Enhanced sorption capacities for lead and uranium using titanium phosphates; sorption, kinetics, equilibrium studies and mechanism implication

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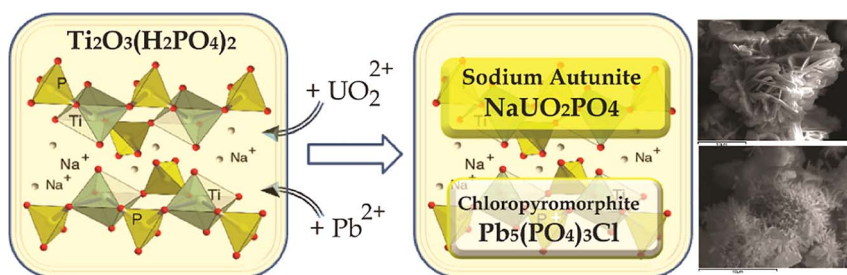[a] Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece
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HIGHLIGHTS

- New titanium phosphates (TiPs) for Pb and U removal from aqueous solutions.
- TiP3 containing Na in its structure exhibited high sorption capacity.
- The sorption on TiP3 was rapid and pH-dependent.
- The mechanism combines ion exchange, surface complexation and surface precipitation.
- TiP3 is a powerful sorbent suitable for industrial and environmental applications.

GRAPHICAL ABSTRACT

ABSTRACT

The application of new synthesized titanium phosphates to the lead and uranium removal from acidic aqueous solutions (pH 2) was explored. Batch sorption experiments were carried out using lead- and uranyl solutions of concentration range 50–6000 and 50–4000 $mg \cdot L^{-1}$ respectively. The effect of pH, concentration, competing cations, temperature and reaction time on the adsorption equilibrium was investigated. The sorbents were examined by FTIR, XRD, XPS and SEM-EDS and characterized as mix salts while the formation of precipitates chloropyromorphite ($Pb_5(PO_4)_3Cl$) and sodium-autunite ($NaUO_2PO_4$) after sorption was demonstrated. Typical sorption isotherms were constructed and modelled by the Langmuir, Freundlich and Temkin equations. The highest sorption capacity values (q_{max}: 2000 $mg \cdot g^{-1}$ Pb and 1250 $mg \cdot g^{-1}$ U) were observed for TiP3 which contains sodium in its structure. The kinetic data, obtained at 298, 308 and 323 K, obeyed a pseudo-second order equation and thermodynamic parameters were calculated. EPA Toxicity Characteristic Leaching Procedure and desorption experiments were performed in order to test the environmental compatibility of the sorbents. The results indicated that the sorption of Pb and U on titanium phosphates can be interpreted by a model combining adsorption and surface complexation toward surface precipitation.

1. Introduction

Sorption is an important method used for the wastewater treatment, and the environmental remediation offering simplicity, high efficiency and relatively low cost compared to other separation techniques (e.g., chemical precipitation, microfiltration, reverse osmosis, ion exchange,

electrolysis). This justifies the increased demand for new sorbents exhibiting high capacity, selectivity and long-term stability [1].

During the last decades a wide range of inorganic sorbents has been synthesized, investigated and applied to the removal of heavy metals and radionuclides from aqueous solutions [2–6].

Lead is one of the metals finding, since the ancient times, a wide range of applications in several fields such as metallurgy (pure metal, alloying element) and industrial activities (motor oil, paints, organic substances). Uses of lead include building materials, pigments, water pipes, lead-acid storage batteries. The effects of lead toxicity on human health are, in most cases permanent and irreversible. Although lead is often considered as "immobile" in soils, high concentrations can do serious harm to humans and animals. The metal and its compounds are highly toxic and cause nerve damage and brain disorders especially in children [7,8].

Uranium is primarily used as a fuel for power generation in nuclear reactors. The nuclear fuel cycle comprises the mining and milling of the uranium ore, fabrication of the fuel, use and treatment after use, and finally, disposal of the wastes [9]. Other sources of uranium into environment are the conventional energy generation by coal burning, the production and use of phosphate fertilizers and the development, testing and use of depleted uranium and nuclear weapons. The threat of uranium is mainly based on its possible chemical toxicity and in lesser extend on its radiation [10,11]. Uranium is a heavy metal and acts similarly to other heavy metals in the body (like molybdenum, lead, or mercury) [12]. Exposure to uranium can lead to kidney failure, health disorders and death [8,9]. U(VI), mainly in the form of uranyl-ion (UO_2^{2+}), is highly soluble in water and very mobile in the environment while U(IV), frequently forming oxides, is less mobile.

Lead and uranium immobilization through phosphate addition is a widely accepted technique for the control of their transfer in the geosphere [13,14]. Phosphate-based materials have been used for the stabilization of heavy metals in soils, water and sediment in the last years [15]. P.Misaelides et al. used Al^{3+}- and Fe^{3+}-modified titanium and zirconium phosphates for the separation of uranium from aqueous solutions achieving a maximum sorption capacity of 56.6 mg·g^{-1} [16]. Wang et al. synthesized a series of zirconium titanium pyrophosphates exhibiting uptake for uranium up to 309.8 mg g^{-1} [17]. Jayswal and Chudasama worked on amorphous zirconium phosphates with lead uptake up to 91.7 mg·g^{-1} [18]. Ma et al. achieved enhanced lead sorption of 149.7 mg·g^{-1} for zirconium phosphates by encapsulation with polysulfone [19].

In this study the ability of newly synthesized titanium phosphates to remove lead and uranium from aqueous solutions is presented. Titanium phosphates exhibit many advantages such as physico-chemical stability, low solubility and a relatively high sorption capacity due to the tendency of phosphate group to form complexes with a large number of metals [16–18].

2. Experimental methods

2.1. Materials and methods

Stock solutions of Pb and U (10000 mg·L^{-1}) were prepared by dissolving appropriate amounts of Pb(NO$_3$)$_2$ and UO$_2$(NO$_3$)$_2$·6H$_2$O in deionized Milli-Q water (resistivity 18.2 MΩ·cm^{-1}). The initial pH of the working solutions was adjusted with dilute HNO$_3$ or NaOH solutions. All reagents used were of analytical reagent grade.

The lead determination was performed by Flame Atomic Absorption Spectroscopy using a Perkin Elmer AA300 spectrophotometer with a hallow cathode lamp and a deuterium background corrector, at the 283.3 nm resonance line using an air-acetylene flame.

Uranium was determined spectrophotometrically at 660 nm on a Shimadzu UV-1601 spectrophotometer (Tokyo, Japan) using 1‰ Arsenazo-III solution as chromogenic reagent [20,21]. The measurements were made in double and the results averaged. The relative uncertainty was less than 5%.

2.2. Sorbents synthesis and characterization

The sorbents were prepared using a previously described synthesis method [22]. In brief, 1M Na$_2$HPO$_4$ aqueous solution was added dropwise into 1M TiCl$_4$ ethanolic solution under continuous stirring at room temperature. Ti:P ratios 1:1.5, 1:2.5 and 1:5.0 were used for the materials TiP1, TiP2 and TiP3, respectively. The gel formed was kept with mother liquor for 20 h. The precipitate was filtered, washed with 1% H$_3$PO$_4$ and distilled water and finally dried at 50 °C. The materials were obtained after grinding and sieving through a 60-mesh sieve. The TiP particles were examined by Fourier Transform Infrared Spectroscopy (FTIR) using a Thermo Scientific Nicolet 6700 FT-IR spectrometer and Powder X-ray diffraction (pXRD) (model X'Pert ProMPD Panalytical, Almelo, The Netherlands with Cu$_{Kα}$ (λ = 0.154 nm) radiation). The 2θ degrees scanning region was 6°–80° (step size: 0.04°) at a scan speed of 0.027° s^{-1}. In addition X-ray Photoelectron Spectroscopy (XPS) was used on a Kratos Analytical AXIS Ultra^{DLD} system, with Aluminum monochromatic X-ray source (λ$_{Ka}$ = 1.4866 Å), under high vacuum conditions (10–8 torr).

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) was applied using a JEOL 840A SEM equipped with an OXFORD ISIS 300 SEM-EDS analyzer. The samples for the SEM-EDS examination were carbon-coated using a JEOL JEE-4X vacuum evaporator.

The point of zero charge was determined by plotting the zeta potentials vs. pH of dilute sorbent suspensions. For the measurements, a Brookhaven Instruments zeta potential analyser utilizing phase analysis light scattering (ZetaPALS) was used, at 25 °C with a refractive index for the aqueous phase of 1.330 and a viscosity of 890cP.

N$_2$ gas adsorption–desorption isotherms for the specific surface area determination were obtained at 77 K by a Thermo Scientific Surfer Analyser gas adsorption porosimeter using the Brunauer–Emmett–Teller (BET) equation in the relative pressure (P/P$_0$) range of 0.06–0.3. The samples were preliminarily heated for 24 h at 200 °C in vacuum. N$_2$ adsorption volumes at the relative pressure of 0.99 were used to determine the pore volumes.

2.3. Sorption studies

For the sorption experiments, lead (concentration: 50–6000 mg·L^{-1}) and uranium (concentration: 50–4000 mg·L^{-1}) solutions were prepared. The initial pH was adjusted by adding 0.1 M HCl or NaOH. The effect of pH, contact time, solid/liquid ratio, competing ions and temperature was investigated. For the batch experiments, 25 mg of the individual sorbents were equilibrated with 10 mL aliquots of the metal solutions in polypropylene tubes at a set temperature for a predetermined period of time. Pb and U concentrations were determined in the supernatant solution after the establishment of equilibrium. All experiments were repeated twice and the results were averaged. The differences were within 5%. The removal (R%) and the adsorption capacity (q$_e$) were calculated as follows:

$$R\% = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \tag{1}$$

$$q_e = \left[\frac{C_i - C_e}{m} \right] \times V \tag{2}$$

where, C_i and C_e (mg·L^{-1}) are the concentrations before and after the contact with the sorbent, V (mL) is the volume of the solution and m (mg) is the mass of the sorbent.

The dependence of the Pb and U sorption on the pH was investigated in the range 1–4, in air using 100 mg·L^{-1} solutions.

2.4. Sorption isotherms

The equilibrium data were analyzed with three isotherm models, i.e., Langmuir, Freundlich and Temkin. The Langmuir equation [23] is