Modelling uranyl-ions sorption by nanostructured composite anatase-based materials

T A Sokolnitskaya¹, V V Zheleznov¹, A P Golikov¹ and A E Plakhutina²

¹ Institute of Chemistry FEB RAS, Prospect 100-letiya Vladivostoka 159.
Vladivostok, 690022, Russia

² – Far Eastern Federal University, Sukhanova str. 8. Vladivostok, 690050, Russia

E-mail: ttt@ich.dvo.ru

Abstract. Influence of complex formation in solution on U sorption has been studied for mesoporous nanostructured anatase-based composites. Uranium sorption degree has been shown to correlate with the stability of the complexes in solution. A model for uranium sorption by titania materials has been suggested presuming two-stage sorption mechanism. It is assumed that initial binding of neutral and positively charged uranyl complexes to negatively charged hydroxyl groups occurs on the first stage, while decomposition of complex ion proceeds on the second stage with the UO₂ being fixed on sorption sites. Prevailing uranium species in solution and kinetics of their ratios have been determined. Calculated rates of evolution of uranyl ion species distribution (therefore, rate and efficiency of the sorption) correlate well with complex stability in solution.

1. Introduction

Intensive mining of Uranium ores produces large amounts of industrial waste such as tailing ponds and ore dumps. As a result of weathering processes Uranium compounds can migrate at large distances which poses significant ecological hazards due their high toxicity. MPC of Uranium in drinking water is 15mkg/L [1], and groundwater concentration can achieve 40mkg/L in contaminated areas [2].

Development of new modern sorption materials tailored for Uranium concentration and recovering is the important area of applied science focused both on further development of industry producing the products containing Uranium and on cleanup of contaminated environment from uranium compounds.

Recent studies show that increasing of sorption capacity and improvement of kinetic characteristics of inorganic compounds can be achieved by regulation of pore structure and increasing the surface area; uptake selectivity can be significantly boosted by using materials with high affinity to Uranil-Ions such as titanium silicates and zirconium silicates.

Sorption of Uranium from low concentration model solutions containing sulphate, fluoride or oxalate ions onto mesoporous nanostructured materials of Titanium oxide doped by Zirconium Oxide has been studied.

2. Results
Approach based on usage of the rigid latex particles with low polydispersity index as templates and meticulous selection of template multy step burning out conditions allows to produce materials with controlled pore structure and developed surface (table 1).

**Table 1.** Composition and structure of several samples

| Sample | Composition, % | Specific surface area, m²/g | Specific pore volume, cm³/g | Phase composition |
|--------|----------------|-----------------------------|-----------------------------|------------------|
|        | TiO₂  | ZrO₂  | SiO₂  |                  |                   |                   |
| ТЭ0    | 95,0  | 0,0   | 5,0   | 155              | 0,45              | anatase           |
| ТЭ5    | 88,4  | 5,6   | 6,0   | 170              | 0,49              | anatase           |

Factors which affect Uranyl -ions sorption:
- Amount and characteristics of active centers on the sorbent surface (it is mostly defined by type and concentration of dope).
- Degree of protonation of active centers (sorption activity and pH of solution dependency).
- Stability of the complexes in solution.

It was shown that materials composed of nanosize TiO₂ have surficial hydroxo complexes due to the surficial and volumetric oxygen vacancies and demonstrating very high reactivity due to excess electron [5]. It is the hydroxo complexes that define sorption activity of TiO₂.

As pH rises above 6-7 the Uranium recovery decline was observed. For neutral pH the degree of recovery approaches 100% after only 2 hours of sorption (Figure 1). As Titanium Oxide has amphoteric properties the sorption from acidic solutions pH slightly increases and in weak alkaline systems pH decreases. Similar dependencies were observed in all three studied systems.

![Figure 1. Sorption kinetics of U (VI). (Sulfate system. C(U) = 4,2·10⁻⁵ mol/l, C (SO₄⁻²) = 5·10⁻² mol/l, S/L = 1/1000).](image)

- Stability of the complexes in solution.

Comparing dependency of U recovery for different systems it was observed that as U complex stability in solution was increasing, pH had less influence on the degree of Uranium extraction (Figure 2); at the same time pH of the solution shifts more during the sorption process.
Figure 2. The degree of extraction U and pH dependency. (C(U) = 4.2·10^{-5} mol/l, time of sorption in the argon atmosphere is 120h, S/L=1/1000, ultrafiltration).

In this study the model of competitive sorption of ions H⁺ and positively (or neutral) charged complexes of Uranyl-ion (sulphate, fluoride, oxalate and hydroxo-complexes) on free sorption centers (deprotonated surface hydroxyl group anatase ) has been used as a foundation for theoretical description of sorption kinetics. The model based on assumption of the two-step sorption mechanism.

It is assumed that the first step is responsible for the preliminary binding of neutral and positively charged complexes of Uranyl-ion with negatively charged hydroxyl groups of anatase (and binding probability is proportional to the charge of complex ion); the second step provides final binding followed by decomposition of complex ion and binding of UO₂²⁺ to the sorption centers.

For the full system description the differential equations of ion equilibrium and material balance were added to the sorption kinetics equations. All ion forms and equilibrium constants have been acquired from well known ion equilibrium in water solutions LLNL database (Lawrence Livermore National Laboratory).

Figure 3. Modeling: change in the concentration of surface UO₂²⁺ groups during sorption of uranium depending on the complexing agent (initial pH 5.4).
Figure 4. Modeling: change in the concentration of surface $\text{UO}_2^{2+}$ groups during sorption of uranium depending on the complexing agent (initial pH 9.9).

The increasing stability of Uranyl-ion complexes in the row oxalates < fluorates < sulfates well known from literature. Modelling of change of concentration of surface $\text{UO}_2^{2+}$ groups during Uranium sorptions dependant on complexing agent (Figures 3 and 4) clearly shows direct relationship with the complex stability in solution and inverse relationship with the remaining concentration of Uranium in solution (Figure 5). This allows to conclude that proposed model accurately describes influence of complexing agent on the Uranyl-ion sorption.

Figure 5. Modeling: Uranium sorption kinetics depending on the complexing agent.
3. Conclusion
Thus we have produced mesoporous nanostructured Titanium Oxides doped by Zirconium ions. The Uranium sorption dependency on the solution pH, type and concentration of complexing agent has been studied. The sorption mechanism were proposed and the sorption process based on them has been modelled.

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