Investigating the potential for recovering REEs from coal fly ash and power plant wastewater with an engineered sorbent

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ABSTRACT

The global demand for rare earth elements (REE) has increased significantly in the past 20 years due to their extensive use in electronics and other applications. Although many recent studies related to quantifying rare earth elements in coal and coal combustion byproducts have been published, methods of extracting rare earth elements are still not economically feasible. The objective of our study is to investigate the potential extraction of the REEs from coal ash and from wastewater sludge collected from a power plant near Detroit, MI. The collected ash and sludge will undergo a hydrothermal extraction process developed by Los Alamos National Laboratory to extract REEs from the sludge or coal ash, resulting in a liquid enriched in dissolved REEs. Batch experiments were conducted using an organosilica adsorbent (Osorb®) and a ligand [P-di(2-ethylhexyl) methanediphosphonic acid (DIPEX)] to extract neodymium from a synthetic hydrothermal extraction solution. DIPEX-associated Osorb media was produced by first dissolving DIPEX into a solvent (e.g., methanol). Different amounts of DIPEX-methanol solution were then added to 0.2g of Osorb to determine the maximum sorption capacity. The methanol was evaporated and, after a rinse step, the DIPEX-Osorb sorbent was used in sorption experiments. A 300 ppm neodymium (Nd) synthetic ash/sludge leachate was tested with the various DIPEX-Osorb media. Results show that DIPEX-Osorb ratios of 4.3, 1.1, 0.5, and 0.05 mL/g sorbed 60, 51, 25, and 7 mg Nd per g media, respectively. Since the 4.3 mL DIPEX/g Osorb media sorbed 100% of the Nd in the solution, a higher capacity is expected and these experiments are ongoing. Breakthrough curve for of the sorption of Nd to Osorb was conducted and showed a higher sorption ratio when the Nd concentration increased. We are also investigating the reusability of the DIPEX-Osorb media by measuring how many cycles the media can be regenerated by extracting the Nd with nitric acid and reusing the sorbent for another cycle.

INTRODUCTION

Rare Earth Elements (REEs) which are lanthanides in addition to yttrium and scandium, play a huge role in the technology industry and are used in components in making several clean energy technologies (Bauer et al. 2010). In the US, 85- 90% of the REEs currently come from China (previously >95%), which creates production vulnerabilities for US technologies that require REEs (Haxel et al. 2002; Massari and Ruberti 2013). In 2010 the demand for REEs was 136,100 tons (Behrmann and Ratnam 2010), the demand for REEs is related to the demand for the end products that require REEs (Humphries 2013). REE extraction is also an energy intensive process that produces various hazardous waste streams, making it important to develop ways to extract REEs efficiently and more environmental friendly.

The world largest percentage of REEs resources are the bastnaesite deposits in the US and China, the second resource is the monazite deposits in several countries including US, China, Australia, Brazil and others (Xie et al. 2014). Newly discovered deposits in the Pacific Ocean near Japan may also add to global inventory, although extraction feasibility is still being investigated (Asanuma 2018). After the mining process, REEs must be extracted from the minerals. The main beneficiation techniques are froth flotation, magnetic, electrostatic, and gravity (Jordens et al. 2013), although strong mineral sorption (such as aqueous Nd sorption to dolomite) has also been observed (Emerson et al. 2018). The separation of REEs from each other can be achieved by ion-exchange and solvent extraction (Xie et al. 2014).

The research in this paper is part of a project that aims to investigate the feasibility of extracting REEs from coal ash, which is generated as a waste product from coal burning power plants. The amount of REEs in coal ash varies based on the source of the feed coal, moreover, power plants might blend more than one source of coal. The concentration of REEs in coal ash can reach up to 600 mg/Kg (Taggart et al. 2016) or even higher in some cases. For this project, coal fly ash samples were collected from power plants in the Detroit, MI area. After the characterization of the coal samples, a hydrothermal process developed and conducted at Los Alamos National Laboratory (LANL) is used to extract the REEs from the collected coal ash samples. The product of the hydrothermal process is a dissolved REE solution. The focus of this paper is the next step, which is to extract the dissolved REEs from the liquid to concentrate it on the surface of a sorbent. To accomplish this, we propose developing an enhanced sorbent media by associated selected ligands to an organosilica sorbent material. The selected ligands will attach to the organosilica through hydrophobic interactions and the dissolved REEs will bind to the attached ligand. This paper will discuss preliminary results for the extraction of a model REE (e.g., neodymium) from an aqueous solution.

MATERIALS AND METHODS

Batch experiments (Figure 1) were conducted to examine the feasibility of extracting neodymium (Nd) from an aqueous solution using an organosilica adsorbent (ABS Materials, Osorb®) and a ligand [P-di(2-ethylhexyl) methanediphosphonic acid (DIPEX)]. Dipex was developed as an extraction resin and has been used for the isolation of actinides from an aqueous solution (Horwitz et al. 1997). Osorb® is an organosilica adsorbent that swells when in contact with an organic solvent (Burkett and Edmiston 2005) and absorb up to six times its weight of solvent. Due to its hydrophobic nature, using water with dry Osorb will make the Osorb float (e.g., it will not be

wetted) and it will not swell. In the following experiments methanol was used as the organic solvent to wet the Osorb and allow for contact with the aqueous solution.

Figure 1. The Batch experiment consist of 50 ml tubes mounted on the rotator with Nd solution, Osorb, and Dipex.

Osorb®-ligand preparation

Reagent-grade methanol (Fisher Chemical) was used as the solvent to dissolve Dipex (Eichrom Technologies Inc). A stock solution was prepared by adding 1.0 g of Dipex to 45 mL of methanol. The stock solution was put on the rotator for 4 hours to make sure that the Dipex is completely dissolved. This stock solution was diluted with methanol to achieve different concentrations used in experiments. Next, 0.2 gram amounts of Osorb were weighed and added to eight polypropylene 50 ml centrifuge tubes. All samples were prepared in duplicate. Various volumes of the diluted stock solution were then added to each tube to achieve a range of final Dipex concentrations (e.g., 0.088, 0.022, .011, and 0.001 grams Dipex / ml methanol).The centrifuge tubes with Osorb and dipex-methanol solution were put on a tube rotator (Fisher Scientific, Fisherbrand) for 24 hours.

After 24 hours of rotation, the centrifuge tubes were removed from the rotator and placed in a vacufuge (Eppendorf, Figure 2) to evaporate the methanol. This is based on the hypothesis that the Dipex will now be loaded on the Osorb surface and no longer dissolved in the methanol. It took roughly 4 hours to evaporate the 10 ml of methanol remaining in solution. To make sure no excess Dipex was in solution, the contents of each tube was washed with 20 ml of ultra-pure water (<18 MΩ cm resistivity). After rinsing, the Osorb-Dipex media particles were left to settle and were ready for use in sorption experiments

Sorption Experiments (control)

Before testing the Dipex- Osorb media for the ability to extract Nd from the solution, control experiments were conducted to evaluate the Nd sorption capacity of Osorb without Dipex added. 0.2 g amounts of Osorb were added to six 50 ml polypropylene centrifuge tubes (3 sets of 2 to serve as duplicates). To wet the hydrophobic Osorb, 10 ml of methanol was added to each tube

and rotated for 24 hours. After 24 hours, the methanol was evaporated using a vacufuge (**Figure *2*Figure *1***) A 300 ppm solution of Nd was made by diluting a 10,000 ppm Nd inductively coupled plasma-mass spectrometry (ICP-MS) standard (High Purity Solutions) with high-purity water. Forty ml of 300 parts per million (ppm) Nd solution with different pH values was added to each tube and rotated for another 24 hours. The pH of the 300 ppm Nd solution was 1.93, and was adjusted up or down using sodium hydroxide (NaOH) and Nitric acid (HNO_3), respectively. The solution (1 ml) from each tube was filtered using a 0.2 µm nylon filter (Basix, 13-1001-08) to be analyzed for Nd concentration using ICP-MS.The results measured from the ICP-MS represent the amount of Nd that was not sorbed to the Osorb.

Sorption Experiments (Dipex-Osorb media)

40 mL of 300 ppm Nd solution (prepared by diluting 10,000 mg/L Nd with high-purity water) was combined with 0.2 g of Osorb-Dipex media in 50 ml polypropylene centrifuge tubes. Two blanks (centrifuge tubes without Osorb-Dipex media) were used with the same Nd concentration to measure sorption to the vessel walls.

Figure 2. The evaporation of methanol from the 50 ml tubes.

After the 24 hours of rotation, ~1 ml of each sample was filtered using 0.2 µm nylon filters, which is a small enough pore opening to ensure the solution is free of Osorb. This 1 ml of filtered solution was used to prepare two sets of dilutions for each sample in a 2 % trace metal nitric acid to be analyzed using ICP-MS. The calibration standard used for ICP-MS was IV-71 (Inorganic Ventures Inc.) and the concentrations ranged from 0.005 µg/L to 200 µg/L. Two standard verification samples and two blanks were added to the analysis in the beginning and after every 10 samples to ensure minimal drift. Results were obtained from the ICP-MS and interpreted.

To examine the desorption of the Nd, we started by using 40 mL of a low concentration nitric acid (~0.1 M). Next, all the samples were decanted and then 40 mL of 2% nitric acid was added to each tube and rotated for 24 hours. ~1 mL of solution was then filtered using 0.2 µm

nylon filter and samples were diluted and analyzed on the ICP-MS to measure the Nd desorbed from the Osorb-Dipex media into the 2 % nitric acid.

RESULTS AND DISCUSSION

Using Osorb as an extractant without adding any ligand showed a small amount of sorption (Figure 3). Over a range of pH from 1-5, the percentage of sorption did not exceed 13 %. Thus, using Osorb alone will not be beneficial as an extractant for Nd.

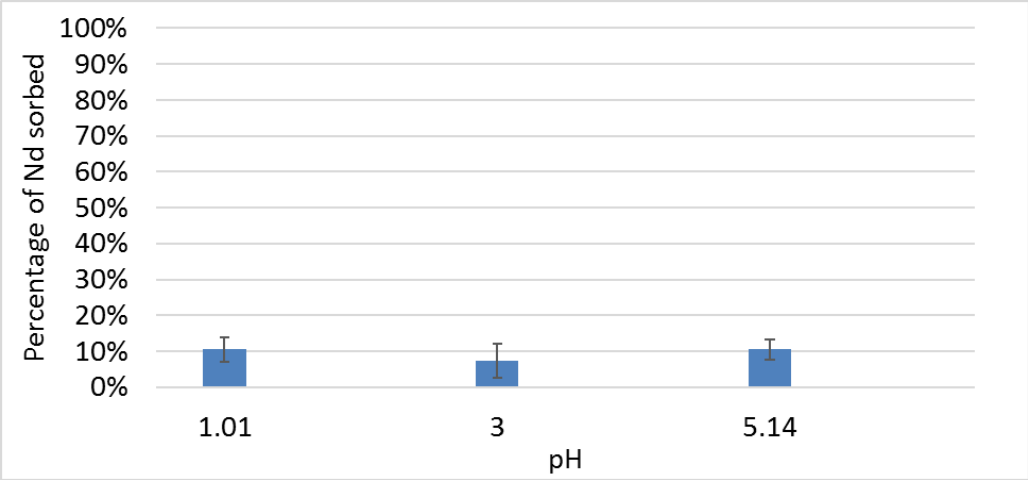

Figure 3. Nd (300 ppm) at different pH using around 0.2 g Osorb.

Dipex concentrations are reported as a Dipex to Osorb ratio. The four sets of samples resulted in four ratios of 4.45, 1.11, 0.55, and 0.055 grams Dipex to grams Osorb. The Dipex /Osorb ratio effected the percentage of Nd sorption as seen in Figure 4. The higher the ratio the higher the sorption until the point where almost all the Nd in solution was sorbed to the media. The error bars in the graph represent the range resulting from the duplicates.

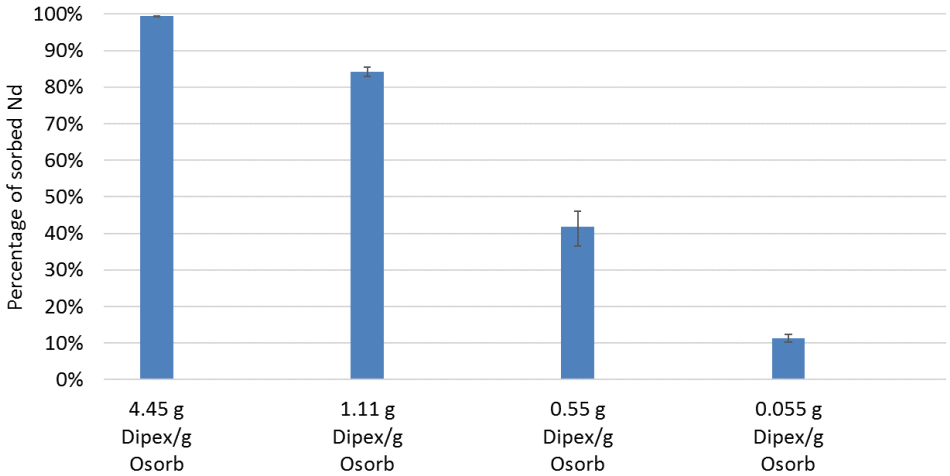

Figure 4. Percentage of Nd sorbed at different Dipex/Osorb ratios.

Starting from the highest Dipex concentration, the amount of Nd sorbed to the Osorb were 57, 52, 26, and 7 mg Nd/g Osorb, respectively. The 4.5 ratio and 1.1 ratio show sorption greater

tan 80% even though the Dipex loading is almost 4 times higher in the 4.5 ratio sample. This is a result of the solution not having an excess of Nd. This suggest that the 100% sorption might be achieved at lower ratio than 4.45 g Dipex/g Osorb, thus, an optimization of the Dipex / Osorb needs to be further investigated.

To have a media that can be used repeatedly (e.g., cycled between sorption, desorption and reuse), a desorption of Nd from the media is an essential goal. Different methods can be used to examine the desorption of Nd; however, we used 2% nitric acid after decanting the solution from the 1.1, 0.6, and 0.06 Dipex/Osorb samples.

Figure 5 shows that the recovery of Nd varies at different Dipex to Osorb ratio. The media with higher concentrations of Dipex desorb less Nd that the lower concentration in a mass basis. This indicates that high ratios sorb Nd very well but make it difficult to recover the Nd with 2% nitric acid. Alternatively, the sample with lowest Dipex to Osorb ratio desorbs more than 80% of the sorbed Nd. A higher concentration of acid has not yet been examined.

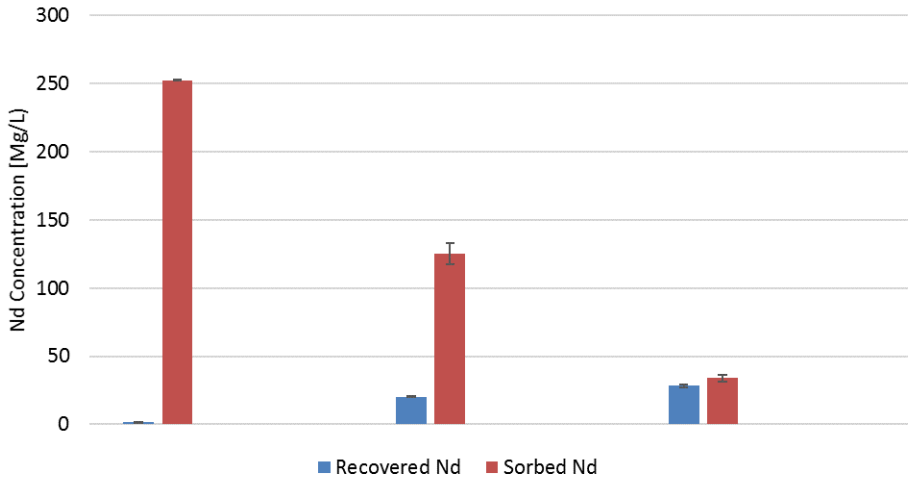

Figure 5. Concentrations of sorbed and recovered Nd

Additional experiments must be conducted to evaluate the kinetics of Dipex loading onto the Osorb surface. For the results shown in this paper, we used 24 hours of contact time, but preliminary kinetic results suggest the loading take much less than 24 hours.

CONCLUSION

Coal ash is considered a potential source of REEs that warrents further investigation. We have demonstrated a proof-of-concept idea to extract the REEs from an aqueous solution that would result from the hydrothermal extraction of REEs from coal ash. An organosilica adsorbent (Osorb®) and a ligand [P-di(2-ethylhexyl) methanediphosphonic acid (DIPEX)] were used to form the concetrating media. Dipex was dissolved in methanol and loaded on the Osorb surface. Nd solution was then added to the media. Different Dipex to Osorb ratios resulted in different percentages of Nd sorption with higher ratios resulting in a higher sorption percentage. Our results demonstrate an media that could reach up to 57 mg Nd/g Osorb. It can be concluded that loading Dipex to the Osorb will increase the extraction significantly. The desorption of Nd from the media was also studied, using 2% nitric acid as a desorption solution, although the recovery was low for

the samples that extracted higher amount of Nd. However, 2% nitric acid desorbed most of the Nd from the low Dipex to Osorb media.

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