Behaviour of modified hexadecyltrimethylammonium bromide bentonite toward uranium species

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A B S T R A C T

Algerian bentonite from Maghnia, has been modified with cationic alkylammonium surfactant (HDTMA-Br) from 30 to 150% of the CEC. A positively charged bilayer of the surfactant cations of HDTMA is created within the structure of the clay. The organic modification changes the bentonite material behavior towards cationic and anionic pollutant species. The unmodified and modified bentonites were characterized with several techniques: X-ray diffraction XRD, infrared spectroscopy measurements FTIR and thermal analysis TG/DTG. The intercalation of the alkylammonium cations in the interlayer space of the bentonite was confirmed by the increasing of the basal spacing from 1.26 to 1.91 nm. Batch adsorption experiments were performed to evaluate the uranium removal efficiency from aqueous solutions on unmodified and modified bentonites in the range pH solution from 3 to 10 for uranium concentration of 10 mg/L. The presence of HDTMA in the interlayer space of the bentonite greatly increased the retention capacity from 8.15 for the base material at pH 3 where UO_2^{2+} is exclusively present to 17.39 mg/L at pH 10 for bentonite exchanged with 120% of the CEC. The modification of the bentonite at 120% by HDTMA enhanced affinity towards anionic species of uranium ($UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$) present at pH 10. Equilibrium sorption experiments of unmodified bentonite and modified bentonite loaded with HDTMA less or equal 1 CEC best fitted to Langmuir isotherm and the kinetic data were found to follow the pseudo second order model.

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1. Introduction

Uranium is a naturally occurring element with an average abundance in the Earth's crust of about 2 mg/kg. Various anthropogenic activities involving the processing or use of materials rich in uranium may modify the natural abundance of uranium in the environment. This abnormal abundance, called pollution, causes devastating health risks for living species. To reduce the impact of pollution in general, that of uranium in particular, several separation methods are used: precipitation, adsorption processes, solvent extraction, membrane dialysis, chromatographic extraction, ion exchange and floatation. Nowadays, the attention is focused on the use of adsorbents based on abundant natural materials like zeolites and clays [1–3].

The clay minerals are the most materials considered because of their properties deemed adsorption and retention of cationic pollutants [2,4] and the possibility of their modification and/or functionalization [5–10] to enhance their anionic adsorption capacity [11,12].

Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature, which makes natural clays ineffective sorbents for organic and anionic compounds [13,14]. Intercalation of organic surfactant between layers of clays changes the surface properties from hydrophilic to hydrophobic. Organic surfactant retention occurs within the interlayer space of clay minerals with a consequent increase of the basal spacing which provides an optimal hydrophobic environment for the retention of anionic pollutants [15]. Organo-clay is considered as an hybrid material [16], it is capable of sorbing organic contaminants [17–20], anions such, TcO_4^-, Cs^+; I^-, Cr^- [21–23] present in the nuclear waste together with cations [24,25]. Bors and al. [21] confirmed the increasing adsorption of I^- and TcO_4^- while Cs^+ and Sr^{2+} showed decreasing adsorption with increasing alkylammonium ion ($HDPy^+$) incorporation into MX80 Bentonite. Chao and Chen [26] confirmed the dual electronic characteristics of HDTMA-zeolite. They concluded that modified

zeolite is an exellent sorbent for both cationic and anionic contaminants in wastwater. Marek and al. [15] concluded that organobentonite reveals sufficient sorption ability towards U(VI) both from the acidic and alkaline solutions.

In this work we focused on:

(i) the modification of the bentonite by intercalating a cationic surfactant (HDTMA-Br). The physicochemical characterization of all materials was done by X-ray diffraction (XRD), IR spectroscopy, thermogravimetric analysis (TGA).
(ii) the sorption of uranium in its cationic and anionic forms using uranium speciation diagram [27] on unmodified and modified bentonite was evaluated.

2. Materials and methods

The starting material used in these experiments was natural bentonite (Bt) provided by ENOF (Entreprise Nationale des Substances Utiles et Matériaux non Ferreux). The bentonite has been washed and freed of pebbles, then dried and crushed to 2 μm. The chemical composition of this clay is shown in Table 1. The presence of Mg in high quantities suggests the presence of dolomite. Its specific surface area is about 54 m²/g and cationic exchange capacity CEC is equal to 100 meq g/100 g.

The surfactant used in this study is hexadecyltrimethylammonium bromide, (HDTMA-Br) ($C_{19}H_{42}NBr$, 96% purity and from Sigma–Aldrich).

Stock Solution of 1000 mg/L of uranium was prepared from synthetic uranyl nitrate (Merck) and suitably diluted to required initial concentrations of uranium (10 mg/L), pH was adjusted by adding either HNO_3 or KOH.

Organo-bentonites were prepared through equilibration of 1 g bentonite with the aqueous solutions of HDTMA-Br for 4 h at 60 °C using a mechanical shaker. The initial amounts of HDTMA-Br in the aqueous phase were equivalent to various percentages of the CEC (30, 75, 100, 120, and 150 meq g/100 g bentonite). After filtration and washing several times with hot deonised water until bromide anions free as indicated by the $AgNO_3$ test. The solid residues were dried at 60 °C. The organo-clays obtained in this way were labeled as Bt0.3, Bt0.75, Bt1, Bt1.2, and Bt1.5 according to the percentage of CEC.

2.1. Characterization of samples

Natural Bt and HDTMA-Bt samples were characterized with several techniques XRD, TG/DTG, FTIR. Phase identification and the change of interlayer distance were measured by wide-angle X-ray diffraction (XRD) using Stoe STADI-P diffractometer with Cu- Kα radiation. The 2θ value was scanned in a range of 2−70°.

Infrared spectroscopy measurements of framework vibrations were conducted using NICOLET 380 apparatus. The KBr pellet technique was used during preparation of the samples.

Thermal decomposition spectra of the samples were recorded with a thermo-analyzer SETARAM-LABSYS using the TG/DTG technique in air atmosphere heating rate, 15°/min from room temperature to 900 °C.

Table 1
Chemical composition of used bentonite clay Bt.

	SiO₂	Al₂O₃	Fe₂O₃	SO₃	MgO	CaO	Na₂O	K₂O	TiO₂	P₂O₅
(%)	65.09	17.10	2.68	0.12	2.82	0.52	2.56	2.53	0.36	0.06

Loss of ignition = 6.06%.

2.2. Adsorption experiments

The experiments are performed in batch in a series of bottles of 200 mL, where a mass of Bt or HDTMA-Bt is in contact with the uranyl nitrate solution. The mixture is stirred on a shaker at 350 rpm. Both solid and liquid phases are separated by centrifugation. The supernatant was analyzed by (UV/Visible) by Arsenazo-III method [28] using atomic absorption spectrometry (Agilon 8543) at a maximum wavelength of (663 nm) to determine the amount of uranium remaining in the solution.

The uranium adsorption percentage R is determined from the difference between the initial and final uranium concentrations using the following equation:

$$R = 100 \times \frac{(C_0 - C_f)}{C_0} \tag{1}$$

where C_0 and C_f are the initial and final uranium concentrations (mg L^{-1}).

2.2.1. Effect of solution pH

The effect of uranium pH removal on Bt and HDTMA-Bt was studied by varying the pH of the solution from 3 to 10 with initial uranium concentration of 10 mg L^{-1} at room temperature and adsorbent dose 3 g/L.

2.2.2. Adsorption isotherms and kinetic studies

The adsorption isotherms and kinetic studies has been done in a batch mode at room temperature and uranium concentration of 10 mg/L at optimum pHs of each material. For kinetic studies the aqueous samples were taken at several time intervals and the uranium concentration measured. The amount of adsorption q_t (mg/g) at time t was calculated by:

$$q_t = (C_0 - C_t)^V/_m \tag{2}$$

Where C_0 (mgL^{-1}) is the initial concentration of the uranium solution, C_t (mg/L) is the concentration at time t, V (L) the volume of the solution and m (g) the mass of Bt or HDTMA −Bt.

For isotherm studies, 0.03 g of Bt or HDTMA-Bt was equilibrated with 10 mL uranium solution having concentrations of 4, 6, 8 and 10 mg/L. The mixtures were shaken at the agitation rate of 350 rpm at room temperature for 3 h, time shown to be sufficient to reach adsorption equilibrium. The mixture was then filtered by centrifugation for 30 min and the filtrate was analyzed. Langmuir isotherm model is used to determine the maximum adsorption capacity. The applicability of the models is judged by correlation coefficient R².

3. Results and discussion

3.1. Characterization of Bt and HDTMA-Bt samples

3.1.1. X-ray diffraction

In Fig. 1, The XRD patterns of the Bt sample shows the peaks of montmorillonite (2θ = 6.99, d$_{(001)}$ = 12.63 Å); (2θ = 19.8° d = 4.48); (2θ = 27.75° d = 3.21) and illite (2θ=19.80°, d = 2.56 Å): (2θ=20.90°, d = 4.25 Å) as secondary phase. The other peaks are the impurities corresponded to quarts and dolomite (MgCa(CO₃)₂). From the results, the crystallographic parameters suggest an interlamellar distance d$_{001}$ of 12.63 Å.

Fig. 2 shows the XRD patterns of the Bt and HDTMA-Bt (Bt0.3; Bt0.75; Bt1; Bt1.2 and Bt1.5). A displacement of the angle 2θ from 6.99° to 4.5° with an obvious increase in the d$_{001}$ value from 12.63 Å for the base material Bt to 19.13 Å for the organophilic-clay Bt1.5, confirming the intercalation of the alkylammonium ions in the interlayer space and by the same the expansion of the layers of