Article

Uranium Sorption on "Tezontle" Volcanic Rock

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Abstract. It is described a study that demonstrates that hexavalent uranium ions were sorbed by the naturally occurring mineral using a batch technique. This mineral is found in abundant quantities in Mexico. Our study focused on the separation of UVI from synthetic aqueous systems of both H_2O-$UO_2(NO_3)_2$.$6H_2O$ (acid) and H_2O-$Na_4[UO_2(CO_3)_3]$ (basic). The chemical speciation was performed by using high voltage electrophoresis, and the uranium content was determined by UV-Vis Spectroscopy. The quantified U(VI) sorption by tezontle from acidic and basic systems was 2.72 and 1.68 µmol/g, respectively, and the sorption behavior is discussed considering the surface charge of the tezontle at different pH values based on the point of zero charge characteristic of this material.
Key words: Uranium, Sorption, Tezontle, Electrophoresis.

Resumen. En este trabajo se demostró que los iones de uranio hexavalente son adsorbidos por el tezontle (roca de origen volcánico proveniente de México), utilizando un procedimiento por lotes. Este estudio se enfoca en la separación de uranio(VI) a partir de sistemas acuosos sintéticos de la forma ácida H_2O-$UO_2(NO_3)_2$.$6H_2O$ así como básica H_2O-$Na_4[UO_2(CO_3)_3]$. La especiación química se realizó utilizando la técnica de electroforesis de alto voltaje. El contenido de uranio se determinó por espectroscopia de UV-Vis. La adsorción del U(VI) por el tezontle a partir de sistemas ácidos y básicos fueron de 2.72 y 1.68 µmol/g, respectivamente. El comportamiento de la adsorción del U(VI) por el tezontle, se discutió considerando la carga superficial del tezontle a diferentes valores de pH con base en el punto de carga cero carcterístico del material.
Palabras clave: Uranio, adsorción, tezontle, electroforesis.

Introduction

Considerable groundwater remediation research has been focused on the removal of contaminated water from the sub-surface, but, while removal of pollutants is desirable from an environmental standpoint, the costs are often prohibitive, and contaminant concentrations are rarely lowered to the required levels. Several processes have been proposed and implemented for the removal of actinides from aqueous media [1-5]. These include precipitation and ion exchange as well as sorption on organic resins, natural zeolites, and clays.

The study of the interaction that occurs between radionuclides in solution and rocks and minerals is an integral part of the environmental safety assessment of the deep geological disposal of radioactive waste [6, 7]. Sorption due to the inter-action of dissolved radionuclides with geological media is among the most important factors in the retardation of radio-nuclide transport. Since uranium is an important constituent of nuclear waste, the prediction of its sorption behavior is of great interest [8].

Differences in mineralogy are important in determining the relative sorption of actinides from solution. A number of reported experimental studies have examined the sorption characterization on granite, sediments, minerals, activated car-bon and cationic resins, exposed to a variety of actinide solu-tions [6, 7, 9, 10-12]

Um et al. [13], reported that the sorption of U(VI) on Hanford fine sand (HFS) with varying Fe-oxide contents showed that U(VI) sorption increase with the incremental addi-tion of synthetic ferrihydrite into HFS. Sorption of uranyl ion, UO_2^{2+}, on $SiO_2.xH_2O$ (silica gel) has been also investigated by

Pathak [14], and reported that the sorption of UO_2^{2+} on silica gel occurs via cation exchange mechanism in the pH range of 2-6. The sorption capacity of the silica gel for UO_2^{2+} was ~ 10^{-7}-10^{-6} mol/g applying the Langmuir and D-R isotherms. In the case of aluminosilicates, Matijasevic [15] investigated and reported the adsorption of uranium (VI) on heulantide/clinopti-lolite rich zeolitic tuff modified with different amounts of hexa-decyltrimethyl ammonium ion (HDTMA). The results showed that uranium (VI) adsorption on unmodified zeolitic tuff was low (0.34 mg U(VI)/g adsorbent), while for the organozeolites, the adsorption increased with increasing amount of HDTMA at the zeolitic surface. The adsorption of uranium (VI) ions onto organozelite at different pH values (3, 6 and 8) showed that the uranium speciation is highly dependent on pH.

To the best of our knowledge, no reports have addressed the sorption properties of the tezontle (volcanic rock) from Mexico as a novel natural adsorbent material to remove U(VI) from aqueous media considering both acid and basic systems. Therefore, the aim of this work was to evaluate the separation of U(VI) from aqueous media at two different pH values 3 and 9 by tezontle considering the uranium chemical speciation in these conditions and the point of zero charge (pzc) characteris-tics of the natural material.

Results and Discussion

Uranium Speciation

A variety of classical and spectroscopic techniques have been used to study aqueous solutions of uranium salts [16-18], and

the direct room temperature electrophoresis technique has been shown to be highly valuable for determining the extent of ionic complex formation [19, 20]. Figure 1 shows the electrophoregram from the basic aqueous uranium system used in the present work. In this figure, the most significant feature is the appearance of two anionic uranium complexes. Extensive research has focused on the uranyl carbonate complexes from solutions. According to Scanlan [18], the tricarbonate and dicarbonate complexes are in equilibrium, and co-exist in approximately equal concentrations. As such, it is reasonable to posit that the H_2O-$Na_4[(UO_2(CO_3)_3]$ system is an equilibrium mixture of tricarbonate $UO_2(CO_3)_3^{4-}$ and dicarbonate $UO_2(CO_3)_2^{2-}$ complexes.

Figure 2 shows the migration of various chemical species of uranium from the acidic system, H_2O-$UO_2(NO_3)_2.6H_2O$. In this figure, a mixture of three cationic species (or three

hydrolysis products) of UO_2^{2+} were observed. In acidic solutions, the uranium +6 oxidation state exists as uranyl ions, UO_2^{2+}, having a linear O-U-O configuration. Mononuclear species of UO_2^{2+} have a strong tendency for dimerization of the $UO_2(OH)^+$ species at 298 K, and the stability of the monomer $(UO_2(OH)^{+)}$ relative to the dimmer $((UO_2)_2(OH_2)^{2+})$ increases at 367 K. The latter species is the principal hydrolysis product of uranium. At high concentration, $(UO_2)_3(OH)_5^+$ and $(UO_2)_3(OH)_4^{2+}$ are the only significant additional species observed in solution. [19] These considerations led us to propose that the H_2O-$UO_2(NO_3)_2.6H_2O$ system is a mixture of $(UO_2)_2(OH_2)^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_4^{2+}$, in which the dominant component is the dimmer. This is in agreement with data reported by Ticknor [9], Cinnéide *et al.* [17], Scanlan [18], and Baes [21].

Sorption Isotherms

Figure 3 shows the uranium sorption from the acidic and basic systems at 298 K on tezontle. Both sorption isotherms were also obtained without a buffer to pH control. In general, the separation of uranium on tezontle from aqueous solutions was higher from the acidic system than the basic system. As evident from this figure, two plateaus were observed in both cases, each likely representing the formation of a complete monolayer [22].

The observed isotherms are of type L2 of the Giles classification and are fitted by the Langmuir equation, which relates the equilibrium solid phase concentration, q_e, with the liquid phase concentration, C_e. The Langmuir equation is expressed as [23]:
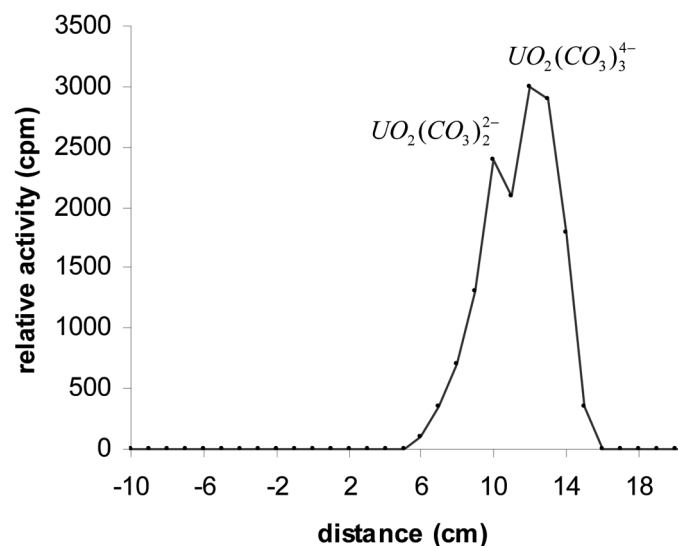
$$qe = \frac{Q_m bCe}{1 + bCe}$$

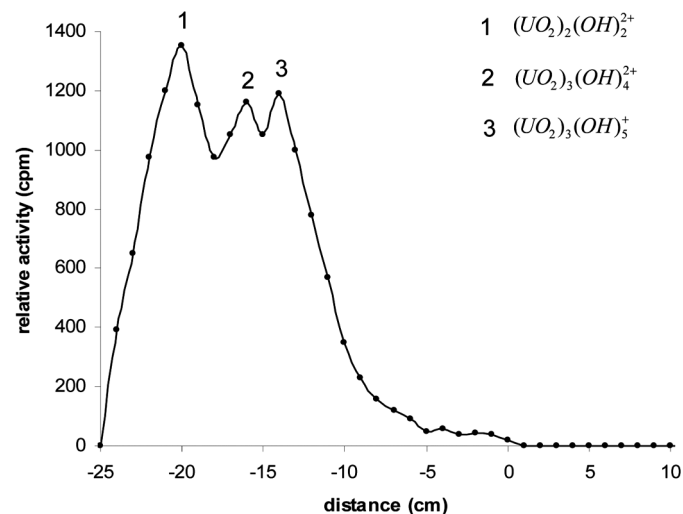**Fig. 1.** Electrophoregram of the U(VI) CO system.
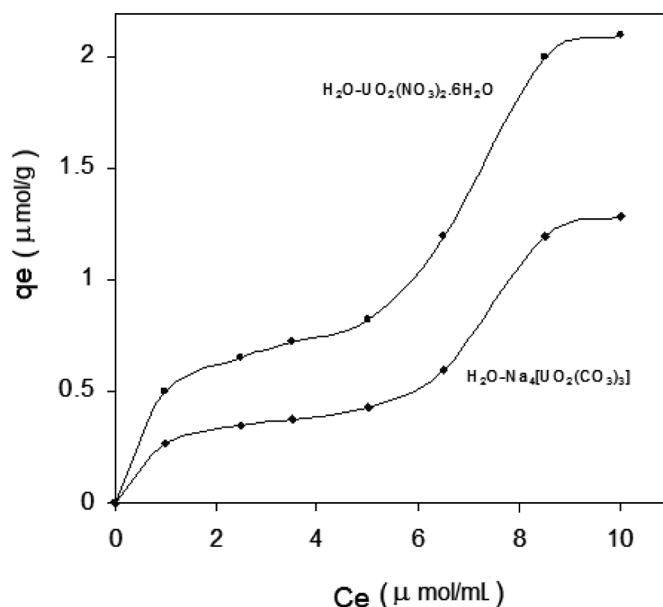

Fig. 2. Electrophoregram of the U(VI) NO system.

Fig. 3. Sorption isotherms of $UO_2(NO_3)_2.6H_2O$ and $Na_4[UO_2(CO_3)_3]$ on T.

Where the lineal equation is:

$$\frac{Ce}{qe} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)Ce$$

from which the sorption capacity, Q_0 (μmol/g), and the constant associated with the energy of adsorption, b (mL/μmol), were calculated (Table 1). These parameters, together the relative affinity of the adsorbate toward the surface of the adsorbent [24], allow it to compile the values of Q_0b (μL/g) for T-NO and T-CO systems (Table 1); the Q_0 value for the nitrate system was 1.6-fold higher than for the carbonate system. Adsorption experimental isotherms are shown in figure 3. Interestingly, the uranium affinity by the tezontle surface represented by Q_0b is higher for the U(VI) cationic T-NO system than for the U(VI) anionic T-CO system.

It was observed (Table 1) that Q_o is 1.6 times higher in T-NO system than in T-CO system. According with the U(VI) adsorption isotherms (figure 3) it is clear that uranium as a cationic specie was preferentiality adsorbed on tezontle than the anionic specie. The higher affinity of the U(VI) cationic species toward tezontle surface is according with the obtained Q_ob value.

Point of zero charge of the tezontle surface

Many natural minerals exhibit ion exchange properties that arise from the existence of a pH-dependent surface charge and that are cationic exchangers in a basic environment when the surface charge is negative. In an acid environment, however, the surface charge is positive, and these species are anion exchangers [25-28]. For these reason the knowledge of the pzc is important. This parameter is defined as the pH value at which the net proton charge of the surface is equals to zero, and it is an important aspect characterizing the adsorption properties of the solids [29-31].

The pzc of natural tezontle is nearly pH 10.8 (figure 4). This value indicates that the overall surface charge is negative. The negative surface charge may be compensated for by $(UO)_2(OH_2)^{2+}$, $(UO^2)_3(OH)_5^+$, and $(UO_2)_3(OH)_4^{2+}$, which are all positive species. It was determined, however, that both cationic ($(UO)_2(OH_2)^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_4^{2+}$) and anionic ($(UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-})$ uranium species were adsorbed on T (figures 1 and 2). Most oxides are amphoteric [32], therefore these results suggest that the charge could be developed on tezontle surface through amphoteric dissociation.

Table 1. Langmuir isotherm parameters from uranium systems.

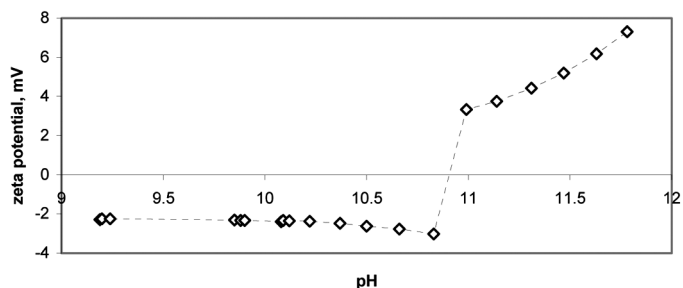| System	Q_0 (μmol/g)	B (mL/μmol)	Q_0b (mL/g)
T-NO	2.72	0.29	0.48
T-CO	1.68	0.03	0.08

Fig. 4. PZC from tezontle.

Experimental

Material

Tezontle samples from Teotenango, State of Mexico (figure 5) were powdered to a 12 mesh particle size and used for all sorption experiments. Next, the samples were washed several times with hot distilled water and dried at 373 K for 24 hours. This tezontle material is referred to as T. The previously reported elemental composition of the tezontle is O, Si, Al, Ca, C, Fe, Mg, and Na, and the principal mineral components are anorthite, cristobalite, diopside, forsterite, quartz, and hematite [33].

Preparation of Uranyl Solutions

Mononuclear uranyl tricarbonate complexes were prepared from a 0.05 M solution of uranyl nitrate hexahydrate and a 0.15 M solution of anhydrous sodium carbonate [19, 34], which were mixed at room temperature. The final aqueous solution had a pH of 8.7, and this basic uranyl solution was termed CO. The corresponding uranyl acid solution, which was termed NO, was prepared from a 0.05 M solution of uranyl nitrate hexahydrate at pH 3.
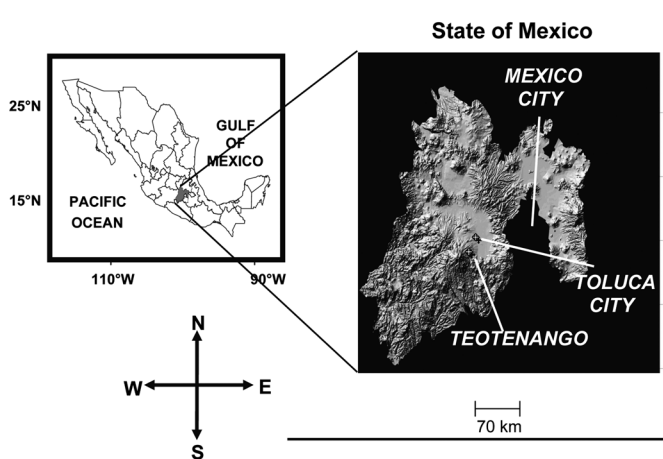

Fig. 5. Location of the sampling site in Teotenango, Mexico.

Uranium Speciation by High Voltage Electrophoresis Method.

The separation of uranium species (anionic, cationic, or neutral) from the NO and CO systems was carried out by high voltage electrophoresis [19, 20], employing 0.1 M solutions of ammonium carbonate and nitric acid electrolytic solutions. A potential of 2500 V was applied for 30 and 20 min for these two solutions, respectively. For experimental measurements, 20 µL of each solution system were deposited on 1×60 cm Whatman No. 2 paper strips. The samples were irradiated for 2 minutes with thermal neutrons in a TRIGA Mark III nuclear reactor at the Centro Nuclear de México, with a 1.19×10^{13} n cm^{-2}s^{-1} neutron flux. The migration of the uranium species in each paper strip was determined by γ-spectrometry with a Ge(Hi) detector coupled to a Canberra 4096 channel analyzer. The ^{238}U activities were measured by integrating the area under the 0.277 MeV γ peak of its daughter ^{239}Np according to the subsequent nuclear reaction:

$$^{238}U(n,\gamma)^{239}U \xrightarrow{\beta-} {}^{239}Np.$$
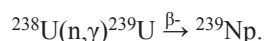
Sorption Isotherms

0.05 M stock solutions of $(UO_2(NO_3)_2.6H_2O$ and $Na_4[UO_2(CO_3)_3])$ were prepared as described and subsequently diluted to varying concentrations from 1 to 10 µmol/mL. One gram of T was placed in contact with a 20 mL solution of UVI (acidic and basic) in a 25 mL glass tube, and the resulting suspensions were agitated and equilibrated for 24 hours at room temperature. The phases were separated by centrifugation, the solutions were filtered through a 0.22 µm pore membrane, and the uranium content of the filtrate was measured. The samples obtained from the CO system were transformed to uranyl nitrate. The uranium was also analyzed spectrophotometrically using a Shimadzu UV/VIS at λ_{max}= 413.7 nm. All experiments were run in triplicate.

Our preliminary experiments indicated that 24 h was sufficient to reach the sorption equilibrium [17].

Point of zero charge of the tezontle surface

Automatic Titration for the determination of the point of zero charge of T was conducted using a Dispersion Technology DT 12000 equipment. Accordingly, samples of T (12 mesh) were washed, dried, and finally powdered The potentiometric titration of the 5 g of a T suspension was carried out by adding small amounts (from 0.5 to 0.3 mL) of acid (1 N HCl) or base (1 N KOH) to the suspension.

Acknowledgements

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