



Flow-enhanced kinetics of uranyl (UO₂) transport into nano-porous silica gel



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ABSTRACT

Uranyl transport into nanoporous silica gel is limited in a static aqueous solution by slow natural diffusion to the open bonding sites. In order to make this process faster, the diffusion dependence was eliminated using pressure driven fluid flow. Uranyl transport and adsorption within nanoporous silica gel was measured using time-dependent fluorescent measurements in an aqueous solution. The transport kinetics was measured under two different conditions: static solution in a standard cuvette and flowing solution through the silica gel. It was determined that the kinetics of uranyl uptake within nanoporous silica gel depends strongly on the liquid flow velocity. Above a certain velocity, the adsorption kinetics increased by at least two orders of magnitude (from about 40 min to 2 s) in comparison to a static solution. In a static solution, the kinetics depends on the porosity of the silica gel, but this dependence was not observed when the liquid flow velocity exceeded a certain value. Flow-enhanced adsorption kinetics has potential applications for fast detection of trace levels of uranyl in water.

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1. Introduction

Uranium is a heavy, naturally occurring radioactive element. Elevated concentrations of uranium in water and soil can be linked to activities such as uranium mining, nuclear fuel preparation and disposal [1–3]. Monitoring the concentration of uranium in the environment is of interest to organizations involved in activities such as national security, non-proliferation, water quality, and environmental impact studies [4,5]. Uranium can be detected in several ways, but the most common method is measuring the high-energy radioactive decay products. However, at low concentration levels in soil or water, uranium radioactivity signals are weak and attenuated and, therefore, difficult to measure outside of a laboratory. Uranium in nature is most commonly found in an oxidized ionic form known as uranyl, with oxidation state +6 and chemical formula UO₂²⁺ [6,7].

The uranyl ion is water soluble and has been known for its distinct green fluorescent emission for over 150 years [8]. The uranyl optical emission signature can have as many as six peaks at wavelengths ranging from 345–600 nm, depending on factors such as pH and temperature [9]. Each of these peaks is due to the vibrational modes of the two smaller oxygen atoms vibrating around the much larger uranium atom [1,2,10].

The fluorescence emitted from the uranyl ion has long been used as a method for determining the presence and concentration of uranyl in

water [11–13]. However, water molecules quench the optical emission making detection at trace concentration levels challenging [8]. Multiple methods have been used to enhance the fluorescence of uranyl in water. One method uses phosphoric acid to alter the pH, which in turn increases the emission intensity. Another method uses low temperatures to enhance the emission [7,9,12,13]. Perhaps the most compelling method for enhancing the fluorescence of uranyl is complexation with silica. Silica has been used to enhance many fluorescent compounds such as La₄Ti₉O₂₄ and Eu³⁺ [11,14]. The silica enhancement method has been used with colloidal silica, and in this paper, porous silica gel was used [11].

Silica gel is hydrophilic and has been used for applications such as chromatography, removal of ions in solution, and desiccant refrigeration [15,16]. Studies of silica in the presence of metal ions have shown that silica has a high adsorption capacity and selectivity, especially when used with uranyl [15]. The selectivity toward uranyl ions is caused by the negatively charged sites on the silica surface, to which the uranyl ions attach [11]. Two important parameters need to be considered when using silica to enhance uranyl fluorescence: the kinetics of the adsorption process and the equilibrium capacity [15]. The equilibrium capacity refers to the total number of silica surface sites available to adsorb a uranyl ion, while the kinetics of adsorption is the time required to fill those sites. Study of equilibrium capacity has focused on maximizing the capacity for removing ions from aqueous solutions [17–20]. The maximization of the equilibrium capacity was achieved by adding functional groups to the surface of the silica gel particles [17,19–22]. The kinetics has been studied for various solutions and with different methods such as in a static or stirred fluid [15]. The tests show that in a static or

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