

Molecular Binding Affinity of Aqueous Uranyl Tricarbonate Towards Basic Surface Functional Groups

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1. Introduction

Uranium (U) is one of the major raw material in the nuclear power plant and military-weapon industries. The U-handling activities have resulted in the widespread contamination of groundwater [1]. Numerous adsorbents including metal-oxide, inorganic, and organic materials have investigated to separate U from aqueous phase. Silica showed high surface area and good physical stability, however, its limited surface density of U binding sites preclude the effective adsorption performance. Recent studies have functionalized the silica surfaces with N, O-ligands and the functionalization process could enhance the adsorption efficiency.

Various types of the N,O-ligands and its derivatives have been confirmed in the increasing silica sorption behavior, but the binding affinity toward U between ligands cannot be directly compared due to the different experimental conditions that would affect the binding characteristics.

In this study, silica surface was functionalized with basic ligands including amine (NH₂), carboxyl (COOH), hydroxyl (OH), and phosphonate (P=O(OH₂)) groups as a monolayer structure, i.e., surface functional groups. Previous spectroscopic studies have reported that uranyl tricarbonate (UO₂(CO₃)₃⁴⁻) is a dominant uranium (U) species in groundwater, therefore, the binding affinity of uranyl carbonate toward surface functional groups were measured and compared in terms of adsorption kinetic/capacity.

2. Materials and Methods

2.1 Preparation of Surface Functional Groups

All the functionalization process was carried out under the anhydrous and anoxic atmosphere (99.999% Ar and H₂O(g)/O₂ < 1 ppm) at room temperature.

Two hundred mL of anhydrous toluene was injected into the amber glass bottle containing 1.2 g of silica. The suspension was magnetically stirred and appropriate amounts of organosilanes ((3-aminopropyl)triethoxysilane (APTES, Sigma 99%), (3-glycidyloxypropyl)trimethoxysilane (GPTMS, Sigma > 98%), 3-(triethoxysilyl)propylsuccinic anhydride (TESPSA, BOC science 95%), and (2-diethylphosphatoethyl)triethoxysilane (DPTS, Gelest 95%)) were added indicating the functionalization process initiate. The particles in the suspension was separated after 16 h by centrifugation (100,000 g for 10 min.). The particles were washed and dried, respectively.

2.2 Batch Sorption Experiments

Uranyl tricarbonate solution was prepared by adding U stock solution (concentration in the mixture: 1×10^{-4} M) into the 1×10^{-2} M CO₃²⁻ solution pH buffered at 7.5 with 2×10^{-2} M HEPES. The exact amount of functionalized silica was transferred into the 200 mL of uranyl tricarbonate solution and the suspension was magnetically stirred at 300 rpm at room temperature. Three mL of the suspension was periodically taken and immediately filtered by membrane filter (Amicon, Ultra-15). The remaining U concentration in the filtrate was quantified by ICP-OES (Agilent 5110).

2.3 Analysis

The functionalized silica was characterized by Attenuated Total Reflection-Fourier Transform Infra-Red (ATR-FTIR, Nicolet iS 50), Elemental Analysis (EA, FlashEA 1112), ThermoGravimetric Analysis (TGA, Netzsch), and Nuclear Magnetic Resonance (NMR, Agilent VNMR600) analysis to verify the formation of monolayer structure organosilanes on the silica surface. The surface charge of functionalized silica was quantified by zeta potential analyzer (ELS-Z2) before and after the adsorption experiments.

3. Result and Discussion

3.1 Surface Functional Groups Characterization

The surface density of functional group on the silica surface was quantified by EA and TGA as shown in Table 1.

Table 1.

Type	NH ₂	COOH	OH	P=O(OH) ₂
density (#/nm ²)	1.38±0.13	1.45±0.16	2.09±0.02	1.11±0.16

The density was in the range of monolayer value and the presence of the surface ligands were identified from ATR-FTIR analysis (data not shown). NMR analysis revealed that the attached organosilane on the silica surface has monolayer structure indicating the surface functional groups were prepared as similar surface density and geometrical structure.

3.2 Molecular Binding Affinity of Aqueous Uranyl Carbonate

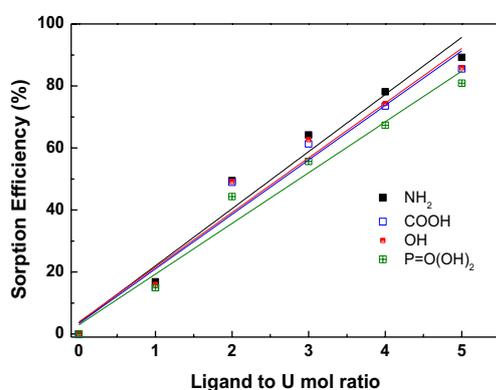


Fig. 1. Uranium adsorption efficiency of the functionalized silica with respect to the molecular ratio of uranium to surface ligand.

Fig. 1 shows the adsorption efficiencies of the functionalized silica for $\text{UO}_2(\text{CO}_3)_3^{4-}$ (aq) at pH 7.5. The efficiencies have linearly increased and complete adsorption were obtained at molecular ratio of 1 to 5 implying that penta-coordinated U-ligand complexes might be formed on the surface. The sorption data have fitted with pseudo-second order kinetic model and the results well followed the model ($R^2 > 0.990$) indicating the calculated adsorption kinetic and capacity values were reliable. In four different basic groups, $\equiv\text{NH}_2$ showed the fastest adsorption kinetic

(1.67×10^{-2} mmol/(mg·min)) while $\equiv\text{COOH}$ had the highest adsorption capacity (32.27 mg/mmol_{ligand}). The charge of NH_2 -surface was the most positively charged (+7.5 mV) and COOH -surface was the most negatively charged one (-25.0 mV). After the interaction with U, the NH_2 -surface charge was shifted to the negative region (-13.5 mV) while that of COOH -surface was maintained. From the obtained results, we propose that the complexation of U with $\equiv\text{N}$ - and $\equiv\text{O}$ -ligand would occur via ionic- and covalent-bonding, respectively (Fig. 2).

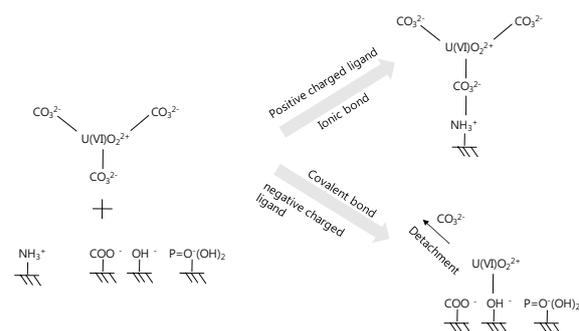


Fig. 2. Proposed binding mechanism of uranyl tricarbonate to the surface ligands.

4. Conclusion

The binding affinity of aqueous uranyl tricarbonate toward basic surface ligands were investigated under the controlled mole ratio of the reactants. Amine group showed the fastest binding kinetic due to its positively charged property in which it could effectively bind with the negatively charged uranyl tricarbonate, i.e., ionic bonding. The highest binding capacity was obtained from the carboxyl group. It might be attributed to the most negatively charged properties of COO^- that could effectively repel the CO_3^{2-} from the $\text{UO}_2(\text{CO}_3)_3^{4-}$ species during the binding process, i.e., covalent bonding.

REFERENCES

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