
Uranium Removal via Sorption Using Peat and Waste Digested Activated Sludge

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Abstract Uranium is a toxic metal used in atomic energy production. Uranium contamination within, or emanating from mine sites can pose a threat to the environment and exposure to uranium is hazardous to health. Although several methods are already available for uranium removal from aqueous solutions, there is still a need for developing alternative, cost-effective and recoverable techniques to deal with the continuing problem of environment contamination. This study focuses on uranium removal by adsorption using widely available, natural sorbents, namely peat and waste digested activated sludge (WDAS) from municipal wastewater treatment.

Key words Waste digested activated sludge, peat, adsorption, fed-batch reactor, hydraulic retention time

Introduction

The global exploration and mining industry currently faces the challenge of discovering and extracting metals from increasingly complex and low grade ores, while still meeting increasing expectations for community acceptance and compliance with principles of ecologically sustainable development. Uranium is an important metal for nuclear energy security. However, the mining of uranium lead to the generation of mine tailing that has low concentration of uranium. On the other hands, the presence of uranium at low concentrations in polymetallic ore deposits is a challenge, as uranium poses threats to humans and the environment due to its chemical and radiological toxicity. Thus, the removal and recovery of uranium from such wastewater will not only prevent the environmental damage but also provide secondary source of uranium.

In 2008, the U.S. Environmental Protection Agency (EPA) set the standard for maximum contaminant levels for uranium in drinking water as 30 µg/L. The World Health Organization (WHO) subsequently revised the recommended limit upwards from 15 µg/L to 30 µg/L in 2011, since according to human studies no clear evidence was found of adverse health effects below that concentration. However, the evaluation of maximum contaminant levels is based on the chemical toxicity of uranium to the kidney instead of its radiological toxicity.

The uranium present in the wastewater is removed by methods such as adsorption, coagulations, precipitation, membrane exchange and chemical or biological reduction (Li et al. 2012). However, some techniques such as coagulation suffers from lower removal rates, chemical reduction methods are not at mature stage on implementation while adsorption in some cases suffers from high cost. In general, adsorption is an efficient method for the

removal of contaminants at low concentration from large volume wastewaters (Hua et al. 2012), which would fit perfectly for removal of uranium from mining wastewaters. The cost-effectiveness of the method can be improved by the use of adsorbents which are produced in large volumes and at low cost.

The activated sludge treatment plants produces large quantity of sludge, where the waste sludge is generally digested under anaerobic process for energy production (Guo et al. 2013). The waste digested activated sludge (WDAS), remaining after the anaerobic digestion process, is generally discarded on land as fertilizer. This WDAS, a waste by-product and present in large quantity, has potential to be a good adsorbent for removal of uranium (Al-Qodah 2006), however, there are no studies that explored this possibility.

As conclusion, adsorption and desorption is a fast and cost-effective process for the removal and recovery of uranium from low concentration, high volume waste streams such as mining wastewaters. This study focuses on uranium removal by adsorption using widely available, natural sorbents, namely peat and WDAS from municipal wastewater treatment.

Peat as an adsorption material

Peat is typically an acidic and heterogeneous organic substance and the quality will vary depending on the physical, chemical and biological properties. These properties include plant origin, elemental content, decomposition degree, pH, cation exchange capacity, hydraulic conductivity, porosity and surface area (Heikkinen et al. 1995, Vymazal 1998). Generally, peat is a complex material with cellulose, hemicellulose and lignin as major constituents. Lignin and humic acid in particular have polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers that can be involved in chemical bonding (Chaney and Hundemann 1979).

In Finland, well-decomposed Carex-Sphagnum peat types with high caloric values are mostly used for energy production. On average, peat has accounted for 5-7% of the total energy consumed in Finland. Also, Sphagnum peat of different decomposition rates are used in agriculture, cultivation, as a growing media in seedling production, tree nurseries, gardening, landscaping and largely in environmental impact management. The important properties of weakly decomposed Sphagnum peat include the porous structure with high water retention capacity, low pH and nutrient content, allowing plant-specific fertilization, no sources of plant diseases, pests or weeds. Weakly decomposed peat has a large specific surface, up to 26.5 m²/g using the nitrogen adsorption method, and a pore volume of more than 90% (Poots and McKay 1979). These properties alone create a high liquid-retention capacity and thus peat has been used in agriculture for manure handling and soil improvement material, composting and as soil litter in different types of farming (Iivonen 2008).

Peat has also been used for the purification of municipal and industrial wastewaters contaminated with dissolved metals. Also, thermally treated peat has been used in the prevention of oil spill related damages because the thermally treated peat absorbs oil but not water.

Peat can also be used in mechanical filters to remove solid particles from the air. Generally, the large surface area of peat removes metal ions, for example, by ion exchange and adsorption. Because of the specific structure and character of the peat, the adsorption potential is high. Peat can provide an effective medium for retention of nitrogen, phosphorus and suspended solids (Kieckbusch and Schrautzer 2007), dissolved metals such as aluminium, iron and nickel (Brown 2000, Räsänen et al. 2001), metals such as Cu, Cd, Zn, Pb, Fe and U(VI) ions (Couillard 1994 and references within that paper, Zhirong and Shaoqi 2010), metalloids such as arsenic (Palmer et al. 2015), pesticides (Roseth and Haarstad 2010), oils and odours (Iivonen 2008).

WDAS adsorption methods

The activated sludge treatment plants used widely for treatment of municipal and some industrial wastewaters produce large quantity of excess waste sludge, which is often anaerobically digested to produce biogas (Appels et al. 2008). The WDAS, remaining after the anaerobic digestion process contains nutrients (e.g. nitrogen and phosphorus) removed from the wastewaters and could be used as agricultural fertilizer. However, municipal wastewater sludges and their digestates can contain trace levels of metals and organic pollutants as well as pharmaceutical residues (Suominen et al. 2014, Mininni et al. 2015) and therefore their land use is restricted in some countries. Because of this WDAS disposal can be a significant cost factor for wastewater treatment plants due to the high quantity of WDAS generation. However, as WDAS consists largely of residues of microbial cells, which have large variety of functional sites such as carboxyl, amino, phosphate and hydroxyl moieties on their surfaces, this waste by-product is a potential adsorbent for metals such as uranium. The use of activated sludge and digested sludge as a biosorbent for removal of metals such as cadmium, copper, lead, nickel and zinc has been studied widely (Bux et al. 1999, Lister and Line 2001, Al-Qodah 2006), but to our knowledge the use of WDAS for biosorption of uranium has not been previously reported.

General methods

Uranium reference standard solution (1000 mg/L) purchased from AccuTrace™ was used as uranium stock solution. All standard solutions were prepared in Milli-Q water and stored at 4-8 °C until use, as were the stock solutions. All other reagents were of commercial p.a. quality. Uranium and other element concentrations in synthetic water samples and solid peat samples were analyzed by S2 Picofox Total Reflection X-ray Fluorescence spectrometer (TXRF, Bruker).

In the case of peat, two-meter-long (diameter ca. 10 cm) sample column was collected from a drained Varkaansuo peatland in Kurkimäki nearby Kuopio. Peat samples for adsorption studies were selected from the top (Peat1), bottom (Peat 5) and three in the middle (Peats 2-4, depth: 0.5, 1.0 and 1.5 m) of the peat column representing different peat types and decomposition degrees of organic material. Typically, ca. 0.4 g of peat was mixed into 100 ml of water containing 10 mg L⁻¹ of uranium for 60 min.

WDAS used in this study was obtained from Viinikanlahti municipal wastewater treatment plant in Tampere. WDAS adsorption experiments were conducted in batch-type shake flasks with ca. 0.2 g (as volatile suspended solids) of WDAS varying initial solution pH (2.2-4.5), uranium concentration (3.3-119 mg L⁻¹) and reaction time (0-960 min), and in 900 mL fed-batch reactor operated with 3.1 mg L⁻¹ of uranium at initial uranium solution pH of 3.2 and varying hydraulic retention times (15-60 min). The experiments were conducted at room temperature (20±2 °C).

Result and discussion

In the case of peat, metal concentration of peat samples 1-5 were measured by using TXRF instrument. As shown in figure 1, amounts of metals are increased from top to bottom. Especially calcium, iron, strontium and lanthanum concentrations are increased dramatically (note that scale in figure 1 is logarithmic).

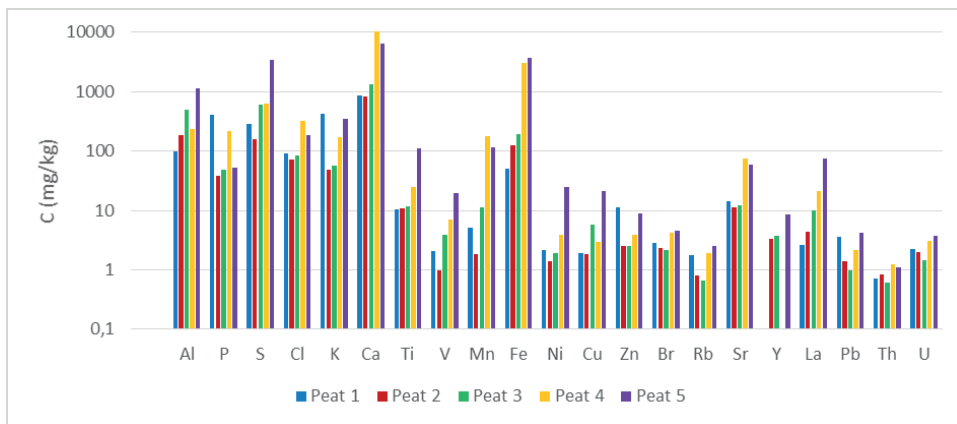


Figure 1. Element concentrations in peat samples.

In batch experiments with peat 96-100% of uranium was removed from the artificial sample solutions. All peat samples removed uranium effectively (Table 1), but the best removal was achieved with peat sample taken from 0.5 m depth. Removal of uranium took place slightly better at pH 7, but functioned well also at lower pH's (e.g. pH 3 in Figure 2).

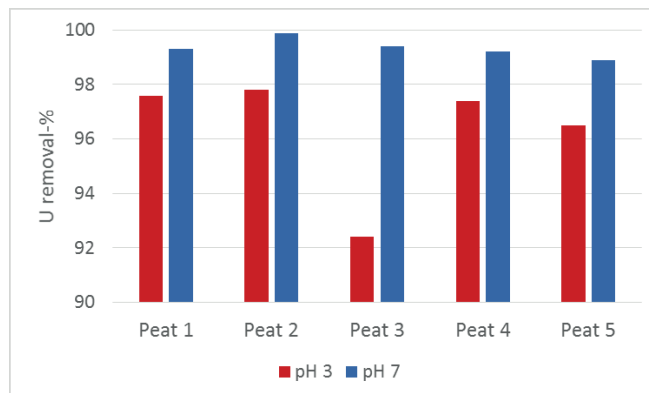
The equilibrium adsorption capacity (Q_e) of WDAS was 100 mg of uranium adsorbed per g of WDAS. The adsorption edge was found at pH 3.0 suggesting the applicability of the WDAS for the mining wastewaters which are generally acidic. Moreover, the fed-batch reactor with WDAS enabled more than 90% uranium removal efficiency even at a very short hydraulic retention time of 15 minutes.

Conclusions

This study indicates that both peat and WDAS are promising options for uranium removal from acidic mining wastewaters and provides a proof-of-concept for the development of a fed-batch system for WDAS based uranium removal.

Table 1. Removal of uranium by using peat.

Adsorbent	Depth (m)	Removal-%	
		pH 3	pH 7
Peat 1	0	97,6	99,3
Peat 2	0,5	97,8	99,9
Peat 3	1	92,4	99,4
Peat 4	1,5	97,4	99,2
Peat 5	2	96,5	98,9

**Figure 2.** Removal of uranium by using peat.

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