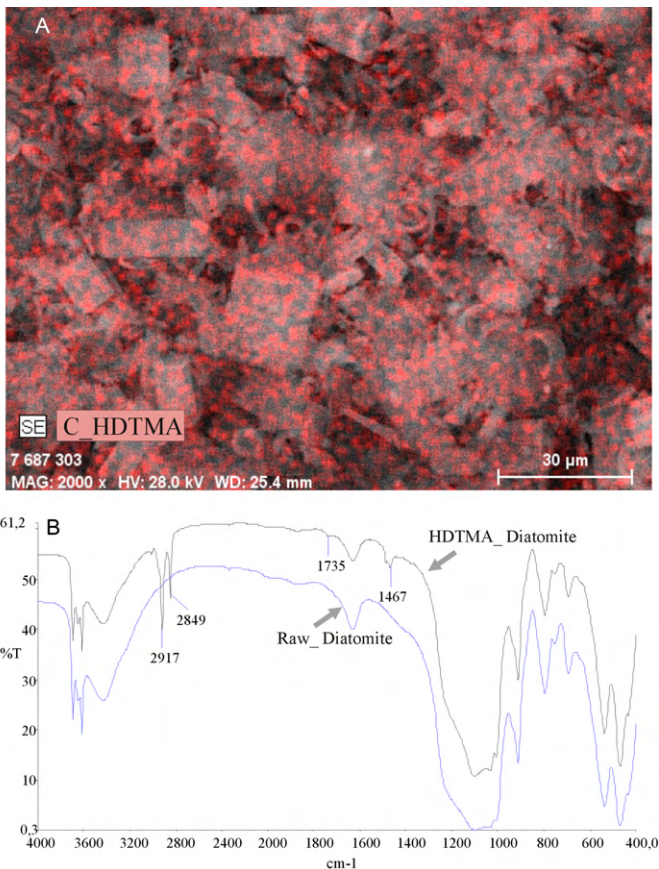
In the FTIR spectrum of the natural diatomite intense bands at 3697, 3621, 1631, 1103, 1015, 913, 796, 694, 537, 469  $\text{cm}^{-1}$  (Figure 2B) were observed. The bands at 3697, 3621 are connected with the free silanol group (SiO–H) and the band at 1631  $\text{cm}^{-1}$  represents H–O–H bonding vibration of water. The bands at 1103, 1015

reflect the siloxane (–Si–O–Si–) group stretching and the 913  $\text{cm}^{-1}$  band corresponds to Si–O stretching of silanol group. Bands at 796 and 694  $\text{cm}^{-1}$  are caused by SiO–H vibration. The absorption peaks around 537, 469  $\text{cm}^{-1}$  are attributed to the Si–O–Si bonding vibration [6,10,18,22]. After modification with HDTMA the aforementioned bands have preserved, but new bands of surfactant groups–2920, 2851, 1471  $\text{cm}^{-1}$  have appeared [25]. As Figure 2B demonstrates the infrared spectra show the strong bands at 2920 and 2851  $\text{cm}^{-1}$  attributed to asymmetric and symmetric stretching vibrations of C–H groups.

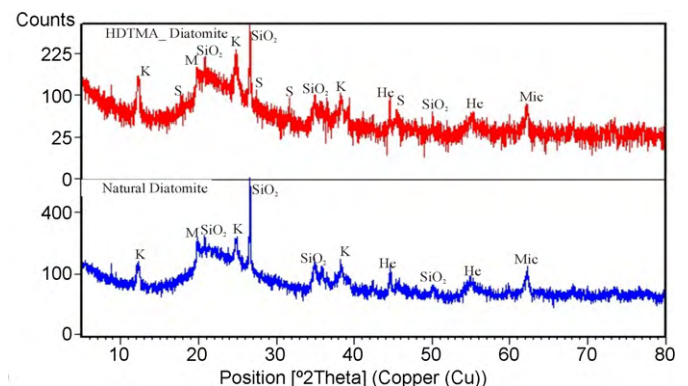
XRD patterns of the natural and the HDTMA-diatomite are shown in Figure 3. As Figure 3 demonstrates, the natural diatomite sample mostly consists of diatoms (SiO<sub>2</sub> amorphous phases) and traces of such minerals as montmorillonite (M), kaolinite (K), hematite (He) and mica (Mic). By this the X-ray pattern of the natural diatomite is also different from the pattern of the treated one. A few new peaks (S) of the surfactant have appeared on X-ray pattern of the modified material. It can be caused by HDTMA cations deposited on the diatomite surface.

### 3.2. Adsorption kinetic study

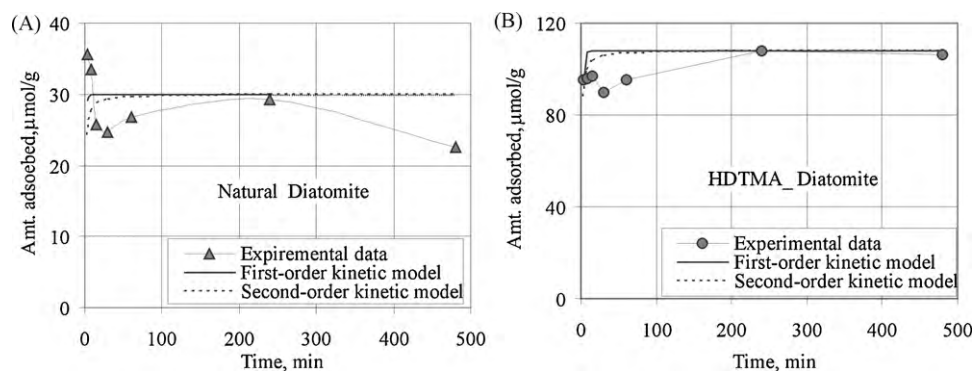
Adsorption kinetics of uranium from the aqueous solutions onto the diatomite was made up to equilibrium. Adsorption of U(VI) on the natural diatomite as a function of the contact time is shown in Figure 4. As one can see in Figure 4A, adsorption of U(VI) increased very quickly at the initial contact time. After 35 minutes from beginning of the adsorption process the maximum amount of uranium adsorbed was achieved. In the next stage of the process (for 40 to 90 minutes after the start) we could observe desorption (about 25%) of uranium previously adsorbed by the diatomite. This inversion period of adsorption may be caused by competition between the exchangeable cations and hydrogen ions from the diatomite



**Figure 2.** Scanning electron micrograph (detector XFlash 4010 Bruker AXS) of the surfactant treated diatomite and FTIR spectra of the natural and the HDTMA treated diatomite.



**Figure 3.** X-ray patterns of the natural and the HDTMA-diatomite.



**Figure 4.** The kinetic of the uranium adsorption on the natural (A) and the HDTMA-diatomite (B).

surface with uranium ions from the solution. The uranium adsorption increased later, but the amount of the adsorbed uranium was significantly lower (about 20%) compared with the first period of the fast adsorption. The kinetic curve of uranium adsorption onto the HDTMA-diatomite is shown in Figure 4B. It can be observed that about 95% of uranium was removed for the first 45 minutes of the adsorption process. The inversion phenomenon with desorption prevalence (near 10%) in this case was apparent from 45 to 90 minutes of the adsorption. Uranium adsorption slowly increased with time reaching a plateau after 250–300 min of the process duration.

The pseudo-first- and the pseudo-second-order kinetics models expressed via Eqs. (5) and (6), respectively were used to study the specific rate constant of U(VI) adsorption by the natural and the HDTMA-diatomite.

$$q = q_e(1 - \exp(-k_1 t)) \quad (3)$$

$$q = (q_e^2 k_2 t) / (1 + q_e k_2 t) \quad (4)$$

where  $k$  is the rate constant,  $q_e$  is the equilibrium adsorption capacity, and  $t$  is the time of adsorption duration. Parameters of the kinetic and isotherm models of uranium ions adsorption are presented in Table 1.

Plotting the experimental data using Eqs. (3) and (4) indicates that the pseudo-first-order kinetics models do not give considerably good fit. The kinetics of U(VI) adsorption onto the natural diatomite and the HDTMA-diatomite can be significantly better described by the pseudo-second-order rate equation (Fig. 4). But

both models did not worked well for the raw diatomite. Furthermore, the values of the rate constants of the uranium adsorption change considerably during the adsorption process. Therefore the kinetic coefficients given in Table 1 were estimated as the average values of the adsorption process and as their values at the first stage. It can be explained by the different types of uranium ions taking part in the adsorption and as a result of the complicated nature of interaction between the uranium ions and the diatomite surface.

### 3.3. Adsorption isotherms study

The adsorption isotherms of uranium ions by the natural and the HDTMA-diatomite were described by the Langmuir and the Freundlich adsorption equations (Fig. 5):

$$q = q_{\max} b C_{\text{equal}} / (1 + b C_{\text{equal}}) \quad (5)$$

$$q = K_f C_{\text{equal}}^n \quad (6)$$

where  $b$  is the Langmuir model parameter,  $q_{\max}$  is the adsorption maximum,  $K_f$  and  $n$  are the empirical constants, with all other symbols having been explained already.

As it is shown in Figure 5, amount of uranium adsorbed increased with increase of the metal concentration until the maximum adsorption ( $q_{\max}$ ) was established. The isotherms illustrate that adsorption capacity of the diatomite towards uranium is greatly improved by modification with HDTMA. The maximum adsorption capacity ( $q_{\max}$ ) of the raw diatomite was 25.63  $\mu\text{mol/g}$ , while the corresponding value of 667.40  $\mu\text{mol/g}$  (158.8 mg/g or 15.9 wt.%) was obtained for the HDTMA-diatomite.

According to the results of Aytas et al. [19], the maximum adsorption capacities of the diatomite were 162  $\mu\text{mol/g}$  or 38.6 mg/g. The isotherms of uranium adsorption are significantly better fitted by the Langmuir model in comparison with the Freundlich model (Table 1).

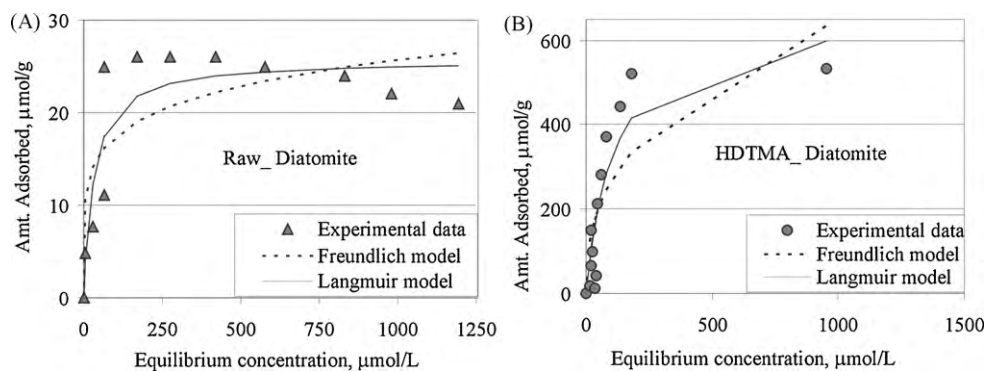
FTIR technique was used to study the interaction between the adsorbate and the active groups on the adsorbent surface. In order to understand the mechanism of uranium adsorption onto diatomite, FTIR of the raw natural diatomite and the natural diatomite with different uranium loading was investigated. Fig. 6(I) shows the infrared spectra of the natural diatomite and the diatomite samples after uranium adsorption. Two bands of small intensity are observed at 2927 and 2857  $\text{cm}^{-1}$ . They can be assigned to  $\text{UO}_2^{2+}$  [6].

According to Vidya et al. [10], the uranyl ions adsorption on mesoporous molecular sieves leads to appearance of bands of small intensity at 902  $\text{cm}^{-1}$  (U=O), 915–833  $\text{cm}^{-1}$  (O=U=O). But we have not observed the same bands in our study for the natural diatomite with the uranium loading. Figure 6 (II) depicts the FTIR spectra of HDTMA-diatomite before and after exchanging with uranyl acetate

**Table 1**

Parameters of the kinetic and isotherm models for the adsorption of the uranium ions.

Model Parameters	Natural Diatomite	HDTMA-Diatomite
First - order kinetic model		
$k_1$	1.1875	0.6800
R	0.6373	0.9556
S	8.2892	10.3645
$k_1$	3.9982 (for 35 min)	1.2931 (for 45 min)
Second - order kinetic model		
$k_2$	0.0483	0.0139
R	0.6686	0.9715
S	7.9987	8.3387
$k_2$	0.3240 (for 45 min)	0.1626 (for 45 min)
Langmuir model		
b	0.0338	0.0092
q max	25.63	667.40
R	0.9069	0.9140
S	4.2210	83.97
Freundlich model		
$K_f$	8.11	45.21
n	0.1672	0.3852
R	0.8258	0.82023
S	5.65	118.43



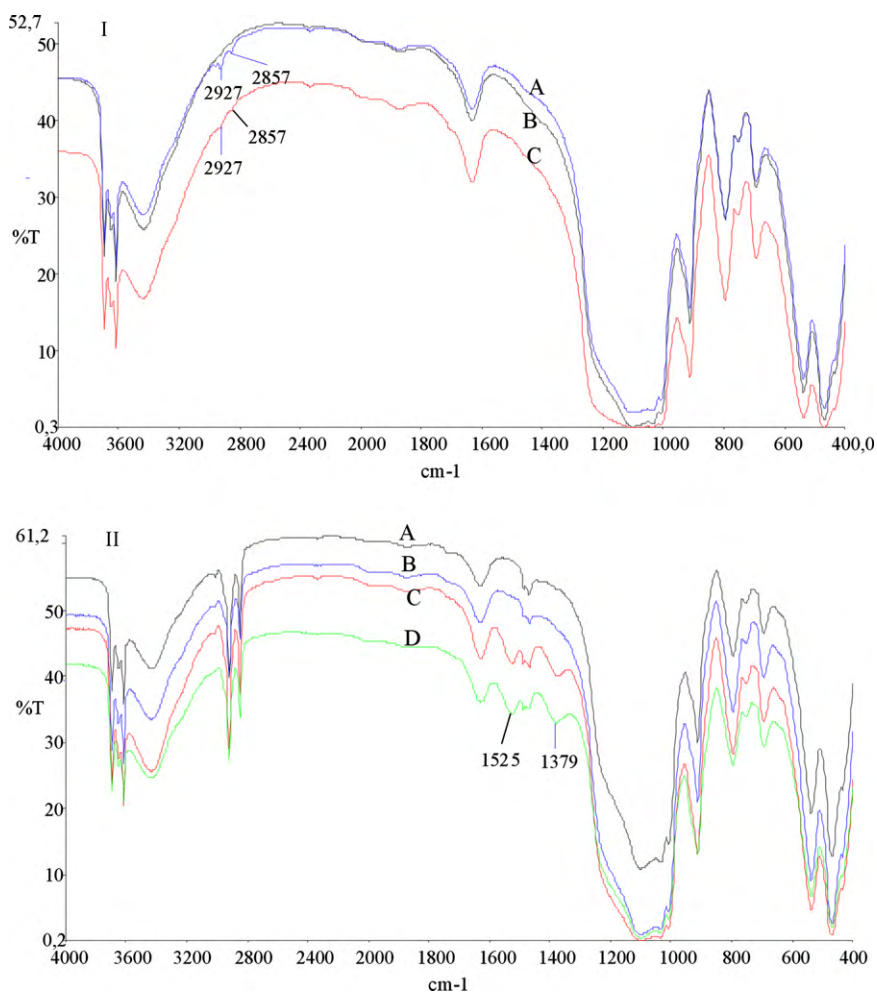
**Figure 5.** The isotherms of uranium adsorption on the natural (A) and the HDTMA-diatomite (B).

solution. The IR bands appearing at  $1525$  and at  $1379\text{ cm}^{-1}$  in the spectra correspond to U connecting with organic compounds.

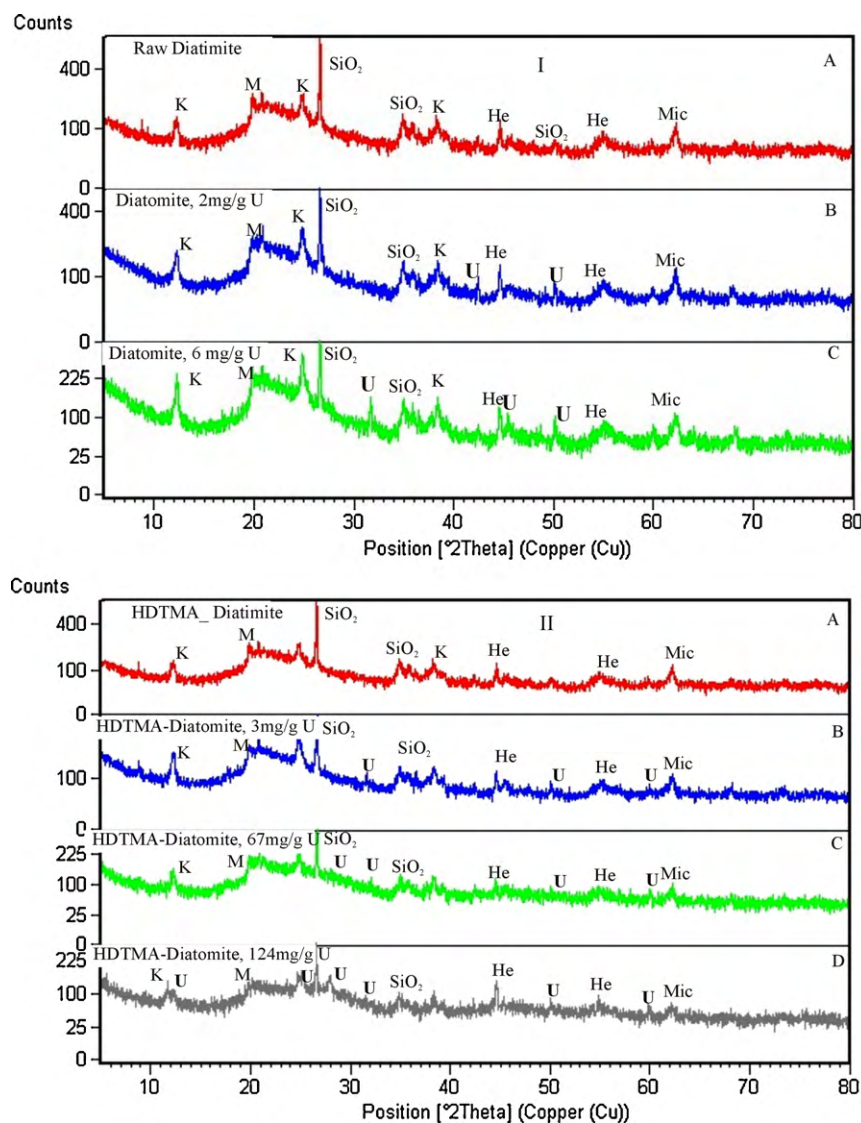
The X-ray diffraction pattern of the diatomite particles with the adsorbed uranium is shown in Figure 7 (I) and Figure 7 (II). As one can see at the X-ray diffractogram (Figure 7 (I)), some new peaks of uranium compounds appeared on the natural diatomite after uranium adsorption. There are peaks in spectrum at  $31.6^\circ$ ,  $42.5^\circ$ ,  $45.5^\circ$  and  $50^\circ$   $2\theta$  values (Figure 5 (I)) that have some resemblance to the peaks identified in the uranium oxides compounds with hypostoichiometric structure such as  $\text{UO}_{2.95}$ ,  $\text{UO}_{2.87}$ ,  $\text{UO}_3$  (peak  $31.6^\circ$   $2\theta$ ) and  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$  (peaks  $42.5^\circ$ – $45.5^\circ$  and  $50^\circ$

$2\theta$ ). The narrow, well-defined and high-intensity peak  $31.6^\circ$   $2\theta$  may indicate the crystalline phase of the uranium oxides.

Different new peaks were evident in XRD patterns of the HDTMA-diatomite after uranium adsorption (Figure 7 (II)). The peaks at  $11.5^\circ$ ,  $25^\circ$ ,  $28^\circ$ ,  $32^\circ$ ,  $50^\circ$  and  $60^\circ$   $2\theta$  values appeared in the sample after uranium loading. It can be determined to consist of two uranium compounds on the modified diatomite surface. It is interesting that the similar peaks were observed by Elzinga et al. [5] as a result of investigation of U (VI) adsorption on the calcite surface. The above authors suggest that the pointed peaks cannot be associated with any unique phase, but can be connected



**Figure 6.** FTIR spectrum of uranium adsorption by the natural diatomite (I) with: a)  $0\text{ mg/g U}$ , b)  $2\text{ mg/g U}$ , c)  $6\text{ mg/g U}$  and FTIR-spectrum of uranium adsorption by the HDTMA-diatomite (II) with: a)  $0\text{ mg/g U}$ , b)  $3\text{ mg/g U}$ , c)  $67\text{ mg/g U}$ , d)  $124\text{ mg/g U}$ .



**Figure 7.** Powder X-ray diffraction patterns of the uranium adsorbed on the natural diatomite (I): a) the natural diatomite before adsorption, b) with adsorbed 2 mg/g U, c) with adsorbed 6 mg/g U and patterns of the uranium adsorbed on the HDTMA-diatomite (II): a) the HDTMA-diatomite before adsorption, b) with adsorbed 3 mg/g U, c) with adsorbed 67 mg/g U, d) with adsorbed 124 mg/g U.

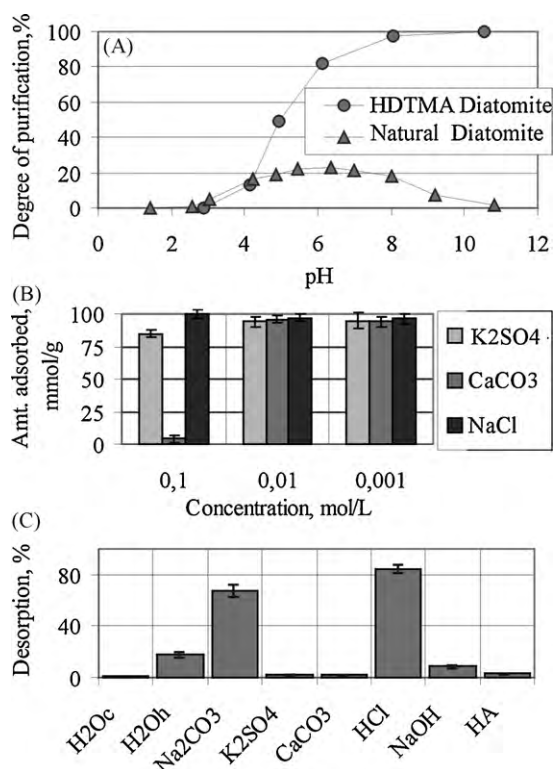
with a wide variety of uranyl hydroxide phases as well as with several synthetic calcium uranyl carbonate hydrates. But in our study the obtained peaks may present multiple phases of uranium and surfactant on the HDTMA-diatomite surface.

### 3.4. Effects of pH

Adsorption values of U(VI) on the natural and the HDTMA-diatomite as a function of pH in 0.01 M NaCl solutions are shown in Figure 8A. The adsorption of U(VI) on the natural diatomite depends on pH; there is the distinct maximum in the adsorption isotherm at pH 5.5–6.5 and the adsorption drastically decreases passing to the acidic and alkaline regions. Such a shape of the pH dependence is caused by both the structural features of the diatomite and the complex aqueous chemistry of U(VI).

At low pH (below pH 4), when the dissociation of Si-OH bonds is suppressed, the adsorption of U(VI) is low. On the other hand, while in acidic solutions the uranyl ion  $\text{UO}_2^{2+}$  is practically the only complex-forming uranium species, with increasing pH uranium species bearing lower positive charge, neutral, or even negatively charged species (hydrolysis products) such

as  $\text{UO}_2\text{OH}^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ,  $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $\text{UO}_2(\text{OH})^2$ ,  $\text{UO}_2\text{CO}_3$ ,  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ , etc are formed [1,32]. However the relative concentration of these species depends on the pH and the concentration of uranyl solution, the higher pH favouring the bulky or high nuclearity species, i.e.,  $(\text{UO}_2)_3(\text{OH})_5^+$  [32]. Thereby the hydrolysis of uranyl ions begins at a solution pH of 3.0 and between pH 3.0 and 4.0 the uranyl ion  $\text{UO}_2^{2+}$  its hydrolysis species  $\text{UO}_2\cdot\text{OH}^+$  and  $(\text{UO}_2)_2(\text{OH})_2^{2+}$  exist in different amounts. The formation of trinuclear uranyl species,  $(\text{UO}_2)_3(\text{OH})_5^+$  begins at pH 4.0, and becomes dominant at pH >4.5 [1]. Since the uranium concentration in the investigated systems is sufficiently high, formation of neutral and negatively charged species is most likely; with pH increase polynuclear colloidal compounds may be also formed. Such uranium speciations are responsible for the observed negligible adsorption of U(VI) from neutral and weakly basic solutions. As it is presented the uranium adsorption increased with pH of the uranyl solution and reached the maximum at around pH 5.5–6.5. This pH range corresponds to the formation of  $(\text{UO}_2)_3(\text{OH})_5^+$ , and thus the maximum loading of uranium can be attributed to the formation of trinuclear,  $(\text{UO}_2)_3(\text{OH})_5^+$  species [10]. The highest uranium adsorption yield was achieved around 24%. The strong adsorption of U(VI) on



**Figure 8.** Effects of pH and inorganic anions on the uranium adsorption onto the diatomite and elution reagents on the uranium desorption from the HDTMA-diatomite.

the diatomite may be attributed to surface complexation or strong chemical adsorption.

The modification of the diatomite strongly affects the shape of the pH dependence of the U(VI) adsorption (Figure 8A). At low pH the adsorption isotherms in the both systems are similar. With pH increase adsorption starts to increase quickly and has arrived at high degree of the solution purification (100%) at pH value 8. Thus, in the alkaline area of pH there is the maximal degree of water purification from uranium by the synthesized adsorbent. Hexadecyltrimethylammonium bromide as a cationic surfactant on the surface of the diatomite strongly connected uranium in complexes with the organic constituents of the adsorbent surface.

### 3.5. Effect of inorganic anions.

Figure 8B shows the value of U(VI) adsorption on the HDTMA-diatomite as a function of ionic strength. It is clear that U(VI) adsorption is independent on NaCl, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> concentrations. Although the value of adsorption is a little higher at low ionic strength than at high ionic strength, it may be considered as very weak influence of ionic strength as the experimental uncertainty [18].

However, the values of U(VI) adsorption on the diatomite is the highest in NaCl solutions and the lowest in K<sub>2</sub>SO<sub>4</sub> solutions. This phenomenon may be attributed to the facts that Cl<sup>-</sup> can form positively charged soluble complexes with U(VI) ion [2], whereas the SO<sub>4</sub><sup>2-</sup> form negatively charged complexes with U(VI) in solution. Idiocratic adsorption of Cl<sup>-</sup> is easier on the solid phase than SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup> adsorption on diatomite surface of changes the surface properties of the diatomite and decreases the availability of binding sites. Carbonate-ions at the low concentration show similar behavior as Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions, but at the high concentration (0.1 M) uranium bonds with carbonate-ions to form uranyl carbonate complexes.

### 3.6. Efficiency of uranium desorption

Some desorptive reagents (solution of HCl, NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, CaCO<sub>3</sub>, humic acid, cool and hot water) were treated with loaded adsorbent to recover uranium. As it is shown in Figure 8C, no significant uranium desorption with K<sub>2</sub>SO<sub>4</sub>, CaCO<sub>3</sub>, humic acid, cool water for the HDTMA-diatomite with uranium consist 124 mg/g was observed. The desorption yields were higher with other desorptive reagents.

After leaching by desorption reagents the uranium concentrations in the HDTMA-diatomite were changed. The highest values of uranium desorption were observed for HCl and Na<sub>2</sub>CO<sub>3</sub>: 86% and 69% respectively, 18% for hot water, 9% for NaOH. These phenomena may be explained by the fact that HCl is the strong acid and it destroys organic compounds and their bonds with uranium compounds.

## 4. Conclusions

Adsorption of uranium (VI) on the natural and the HDTMA-diatomite varies with initial uranium concentration, sorbent-solution contact time and pH values of solution. Three distinct kinetic stages of the uranium adsorption are observed: active adsorption, inversion and stabilization stage. Over 90% of the total uranium adsorption occurs within the first 30 min. The isotherms of uranium adsorption are significantly better fitted by the Langmuir model in comparison with the Freundlich model. The maximum adsorption capacity of the diatomite was 25.63 μmol/g, while the corresponding value of 667.40 μmol/g (158.8 mg/g or 15.9 wt. %) was obtained for the HDTMA-diatomite. After leaching by desorption reagents the uranium concentration in the HDTMA-diatomite changed. The highest values of the uranium desorption were observed using the HCl and Na<sub>2</sub>CO<sub>3</sub> solutions as desorption reagents with efficiency of 69 and 86% respectively. The results presented in this paper clearly reveal that the HDTMA-diatomite may be used as an efficient adsorbent for uranium ions removal from aqueous solutions.

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