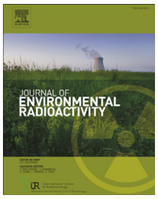
Journal of Environmental Radioactivity 180 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Removing uranium (VI) from aqueous solution with insoluble humic acid derived from leonardite

Fande Meng [a, b, c], Guodong Yuan [d], Steven L. Larson [e], John H. Ballard [e], Charles A. Waggoner [f], Zikri Arslan [a], Fengxiang X. Han [a, *]

[a] *Department of Chemistry and Biochemistry, Jackson State University, 1400 J. R. Lynch Street, P.O. Box 17910, Jackson, MS 39217, USA*
[b] *Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, China*
[c] *University of Chinese Academy of Sciences, Beijing 100049, China*
[d] *Zhaoqing University, Zhaoqing, Guangdong 526061, China*
[e] *U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Rd., Vicksburg, MS 39180-6199, USA*
[f] *Institute for Clean Energy Technology, Mississippi State University, 205 Research Blvd, Starkville, MS 39759, USA*

ARTICLE INFO

Article history:
Received 27 May 2017
Received in revised form
31 August 2017
Accepted 23 September 2017

Keywords:
Uranium contamination
Depleted uranium
Leonardite
Humic acid
Artificial seawater
Desorption
Soil

ABSTRACT

The occurrence of uranium (U) and depleted uranium (DU)-contaminated wastes from anthropogenic activities is an important environmental problem. Insoluble humic acid derived from leonardite (L-HA) was investigated as a potential adsorbent for immobilizing U in the environment. The effect of initial pH, contact time, U concentration, and temperature on U(VI) adsorption onto L-HA was assessed. The U(VI) adsorption was pH-dependent and achieved equilibrium in 2 h. It could be well described with pseudo-second-order model, indicating that U(VI) adsorption onto L-HA involved chemisorption. The U(VI) adsorption mass increased with increasing temperature with maximum adsorption capacities of 91, 112 and 120 mg g^{-1} at 298, 308 and 318 K, respectively. The adsorption reaction was spontaneous and endothermic. We explored the processes of U(VI) desorption from the L-HA-U complex through batch desorption experiments in 1 mM $NaNO_3$ and in artificial seawater. The desorption process could be well described by pseudo-first-order model and reached equilibrium in 3 h. L-HA possessed a high propensity to adsorb U(VI). Once adsorbed, the release of U(VI) from L-HA-U complex was minimal in both 1 mM $NaNO_3$and artificial seawater (0.06% and 0.40%, respectively). Being abundant, inexpensive, and safe, L-HA has good potential for use as a U adsorbent from aqueous solution or immobilizing U in soils.

1. Introduction

Uranium (U) occurs naturally in several minerals as a mixture of three isotopes, U-238, U-235, and U-234 (Cordfunke, 1970). Depleted uranium (DU) is a by-product of the production of enriched uranium containing U-235 and U-234 at lower concentrations than natural U (AEPI, 1995). DU is used in kinetic energy penetrators and armor plating as well as having widespread applications as aircraft counterweights and radiation shielding in medical radiation therapy (Betti, 2003; Global Security, 2008). Leaching of U to water occurs naturally due to interaction with soil minerals (Choy et al., 2006; Munasinghe et al., 2015). Anthropogenic contamination also arises from U ore mining/processing, medical waste, nuclear power station operation, accidents, and weapons testing. Acid drainage water from U mine tailings contains U and other radionuclides at low pH, reported from sites worldwide, including Australia (Mudd and Patterson, 2010), Germany (Biehler and Falck, 1999), Canada (Berthelot et al., 1999), and Brazil (Campos et al., 2011). This has resulted in the release of U-and DU-containing wastes into soil and groundwater environments, posing risks to surface water and human health (Lienert et al., 1994; Krestou et al., 2004; Todorov and Ilieva, 2006; Gavrilescu et al., 2009; Steinhauser et al., 2014). U usually occurs as U^{6+} and U^{4+} oxidation states in soil and water environments and U^{6+} is the main stable valence under oxidizing conditions. The daily intake of U, as established by the World Health Organization (WHO), is 0.6 μg kg^{-1} of body weight/day; the maximum U concentration in drinking water at 15 μg L^{-1} (WHO, 2008) or30 μg/L (U.S. Environmental Protection Agency, 2012).

---

[*] Corresponding author.
E-mail address: Fengxiang.han@jsums.edu (F.X. Han).

https://doi.org/10.1016/j.jenvrad.2017.09.019
0265-931X/

A range of technologies have been developed for removing U from water, including adsorption, membrane processes, chemical precipitation, and ion-exchange (Dulama et al., 2013). Adsorption has become a popular choice due to its cost-effectiveness and ease of operation. Adsorbents used to remove U from water, include microbial biomass (Kalin et al., 2004), activated carbon (Mellah et al., 2006), hematite (Xie et al., 2009), sepiolite (Donat, 2009), clay materials (Campos et al., 2013) and clay-humic complexes (Anirudhan et al., 2010). Recently, biopolymers, such as insoluble humic acids (HA), have been extensively used as adsorbents of heavy metals (Havelcová et al., 2009; Shaker and Albishri, 2014; Khalili and Al-Banna, 2015; Meng et al., 2016). HAs are naturally occurring in water and soil environments and play a vital role in environmental detoxification (Kochany and Smith, 2001; Yuan and Theng, 2012; Ziółkowska, 2015). They could also be extracted from leonardite and lignite. With abundant functional groups (e.g., quinone, amino, carboxylic, phenolic), leonardite-derived HA (L-HA) has a good propensity to bind metal cations (Olivella et al., 2002; Yang et al., 2015).

The objective of this work was to investigate the potential use of L-HA as a U adsorbent from U waste water such as mining tailing as well as other U contaminated sites such as army shooting ranges. To this end, the effects of pH, contact time, temperature, and initial U(VI) concentrations on U adsorption were assessed through kinetics adsorption experiments at 298 K and batch isotherm experiments at 298, 308 and 318 K. Further, the process of U(VI) desorption from the L-HA-U complex was investigated with batch kinetics desorption experiments at 298 K. Desorption studies were performed using diluted $NaNO_3$ as a background electrolyte to simulate a normal soil solution (Harter and Naidu, 2001) and artificial seawater as a marine environment simulant to study the tendency of U(VI) release from L-HA-U complex.

2. Experimental

2.1. Materials, reagents and preparation of solutions

Leonardite was purchased from Xinjiang Uyghur Autonomous Region, China, which was similar in physical and chemical properties to leonardite from North Dakota, US. All reagents used in this study were of analytical grade. Nitric acid and sodium hydroxide, used for adjusting pH, were purchased from Thermo Fisher. Uranyl nitrate, 1% aqueous, was purchased from Poly Scientific R&D Corp. A series of U(VI) solutions were prepared by successively diluting the uranyl nitrate 1% aqueous with 1 mM $NaNO_3$. A single element standard for U was obtained from SPEX CertiPrep and used to prepare standard curves for quantitation. Artificial seawater was prepared according to the methods of Yu et al. (2011) and consisted of 26.5 g/L NaCl + 24 g/L $MgCl_2$ + 0.73 g/L KCl + 3.3 g/L $MgSO_4$ + 0.2 g/L $NaHCO_3$ + 1.1 g/L $CaCl_2$ + 0.28 g/L NaBr.

2.2. Preparation and characterization of L-HA

The traditional alkaline-acid procedure was used to obtain HA from leonardite (Havelcová et al., 2009; Meng et al., 2016). Briefly, 50 g leonardite were added to 500 mL of 0.1 M NaOH solution in a Teflon-lined container, heated to 40 °C, then sonicated for 30 min. After standing overnight in the sealed container, the supernatant liquid was slowly poured off and 0.1 M NaOH was added to the solid residue. This extraction procedure was repeated six times. The L-HA was obtained by adding 6 M HCl to the collected supernatant liquid while stirring to pH 2, centrifuging at 3000 $r\bullet min^{-1}$ for 15 min and washing the precipitate with deionized water, and centrifuging for three times. The final precipitation with pH 4.02 was freeze-dried for use.

The L-HA was analyzed for its physical and chemical properties. Ash content of the L-HA was determined by heating samples in a muffle furnace at 800 °C for 4 h under air atmosphere. Elemental contents were determined by an elemental analyzer (Vario micro cube, Elementar, Germany) for dried sample. The pH was determined in boiled, distilled water with a pH meter at a solid-liquid ratio of 1: 10 (Mettler Toledo, Switzerland). Surface morphology was observed with a Scanning Electron Microscope (SEM, Hitachi S-4800, Japan, 3 kV). Functional groups were analyzed with Fourier transform infrared spectroscopy (Thermo Nicolet, 470 FTIR, USA). Acidic functional groups were quantified according to the method of International Humic Substances Society (http://www.humicsubstances.org/acidity.html). Briefly, a solution containing 0.36 ± 0.01 g L^{-1} (base on a dry ash-free) of HA (with pH adjusted to 3.0 with HCl and 0.1 M NaCl as background electrolyte) was titrated with carbonate-free 0.1 M NaOH at 25 °C to pH 8.0 and 10.0. The contents of carboxyl and phenolic-OH groups were calculated from NaOH consumption between pH 3.0 and 8.0 and between 8.0 and 10.0, respectively.

2.3. Batch experiments

2.3.1. Batch adsorption experiments

First, initial U solutions (60 mg/L) were prepared. The pH values of the U solutions were adjusted to pH 3, 4, 5, 6, 7, 8 with 0.1 M HNO_3 or NaOH solutions before mixing with L-HA. Dissolved U in pH adjusted solutions was measured again. Twenty mg (accurate to 0.0001 g) L-HA was added to 50 mL centrifuge tubes containing 30 mL U solution. The tubes were capped and placed on a temperature controlled shaker at 298 K. After 12 h of shaking the tubes were centrifuged, and the supernatants filtered through 0.45-μm membrane (Whatman, UK). The clear supernatants were diluted with 1% HNO_3 for U analysis with a Varian 820-ICP-MS, (Varian Inc., USA) where the U concentrations should be less than 100 μg/L. The kinetic study was conducted in the solution with pH 5.0 at 298 K for 0.1, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 4 h. The initial U concentrations are high for most U contaminated sites, however, this research effort is partially directed toward military shooting ranges, where U concentrations in soil have been reported as high as 2700 mg/kg (Larson et al., 2009). To simulate high concentrations of absorbed U in a solid matrix, a relatively high initial U concentration such as those used in the present study seemed desirable.

Adsorption thermodynamics were assessed with initial U(VI) concentrations from 5 to 120 mg L^{-1} at three temperatures (298, 308 and 318 K). Thirty mL of the U(VI) solutions were added into 50 mL centrifuge tubes containing 20 mg L-HA. The initial pH of U(VI) solution was adjusted to 5 ± 0.05 and shaken for 12 h.

2.3.2. Batch desorption experiments

A L-HA-U complex was prepared for the desorption experiments by adding 1 g L-HA to a PTEE bottle with 250 mL of 120 mg L^{-1} of U solution. The initial pH was adjusted to 5.0 ± 0.1 using HNO_3 or NaOH. After shaking for 12 h at 298 K, the bottle was centrifuged and the obtained residue (L-HA-U complex) was dried at 105 °C until constant weight.

Desorption of the U(VI) from the L-HA matrix was studied using 1 mM $NaNO_3$ (as a simulated soil solution) (Harter and Naidu, 2001) or artificial seawater. Twenty mg of the L-HA-U were placed into 50 mL tubes containing 30 mL of a 1 mM $NaNO_3$ solution with a pH 5.03, or artificial seawater with a pH 6.98. The tubes were capped and continuously shaken in a temperature controlled shaker at 298 K. The shaking time are 0.25, 0.5, 0.75, 1, 1.5, 2, 3 and 4 h for artificial seawater, and 0.25, 0.5, 0.75, 1, 1.5, 2, 3, 4, 6 and 8 h for 1 mM $NaNO_3$. The supernatants were filtered and analyzed for U concentration by ICP-MS.