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Effect of short chain aliphatic carboxylic acids for sorption of uranyl on rutile Zeta potential and *in situ* ATR-FTIR studies

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ABSTRACT

Migration of radionuclides in aqueous system is a matter of great environmental concern due to their acute and long-term toxicity. This study seeks to address the sorption of uranyl on rutile in presence of short-chain aliphatic carboxylic acids by zeta potential analysis and *in situ* ATR-IR spectroscopy. Point of zero charge of rutile was significantly shifted with the addition of carboxylic acids/uranyl ions separately in solution but it was negligible when organics and uranyl ions were added in the suspension. *In situ* ATR-IR data for uranyl sorption was evidenced by an absorption band of uranyl *as*(UO_2) at 915 cm^{-1}.

1. Introduction

The short-chain carboxylic acids significantly release in the environment through the decay of plant matter, animal residue and microbial tissues. They can alter the rate of sorption of the pollutants and metal ions as they may affect the surface property of the mineral [1]. Adsorption behaviour of carboxylic acids on mineral oxide surfaces in contact with aqueous media could be significant in various aspects such as; surface reactions in environment, application of mineral particles for pollutant degradation, etc. Sorption of carboxylic acids eventually influences the competitive adsorption of other water constituents and pollutants (such as transition metals or radiotoxic elements), dissolution of mineral oxides and the transport of colloids [2]. The migration of radionuclides/metal ions present in the aqueous media may also be affected by the presence of different minerals [3–5].

Point of zero charge (pHzpc)usually obtained by zeta potential measurements, is an important property of colloidal particles. The determination of zeta potential by electro-kinetic methods and shift in the pHpzc of mineral surfaces with different ions is a common way to determine the interactions of a wide variety of charged particles (colloids to nanoparticles), particularly with the cations/anions that can be sorbed on surfaces. Titanium oxide has been widely regarded as a model mineral in sorption due to its lower solubility and surface charge property [6,7]. Different types of electrolytes and organic additives also influence the zeta potential of TiO_2 and PLZST ($Pb_{0.97}La_{0.02}Zr_{0.66}Sn_{0.25}Ti_{0.09}$), respectively [8–17]. Scales et al. and O'Brien et al. investigated the influences of electrolyte concentration, solids fraction, particle size, polydispersity, density difference between the particles and the fluid on zeta potential calculated from the electroacoustic signal [18–20].

Among various spectroscopic methods, Attenuated Total Reflection Infra-Red (ATR-IR) spectroscopy has been successfully applied for analysis of ions and organic molecules [21]. Moreover, this technique was significantly used for the structure determination of organic molecules sorbed on surfaces [22–24]. Number of *in-situ* ATR-IR spectroscopic studies of metal oxide–aqueous interfacial systems were carried out to probe molecular interaction of different adsorbates with the thin films of metal oxides [25–30]. A few also substantially reported ATR-IR spectroscopy of uranyl [31,32] and carboxylic acid [33,34] as binary systems; rutile–uranyl and rutile–carboxylic acids. Hitherto, to the best of our knowledge, the determination of pHpzc of rutile in the presence of uranyl and short chain organic molecules (ternary systems) has not been reported. The study would provide an essential observation in the broader spectrum of environmental concerns.

Herein, we investigated the evolution of zeta potential of rutile in presence of organics/uranyl at various conditions (pH, different

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concentrations of uranyl and carboxylic acids). The study is further extended with *in-situ* ATR-IR spectroscopy and TOC measurements. The application of these complementary techniques was both; to determine the role of carboxylic acids in sorption of uranyl by rutile surface and to precise the uranyl–organic complexes onto the rutile or/aqueous solution. Our work is in a general frame of the long-term safety of radioactive waste repositories. The study provides sorption of uranyl ions onto rutile in the presence of short-chain carboxylic acids such as; formic acid (FA), acetic acid (AA) and propionic acid (PA). The organics have been chosen as the models of the natural organic matter (NOM) and representative of cellulose degradation products.

2. Materials and methods

2.1. Materials

All the chemicals were of analytical reagent grade. Formic, acetic, propionic acid and sodium perchlorate hydrate were purchased from Sigma–Aldrich. The stock solution of $UO_2(ClO_4)_2$ of 10^{-2} M in 1 M $HClO_4$ was obtained by dissolving $UO_2(NO_3)_2{\cdot}6H_2O$ (>99% FLUKA) in 4 M $HClO_4$ (MERCK, Suprapur) and the resulting solution was evaporated up to dryness. The residue was dissolved in concentrated $HClO_4$ and evaporated twice. Rutile powders of size 325 mesh (supplied from CERAC) were used for zeta potential measurements and ~20 nm (supplied from PI-Kem) for ATR-FTIR experiments. All the aqueous solutions and suspensions were prepared in deionized water (Millipore direct *Q*, *R* = 18.3 MΩ/cm).

2.2. Characterization of material

Rutile powder was analyzed by X-ray diffraction and cold field emission scanning electron microscopy (FE-SEM). PXRD patterns were recorded on a Rigaku X-ray diffractometer equipped with Cu KR radiation (35 kV, 200 mA) at a rate 5°/min over a 2θ range of 15−80°. Hitachi 800 cold-field-emission scanning electron microscope (FE-SEM) was used for morphology of the rutile powder.

2.3. Zeta potential measurements

Malvern® Nano Szetasizer was used for the zeta potential measurements. Fresh zetasizer cells (Malvern® DTS 1061) were used for each experiment. 20 mg of rutile powder was suspended in 10 mL of deionized water (2 g/L) in a polypropylene tube. After an equilibration time (~12 h), the pH of the suspension was adjusted by the addition of dilute $HClO_4$ and NaOH solutions. Calculated volume of solution was replaced by electrolyte ($NaClO_4$) to maintain the ionic strength of the hydrated samples. The pH of the suspension was measured and re-adjusted to the desired values if necessary. Samples were equilibrated for 12 h to ensure and attain the equilibrium conditions. Seven samples at different pH ranging from ~2 to 8 were prepared for each set of experiments. For binary (rutile–uranyl) and ternary (rutile–uranyl–organics) systems, all the samples were prepared as aforementioned except the addition of the calculated amount of the uranyl ions and acids into the suspension. For ternary systems, the time of equilibration of the rutile with organics and uranyl was kept 48 h. Ionic strength was maintained at 0.1 M $NaClO_4$ in all the samples. Prior to their introduction to the zetasizer cell, samples were sonicated for 2 min in ultrasonic water bath. The instrument calibration was checked by a standard zeta potential solution from Malvern®. Each zeta experiment was repeated thrice to ensure the reproducibility of the results and an average value was taken for a set of measurement. All the data were plotted by adding error bars at each point.

2.4. ATR-FTIR spectroscopy

Infrared spectra were performed in a dry air-purged compartment of a Thermo Scientific Nicolet 6700® spectrometer equipped with a mercury cadmium telluride (MCT) detector. ATR-FTIR spectra were collected using OMNIC® software for the data processing. A thin layer of rutile (aqueous suspension of rutile @ 10 g/L) was deposited onto the ATR diamond crystal by using 3 drops of 1 μL. Each drop was slowly dried with nitrogen gas to obtain a homogeneous layer. 10^{-2} M NaCl was used as ideal background electrolyte (NaCl does not absorb in the spectral range 400–4000 cm^{-1}). Nitrogen gas was constantly purged in ATR cell to avoid the atmospheric CO_2 in the solution. Rutile layer was first equilibrated by 10^{-2} M NaCl electrolyte solution and the ATR spectra were recorded till the stabilization of rutile layer under the electrolyte solution. Flow rate of aqueous solution to the layer was sustained to 0.5 mL/min. After stabilization of rutile layer, uranyl (5×10^{-5} M) or/and organic acids (5×10^{-3} M and 10^{-2} M) were added in the ATR cell to perform *in situ* sorption experiments. A spectrum was acquired for 3 min (256 scans) during the mineral layer stabilization at resolution of 4 cm^{-1}. Background spectra were usually recorded after stabilization of rutile layer, saturation of the rutile surface by uranyl ions (rutile–uranyl) and before the subsequent addition of carboxylic acids (rutile–uranyl–organics).

2.5. Total organic carbon analysis

Total organic carbon (TOC) analysis was performed by TOC–V Shimadzu analyzer® (Institut de Physique Nucléaire Orsay, France). A pH meter GLP 21 (Crison Instruments®, France) was used after calibration against NIST standards (4.01 and 7.00, Crison Instruments®). Sorption experiments of formic, acetic and propionic acids onto rutile (10 g/L) were carried out at various conditions (time of equilibration, pH and acid concentration). Experiments were made in polypropylene tubes by adding 100 mg of rutile in 10 mL of deionized water. The suspensions were left for overnight. pH and ionic strength were adjusted by replacing calculated volume of solution from supernatant after centrifugation (@3500 rpm) followed by the addition of acids. pH of the suspension was re-adjusted to the prefixed values by the addition of 0.1 M $HClO_4$ and 0.1 M NaOH solutions. To avoid the presence of rutile particles, the supernatant was filtered by membrane filter paper (~20 μm diameter).

3. Results and discussion

Fig. 1 represents the XRD pattern of rutile powder. Fig. 2 gives low and high magnification FE-SEM images of rutile powder which shows an average particle size of ~250 nm.

3.1. Zeta potential measurements

Fig. 3 depicts relative curves of zeta potential for rutile in the pH range ~2 to 8 at ionic strength of 0.1 M $NaClO_4$. Zeta potential curves for binary systems (rutile–uranyl) at rutile concentration of 2 g/L and 10 g/L are also incorporated in the same figure. For pHpzc of rutile only (black curve with square points), the concentration of rutile was kept constant at 2 g/L and the suspension was equilibrated for 12 h. The range of zeta potential was obtained between 40 mV to −35 mV. pHpzc of rutile was found to be 4.8, very close to the previously reported data [35].

The complexation of short chain aliphatic carboxylic acids (FA, AA and PA) with Uranyl has been illustrated in the scheme 1.

In case of binary systems (rutile–uranyl), the rutile concentration was varied to 2 g/L and 10 g/L to check the effect of surface