analytical chemistry

Letter

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Photoinitiated Polymerization of 4-Vinylpyridine on polyHIPE Foam Surface toward Improved Pu Separations

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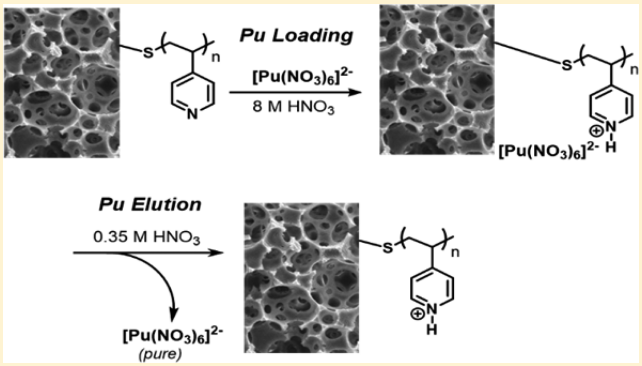
Supporting Information

ABSTRACT: The separation of hazardous metals from contaminated sources is commonly achieved with ion-exchange resins. The resins have a high surface area decorated with many ion-exchange sites and thus a high sorption capacity for the analyte of interest. However, these sites are primarily accessed by diffusion which limits the throughput and quality of the separation. Reported herein is a study of monolithic polyHIPE foam columns surface-grafted with a brush of polymer containing ion-exchange functionality for the separation of Pu. It was found that the loading curves of the foam material are steeper than a similarly scaled resin-based column, and the elution profiles of the foams were narrower than the resin, generating more concentrated eluate relative to the amount of Pu loaded onto the foam columns. On a gravimetric basis, the foams had a similar or greater Pu capacity than the resin with fewer ion-exchange sites per unit mass. These characteristics are mainly due to the convective mass transport which dominates the separation in the polyHIPE materials, suggesting that these materials may be useful for more efficient hazardous metal separations.



Because of their versatility, polymeric high internal-phase emulsion (polyHIPE) foams have garnered attention for many diverse applications including flow-through chemistry,[1−3] separation media and supports for biomolecules,[4−6] sequestration of small organic molecules,[7] and ion-exchange supports to separate metals[8−13] and other ions.[14−16] Materials known as polyHIPE foams are macroporous, emulsion-templated polymeric materials formed from an emulsion with an internally dispersed phase, which is greater than or equal to 74% of the total emulsion by volume.[17] Upon curing, an interconnected pore morphology can be formed with pore sizes on the order of 10−250 μm.[17−20] By virtue of the synthetic process used to make polyHIPE foams, structural parameters such as pore volume fraction, pore connectivity, pore size, and surface functionality are each highly tunable.[21,22] In addition to the synthetic ease of modifying these parameters, polyHIPE foams are particularly well-appointed for separations processes because of the ability to incorporate chemical functionality on the surface of the macropores which has the effect of minimizing diffusional path lengths and allowing for almost no chromatographic overlap as a result of convective mass transport.[23]

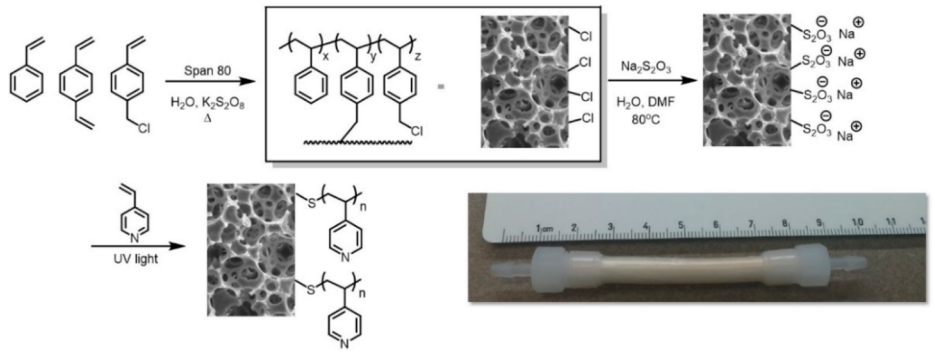
Ion-exchange processes used to remove hazardous metals from contaminated sources commonly rely on the use of polymeric resins which have been extensively studied and produced commercially.[8,9] The bulk of ion-exchange sites contained within the resin beads are accessed by diffusion into small pores on the surface. The use of smaller beads has the benefit of shorter ion diffusion path lengths; however, in a packed-bed column the use of small beads results in high column backpressures.[24] In applications where high backpressure is undesirable or impractical, larger beads are used at the expense of longer ion diffusion path lengths which creates the need for longer contact times with the resin to complete the ion-exchange process.[24] Ideally, ion-exchange materials should rely minimally on diffusive mass transport and instead employ a primarily convective mechanism of mass transport to maximize throughput and separation efficiency.[24]

A promising alternative to ion-exchange resins are polyHIPE foams surface-functionalized with ion-exchange sites on the surface of the macropores.[24] To date, most functionalized polyHIPE foams synthesized and tested for ion-exchange applications have monomeric ion-exchange or other functionality tethered or coated onto the foam surface to perform the separation.[8−16] Described herein is an approach which takes advantage of the convective mass transport offered by the polyHIPE foams and introduces ion-exchange functionality onto the surface of the foam by growing a "brush" of polymer

Received: March 28, 2017
Accepted: April 29, 2017
Published: April 30, 2017

 © 2017 American Chemical Society DOI: 10.1021/acs.analchem.7b01153

Scheme 1. Synthetic Route to Prepare HIPE Foams with Surface-Grafted Chains of Poly(4-vinyl pyridine) (P4VP) and Monolithic Column Prepared for Testing (Inset)



chains from surface initiating sites in a similar manner to previous reports.[12,25−27] Use of a functional monomer endows each repeat unit of the grafted chains with ion-exchange functionality. The aim of this work is to better understand the parameters which will result in a more efficient ion-exchange process and to gain an understanding of the separation characteristics under flow conditions of this type of material. The specific application being studied is the purification of plutonium by anion-exchange utilizing a quaternary amine functional group.

EXPERIMENTAL SECTION

Materials and Instrumentation. All materials were purchased from either Sigma-Aldrich or McMaster-Carr and were used as received unless otherwise specified. Prior to use, styrene, 4-vinyl benzyl chloride, and divinylbenzene (mixed isomers) were each passed through a column of basic alumina to remove the inhibitor. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol and stored at −30 °C prior to use. 4-Vinylpyridine was distilled under reduced pressure and stored under nitrogen prior to use. Scanning electron microscopy (SEM) images of the foams were observed with a Zeiss Ultraplus thermal field emission SEM using an acceleration voltage of 8 kV. Prior to SEM imaging, the foam samples were rendered conductive via sputter coating using a Pd/Au target. Elemental analysis was performed at Midwest Microlab, Indianapolis, IN. Pu concentration was determined by gamma spectroscopy using either a Canberra or Ortec high-purity germanium detector instrument.

Preparation of polyHIPE Foam Monoliths. The general procedure for the synthesis of each polyHIPE foam monolith is as follows. The components of the oil phase including styrene (0.68 g, 45 wt %), divinylbenzene (0.378 g, 25 wt %), 4-vinyl benzyl chloride (0.453 g, 30 wt %), sorbitan monooleate (SPAN 80, 0.288 g, 20 wt % relative to monomers), and AIBN (0.010 g) as initiator were weighed out and combined in a small resin kettle equipped with a glass paddle stirrer. The aqueous phase comprised of distilled water (15 g) was placed in a dropwise addition funnel and was added slowly to the stirring oil phase (350 rpm) over the course of 15 min. After complete addition of the aqueous phase, the resulting emulsion was allowed to stir 5 additional minutes to ensure even mixing. The resulting emulsion was deposited via a syringe into thin glass tubing and cured overnight at 70 °C. The monoliths were removed from the glass tubes by breaking the glass and were washed for 24 h in a Soxhlet extractor with ethanol as the extraction solvent. The monoliths were dried overnight in an 80 °C oven prior to further use.

Reaction of Surface Chloromethyl Groups with Sodium Thiosulfate. Approximately 0.5 g of polyHIPE foam monoliths were added to a 250 mL round-bottom flask equipped with a 1-in. magnetic stir bar. To the flask was added 100 mL of a 50/50 (%v/v) mixture of distilled water and *N*,*N*-dimethylformamide and 1.6 g (excess) of anhydrous sodium thiosulfate. The contents of the flask were allowed to stir slowly overnight at 70 °C. The resulting thiosulfate modified foams were washed for 24 h in a Soxhlet extractor with ethanol as the extraction solvent, then dried in an 80 °C oven overnight prior to further use. Successful thiosulfate modification was confirmed via elemental analysis (Table S1).

UV-Initiated Surface Polymerization of P4VP. A monolith of thiosulfate-functionalized polyHIPE was placed into a 25 mL Schlenk flask equipped with a rubber septum and a glass stopcock. The foam was deoxygenated by 3 cycles of evacuating and backfilling with nitrogen. Freshly distilled 4-vinylpyridine (∼3 mL) was added via gastight syringe to saturate the prepared monolith. The flask was sealed under nitrogen then placed 10 cm from a high intensity UV lamp for varying time intervals. After the surface polymerization was complete, the monoliths were washed for 24 h in a Soxhlet extractor with ethanol as the extraction solvent.

Assembly of Column Prototypes. The column prototypes were prepared using the following procedure. The foam monolith was first wrapped in a layer of PTFE tape, encapsulated in one layer of PVDF heat-shrink tubing, then one layer of high-strength heat shrink tubing. PVDF hose connectors were attached to the end of the column and secured with one additional layer of high-strength heat shrink tubing. Specific column dimensions for each sample are shown in Table S1.

Pu Uptake and Elution Studies. Plutonium sorption capacity and elution characteristics of the synthesized materials were studied using a feed solution of 3.28 g/L Pu solution in 8 M nitric acid which approximates the conditions for this separation process at the Savannah River Site. The feed solution was treated with ascorbic acid prior to use to reduce any Pu(VI) to Pu(III). Upon adjusting the acid concentration to 8 M, the Pu(III) was oxidized to Pu(IV), forming the $[Pu(NO_3)_6]^{2-}$ complex which readily loads onto the anion exchange sites. Each prepared column was first conditioned with approximately 10 mL of 8 M nitric acid using a syringe pump at a flow rate of 0.75 mL/min to protonate the pyridine groups and to flush any water or dilute acid from the material.

DOI: 10.1021/acs.analchem.7b01152

Table 1. Chemical and Physical Characteristics of Synthesized polyHIPE Foam Columns and Reillex HPQ

sample	internal phase (vol %)	cross-linker content (wt %)	weight gain (%)	polymerization time (h)	% N	density[b] (g/mL)
A	89	25	0	0	0	0.077
B	89	25	34	6	3.58	0.111
C	89	25	70	10.5	5.54	0.136
D	89	25	77.2	10.5	6.24	0.152
Reillex HPQ		25			8.75[a]	0.890

[a]Calculated theoretical value for nitrogen content. [b]Calculated from column dimensions listed in Table S1

The Pu feed solution was then fed at 0.5 mL/min, and 1 mL aliquots were collected until breakthrough was observed visually, followed by a 10 mL wash of 8 M nitric acid at a flow rate of 0.75 mL/min to remove any impure solution, in effect purifying the loaded Pu. The sorbed Pu was then eluted by flowing 0.35 M nitric acid through the column at a flow rate of 0.5 mL/min with 1 mL aliquots taken until elution was complete. The low nitrate concentration allowed the Pu complex to desorb from the anion exchange sites to be collected in a purified form. The sorption and elution results of these experiments were compared to a similarly scaled glass column packed with Reillex HPQ ion-exchange resin which was also tested using the procedure described above.

RESULTS AND DISCUSSION

To study the sorption and elution properties of the P4VP-grafted polyHIPE foams, a series of P4VP-grafted polyHIPE foam columns with differing nitrogen contents were prepared according to Scheme 1. The physical and chemical characteristics of the synthesized materials are shown in Table 1. Differing nitrogen content between samples correlates to the amount of grafted P4VP, since there was no nitrogen present in the unmodified material. The typical open-celled morphology of the polyHIPE foams pre- and post- surface polymerization are shown in Figure 1. Surface modification of the polyHIPE

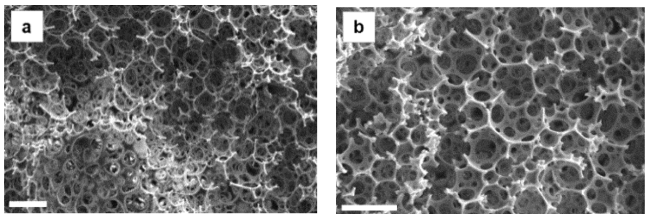


Figure 1. Representative SEM images of polyHIPE foams (a) before surface polymerization and (b) with grafted P4VP (scale bars are 20 μm).

with grafted P4VP appeared to slightly smooth the surface texture which was observed by microscopy (Figure S1), and the open-celled morphology generated by nearly 90% internal phase in the initial emulsion was amenable to flow testing.

The loading and elution characteristics of the grafted polyHIPE foam columns were tested using prepared columns which were subjected to a similar procedure used for the ion-exchange separation of Pu at the Savannah River Site. These results were compared to the same testing of a similarly scaled column of the ion-exchange resin currently used for this separation, Reillex HPQ (an N-methylated cross-linked P4VP resin). Because of the similarity in functionality between the resin and the grafted P4VP chains, the reactivity of the resin and the grafted chains was expected to be very similar (the grafted P4VP became quaternized under the strongly acidic conditions of the feed solution). It has been previously demonstrated that this type of material demonstrates faster uptake kinetics than resin materials bearing similar functionality.[12] The loading and elution data for the synthesized columns are shown in Figure 2. Because of a large difference in

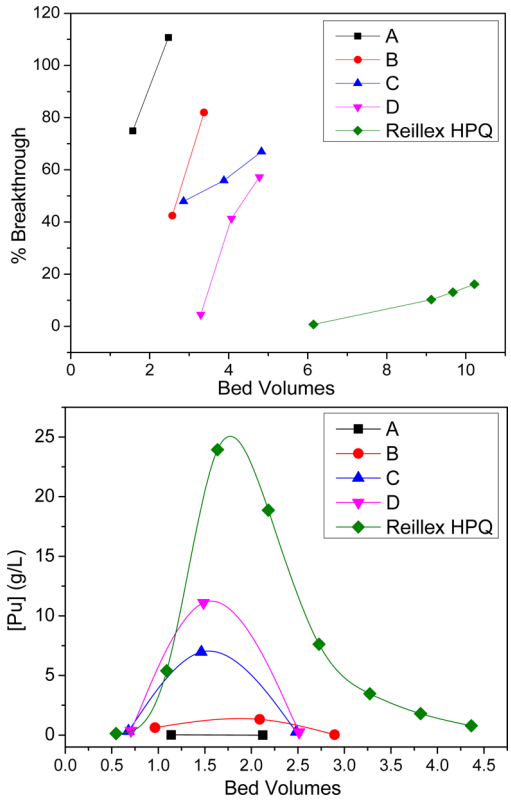


Figure 2. Pu loading curves for foam and Reillex HPQ columns (top) and Pu elution curves for foam and Reillex HPQ columns (bottom).

density between the foam materials and the resin (Table 1), both loading and elution characteristics were plotted as a function of bed volume so that the materials were compared on a volumetric basis.

In general, as the nitrogen content of the foam samples increased (indicative of larger amounts of grafted P4VP), the number of bed volumes until breakthrough also increased which indicates that the amount of grafted P4VP is correlated with the capacity of the material. In this case, % Breakthrough is defined as the concentration of Pu detected in the collected eluate divided by the initial concentration of the feed. Compared to the Reillex HPQ, which has a theoretical nitrogen content of 8.75%, the volumetric capacity of the polyHIPE with the largest amount of grafted P4VP (Sample D, Figure 2, top) was about half the volumetric Pu capacity of the resin, and the breakthrough curves of the foams are noticeably steeper than

DOI: 10.1021/acs.analchem.7b01152

the resin. The steepness of the curves is likely an artifact of the difference in mass transport between the materials. Because of the convective mass transport employed by the foams, the ion-exchange sites were efficiently used until no more existed. This process caused a steep breakthrough curve for the foam samples once all sites were used while the resin had more of a gradient breakthrough trend due to diffusional mass transport. The elution profiles (Figure 2, bottom) more clearly demonstrate the advantage of the foam over the resin. The complete elution of adsorbed Pu was completed in less than two bed volumes on average for the P4VP-grafted polyHIPE foams compared to nearly 4 bed volumes for the resin. The demonstrated narrow elution profiles are a substantial improvement in the efficiency of the separation because the separated material is obtained in a more concentrated form relative to the Pu eluted from the resin (which shows an elution tail, diluting the eluate).

When these two types of materials were compared on a gravimetric basis (the mass of Pu sorbed per gram of material), the foam demonstrated a higher Pu capacity than the resin even with relatively modest amounts of grafted P4VP (Figure 3). In applications such as capture and storage, the mass fraction capability is important to consider in minimizing the amount of hazardous material which must be sequestered. Because the Pu is sorbed by the grafted chains which are in a solution-like environment, all ion-exchange sites are more freely accessible which helps explain why the foam, despite having modest levels of grafted P4VP (and fewer ion exchange sites per unit mass) compared to the resin, exceeded the sorption capacity of the resin on a gravimetric basis.

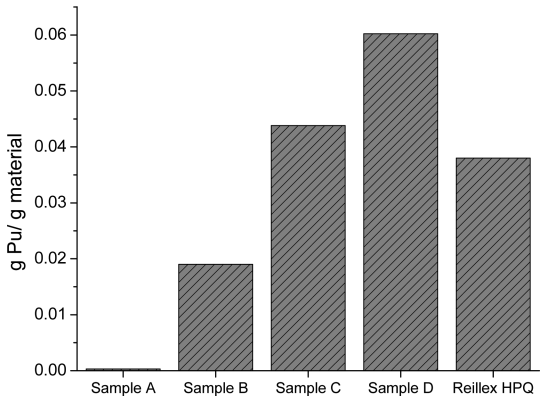


Figure 3. Gravimetric comparison of Pu loading between foam columns and Reillex HPQ resin.

CONCLUSIONS

This work demonstrated the potential for polyHIPE foams surface-grafted with polymers containing ion-exchange functionality to improve the efficiency of the current resin-based ion-exchange separation of Pu from contaminated sources. Because of the convective mass transport afforded by the macroporous structure of the polyHIPE materials tested, the loading curves were steep and the elution profiles were narrow relative to the resin material currently used for this separation. The Pu sorption capacity of the polyHIPE foam increased as the nitrogen content of the foam increased, suggesting that sorption capacity and amount of grafted polymer are correlated. On a gravimetric basis, the polyHIPE foams demonstrated a higher Pu capacity than the resin which could prove useful for capture and storage applications of hazardous materials. Further inquiry into the synthesis of these materials with the goal of incorporating more functionality (either higher density of surface chains or higher chain molecular weights) could give materials with equal or greater volumetric sorption capacity with the advantage of recovering more concentrated Pu during the elution step compared to the resin. It is also possible that tailoring the chemistry of the grafted polymer for other types of separations could render this material useful for other separation processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b01153.

Column dimensions, additional elemental analysis data, and high magnification SEM images of foam surface before and after polymer modification (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this work from Savannah River National Lab LDRD Program No. LDRD-2016-00026.

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DOI: 10.1021/acs.analchem.7b01152