



Neutron activation analysis for the characterization of seawater uranium adsorbents

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HIGHLIGHTS

- Detailed an iterative NAA workflow to quantify metal uptake in organic adsorbents.
- Successfully characterized surrogate adsorbents for the recovery of seawater uranium.
- Eliminated adsorbent composition as a source of performance variability.
- Devised an improved form of adsorbent with decreased performance variability.

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ABSTRACT

This work details the development of an iterative neutron activation analysis (NAA) based workflow to precisely quantify metal ion uptake in an adsorbent. The workflow is iterative because it explores the dependence between independent variables defining the adsorbent fabrication procedure and the time-dependent uptake. It can be adapted to other adsorbents provided they have an affinity for ions which are amenable to efficient quantification using NAA. For this work, the ability of silver nanoparticles to mitigate the negative effects of biofouling on uranium transfer to an adsorbent was ultimately of interest, and hence motivates the development of this method. The limits of U detection and quantification were found to be 0.609 and 3.01 $\mu\text{g g}^{-1}$, respectively; these were obtained using modest irradiation and counting times. The uncertainties arising from the NAA procedure were no more than 9.9%, far smaller than other sources of uncertainty present in the analysis. These results provided solid evidence that adsorbent shape and structure, rather than uniformity of composition, drives variability in adsorption of uranium.

1. Introduction

The ability to economically recover the nearly limitless supply of uranium naturally contained within the world's oceans (Ku et al., 1977) can reduce long term uncertainty regarding the cost and sustainability of nuclear power. Recognizing the potential to dramatically alter the relationship between the fuel cycle and the recovery of naturally occurring radionuclides, a consortium of national laboratory and university partners, led by Oak Ridge and Pacific Northwest National Laboratories (ORNL and PNNL), has pursued the development of polymer fibers capable of passively adsorbing uranyl ions out of seawater.

A notable obstacle to the economic competitiveness of seawater uranium, which offers environmental and supply security benefits at any cost, is the hampering of adsorbent uptake due to marine biofouling (Byers and Schneider, 2016; Park et al., 2016; Kim et al., 2013). Therefore, work at the University of Texas ultimately seeks to mitigate this issue by applying the known antibacterial properties of silver

nanoparticles to this novel application.

Early experimentation identified reproducibility of adsorbent behavior in lab studies as a major hindrance in the ability to test the effectiveness of silver nanoparticles. Therefore this work set out to determine the cause of and ultimately reduce variability in adsorbent performance. Knowing that the adsorption equilibrium is governed by uranium concentration in solution and number of available surface binding sites (Caccin et al., 2013; Mellah et al., 2006), it is assumed that inconsistencies in adsorbent composition within and across adsorbent batches, due to inadequate mixing, drives the observed variance in adsorbent performance. Therefore this work details the development of a neutron activation analysis (NAA) based method for quantifying adsorbent inhomogeneity in an effort to normalize uptake results.

A previous publication identified NAA as a technique capable of measuring uranium uptake in surrogate adsorbents (Eder et al., 2017). This work thus builds on that conclusion by utilizing NAA to pre-characterize adsorbents in order to consider adsorbent performance in

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light of initial composition to examine correlation.

2. Methodology

Since the ORNL uranium adsorbent fibers are very costly to produce and require the use of specialized equipment, it was decided that surrogate adsorbent materials would be used when testing the efficacy of silver nanoparticles to restore capacity by providing a means of marine biofouling mitigation. Additionally, the relatively slow adsorption kinetics of ORNL adsorbent fibers led to the decision to seek surrogate adsorbents allowing the completion of uptake and fouling trials at a much faster rate and lower cost.

After a down selection of commercially available products, composites made of activated carbon in a high density polyethylene (HDPE) matrix were determined to be the most appropriate choice (Eder et al., 2017) to approximate the behavior of the amidoxime grafted HDPE adsorbents produced by ORNL. While there was no intention of producing ultra-fine fibers on the same scale as the ORNL materials, 20–30 μm (Das et al., 2015, 2016) methods of constructing adsorbent filaments with diameters of 1.75 mm were successfully achieved by combining a blend of HDPE and activated carbon using a single screw extrusion device.

2.1. Quantification of adsorbent uptake performance

NAA was hypothesized to be the analytical technique most suitable for quantifying uptake behavior due to its ability to detect the presence of an array of materials at sensitivities as low as nanograms per gram in solid and liquid samples. That notion was tested and confirmed in this work as well as in a previous publication (Eder et al., 2017). All irradiations were conducted using the 1.1 MW TRIGA Mark II reactor with pneumatic facilities available at the University of Texas Nuclear Engineering Teaching Laboratory (NETL). A previously published software, Neutron Activation Data Analysis (NADA), was used to employ a comparator method for the calculation of elemental concentration (Landsberger et al., 1992, 1994).

A time series exposure experiment was conducted to test the ability of NAA to measure the uranium uptake of unfouled adsorbents deployed in aqueous solution spiked to contain 1,000 $\mu\text{g g}^{-1}$ uranium. These batch experiments allowed for the analysis of uranium concentration at appreciating levels as well as establishment of a loading curve to attempt to identify the saturation point, which will be necessary in future fouling trials. The adsorbents used in these experiments contained 5 wt% activated carbon and were synthesized using 7 iterative extrusions in an effort to achieve homogeneity (Eder et al., 2017).

In quantifying the resulting uptake, a uranium daughter, ^{239}Np was used due to the very low energy, 74.7 keV, gamma rays emitted by ^{239}U , which are subject to high background noise, as well as the short half-life of ^{239}U , 25 min, which would require an inefficient manual irradiation and counting procedure. The gamma rays emitted by ^{239}Np are still relatively low energy, 277.6 keV, and are thus counted using a High Purity Germanium (HPGe) detector with a 30% efficiency and 2.0 KeV full width half maximum (FWHM) resolution for the 1332 KeV gamma ray of ^{60}Co .

2.2. Characterization of individual adsorbent filaments

Having initially hypothesized that variation in adsorbent behavior may stem from heterogeneous composition across adsorbent samples, a method of using NAA to trace individual adsorbent performance back to its specific composition was designed. The objective of this method was to determine the uptake of uranium per unit activated carbon, rather than on a per unit of adsorbent basis, in hopes of achieving a more Gaussian performance distribution. The inability of NAA to quantify isotopes of naturally existing carbon however presented an issue. Therefore, an observed ^{55}Mn impurity pre-existing in the purchased

Table 1
Neutron Activation Analysis parameters used for the characterization of individual adsorbent samples.

	Pre-deployment Characterization	Post-deployment Performance
Activation Reaction of Interest	$^{55}_{25}\text{Mn} + n \rightarrow ^{56}_{25}\text{Mn}$	$^{238}_{92}\text{U} + n \rightarrow ^{239}_{92}\text{U}$
Decay Observed for Counting	$^{56}_{25}\text{Mn} \rightarrow ^{56}_{26}\text{Fe}$	$^{239}_{93}\text{Np} \rightarrow ^{239}_{94}\text{Pu}$
Gamma Ray Analyzed	847 keV	278 keV
Neutron Energy	Thermal	Epithermal
Power Level	500	500
Irradiation Time (s)	1800	120

raw activated carbon was leveraged as a surrogate for activated carbon content in the fabricated adsorbent polymer matrix. This allowed for individual filament characterization by quantifying the ^{55}Mn content of each adsorbent filament to be deployed so the level of uranium uptake could be correlated to the relative activated carbon content.

The desire to quantify these two different isotopes of interest, each with their own unique NAA relevant characteristics, required the use of very different NAA parameters. The two different NAA techniques used to characterize adsorbent filaments before and after exposure to uranium spiked solution are outlined in Table 1 and will be described in further detail below.

The specific implementation of NAA used for elemental quantification of both ^{56}Mn and ^{238}U uptake in adsorbent filaments, previously discussed in Eder et al. (2017), left the analyzed filaments unsuitable for subsequent deployment in uranium spiked solution. Specifically, the use of the existing pneumatic system to insert and retrieve samples to and from the reactor core requires that each sample be contained in a polyethylene vial of height 5.5 cm. Furthermore, use of the HPGe detector to count the irradiated samples again requires the use of the small polyethylene vials. Once the filaments have been divided into these small pieces they are too small for deployment in the current aqueous exposure system. While the deployment system could be altered to accommodate the very small adsorbent filament segments, this was assumed to exacerbate variation within adsorbent samples. Therefore the means of both irradiating and counting were altered to be able to analyze filaments on the order of 15–20 cm long weighing around 0.3 g.

The rotary sample rack (RSR) at NETL allows for up to 30 samples to be co-irradiated as they circle around the outside of the core. The primary benefit of the RSR, in this particular application, is the larger size of the sample vessels, which are capable of housing an adsorbent sample of the aforementioned size in its entirety. Use of the RSR did present an obstacle with regards to the longer sample retrieval times. Unlike the pneumatic system, which automatically returns samples to the experimenter for counting within seconds after irradiation, the RSR requires manual unloading of the entire sample batch at once, which takes on the order of 30 min. This typically does not pose a problem as the RSR is intended for analysis of isotopes requiring long irradiation and counting periods. In this instance however, the 30 min delay time is somewhat of an obstacle, albeit non-insurmountable, given it comprises a non-trivial fraction of the 2.5 h half-life of ^{56}Mn . Additionally, the irradiation of all samples at once further extended the decay time between irradiation and counting, at least of the latter counted samples, as compared to the method of sequential irradiation followed by immediate counting of filaments, which is possible with the pneumatic system. Therefore calculations, and a trail experimentation, of the necessary power level and irradiation time were performed in order to secure a sufficient number of decays could be observed for the last sample counted.

The neutron flux experienced by samples inserted into the core at a power of 500 kW is approximately $2.25 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ (including thermal and epithermal neutrons) while those irradiated at 500 kW by

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