



Selective removal of lanthanides from natural waters, acidic streams and dialysate

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ABSTRACT

The increased demand for the lanthanides in commercial products result in increased production of lanthanide containing ores, which increases public exposure to the lanthanides, both from various commercial products and from production wastes/effluents. This work investigates lanthanide (La, Ce, Pr, Nd, Eu, Gd and Lu) binding properties of self-assembled monolayers on mesoporous silica supports (SAMMSTM), that were functionalized with diphosphonic acid (DiPhos), acetamide phosphonic acid (AcPhos), propionamide phosphonic acid (Prop-Phos), and 1-hydroxy-2-pyridinone (1,2-HOPO), from natural waters (river, ground and sea waters), acid solutions (to mimic certain industrial process streams), and dialysate. The affinity, capacity, and kinetics of the lanthanide sorption, as well as regenerability of SAMMS materials were investigated. Going from the acid side over to the alkaline side, the AcPhos- and DiPhos-SAMMS maintain their outstanding affinity for lanthanides, which enable the use of the materials in the systems where the pH may fluctuate. In acid solutions, Prop-Phos- and 1,2-HOPO-SAMMS have differing affinity along the lanthanide series, suggesting their use in chromatographic lanthanide separation. Over 95% of 100 µg/L of Gd in dialysate was removed by the Prop-Phos-SAMMS after 1 min and 99% over 10 min. SAMMS can be regenerated with an acid wash (0.5 M HCl) without losing the binding properties. Thus, they have a great potential to be used as in large-scale treatment of lanthanides, lanthanide separation prior to analytical instruments, and in sorbent dialyzers for treatment of acute lanthanide poisoning.

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1. Introduction

Lanthanide-based materials are gaining increasing importance, both in terms of research activity, and in terms of commercial products [1]. For example, the electroluminescent properties of various lanthanide complexes have made them popular as emitters in electroluminescent devices [2–6]. Lanthanide-based reagents have also become increasingly popular in organic synthesis [7,8], as well as asymmetric catalysis [9,10]. Lanthanides are an important component of plastic fiber optic lasers [11], ionic conducting oxides (a key component of fuel cells) [12], MOCVD of oxides used in microelectronics [13], and even liquid crystals and surfactants [14].

This increased demand for the lanthanides means two things—increased production of lanthanide containing ores (i.e. mining), and increased public exposure to the lanthanides, both from various commercial products and from production

wastes/effluents. Increased mining activity has been shown to result in increased rare earth releases and mobility, whether this mining is of the rare earth materials themselves [15], of other metals [16–19] or even coal [20,21]. In regions with high levels of rare earth elements (REE), elevated levels of REE are found in humans [15,22], and other organisms [23]. Metabolism and toxicity of rare earth compounds was previously reviewed [24]. Recent toxicology studies of the rare earth chlorides have shown that as a group they tend to have similar toxicities, and are similar to CdCl₂, which has long been considered toxic [25].

Historically, lanthanide separations have commonly focused on purification of the raw ore (e.g. [26,27]), or separation of the lanthanides from spent nuclear fuels (e.g. [7,28]). These studies commonly focused on ligand design and solvent extraction studies (e.g. [29,30]), solid-phase extraction (e.g. [31,32]), or chromatography (e.g. [33,34]). As a general statement, these methods are not amenable to large-scale treatment of contaminated groundwater or drinking water. Purification of water contaminated with lanthanides requires the ability to selectively remove the lanthanides in the presence of common, harmless ions like Ca and Mg. Therefore,

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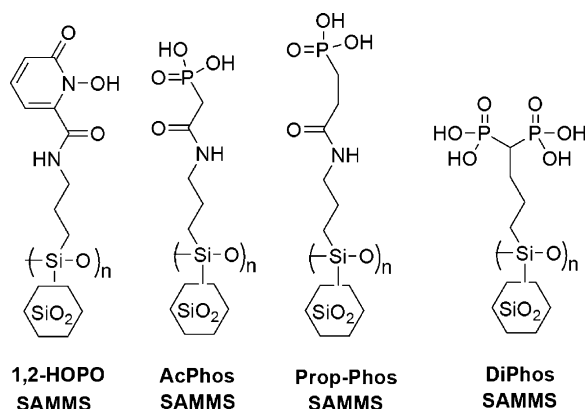


Fig. 1. Chemical structures of SAMMS with various organic groups.

it may be of value to design and build a chemically selective sorbent material, capable of selectively sequestering the lanthanides from waste streams, ground water and drinking water, without the need for any additional reagents, solvents, or treatment processes.

Self-assembled monolayers on mesoporous supports (SAMMSTM) are versatile functional materials. Simply by varying the terminal functionality of the monolayer interface, it has been possible to tailor the affinity of these nanoporous sorbent materials to very effectively capture “soft” heavy metals [35–38], oxometallate anions [37,39–43], radioiodine [44,45], and cesium [46]. Of particular relevance to this discussion is the demonstrated ability of certain “flavors” of SAMMS to bind the rare earth actinides [47,48] and lanthanides [49,50]. However, it is important to recognize that the previous work focused on design and synthesis of the materials. Also sorption characterization has been done in simple laboratory buffers, and matrix effects (in particular complexing anions) are known to have a significant impact on lanthanide speciation, and therefore chemical behavior.

This manuscript summarizes our studies using these nanoporous sorbent materials to sequester lanthanides from acidic streams (to mimic industrial wastes), natural waters, and dialysate, the latter two contain strong complexing anions for lanthanides, including carbonate [51], phosphate [52], and sulfate [53]. Successful capturing of lanthanides from these matrices will provide a complete strategy for managing of lanthanides from lowering discharge levels (e.g. waste water treatment), lowering environmental exposure levels (e.g. lanthanide removal from drinking and natural waters), to treatment of lanthanide poisoning (e.g. with sorbent dialysis).

2. Experimental

2.1. Sorbent materials

Synthesis and characterization of functional mesoporous silica materials were described elsewhere, including those functionalized with acetamide phosphonic acid (AcPhos) [49], propionamide phosphonic acid (Prop-Phos) [49], and 1-hydroxy-2-pyridinone (1,2-HOPO) [50]. The chemical structures of the SAMMS materials are presented in Fig. 1. For comparison, high surface area activated carbon (Darco KB-B, Sigma–Aldrich) were also tested along with the SAMMS materials.

2.2. Test matrices

Batch metal sorption experiments were performed with natural waters, simulated acid wastes, and dialysate. The natural waters include river water (Columbia River, Richland, WA),

seawater (Sequim Bay, WA), and groundwater (Hanford, WA) which were used after filtering through a 0.45 μm cellulose membrane (MF-MilliporeTM). Simulated acid wastes include pH-adjusted 0.1 M nitrate (0.01 M HNO_3 /0.09 M HNO_3 , pH 1.82) and 0.1 M chloride (0.01 M HCl /0.09 M NaCl , pH 2.42). The dialysate (PrismaSate[®], BGK4/2.5 from Gambo Inc., Lakewood, CO) consists of 2.5 mequiv./L of Ca^{2+} , 1.5 mequiv./L of Mg^{2+} , 140 mequiv./L of Na^+ , 4 mequiv./L of K^+ , 113 mequiv./L of Cl^- , 3 mequiv./L of lactate, 32 mequiv./L of HCO_3^- , 110 mg/dL of glucose, and osmolarity of 300 mOsm/L.

2.3. K_d measurements

For K_d measurements, the test solutions were spiked with trivalent lanthanides (La, Ce, Pr, Nd, Eu, Gd and Lu) to obtain 50 $\mu\text{g/L}$ each. After 30 min of incubation, it was aliquoted into 4.9 mL volumes in a 20 mL polypropylene vial. The solution was then spiked with 0.1 mL of a suspension of solid sorbent and deionized distilled (DI) water at liquid per solid ratio (L/S in the unit of mL/g throughout) of 100. This resulted in a final L/S of 5000. The sample was then shaken for 2 h at 160 rpm on an orbital shaker. After 2 h, the solution was removed by filtering thru 0.20- μm syringe Nylon-membrane filters and the filtrate was kept in 1 vol.% HNO_3 prior to the analysis of lanthanides. The control was performed in the same fashion but without solid sorbent. The filtrates from the controls were analyzed against the starting solutions to ensure no lanthanide precipitation. The lanthanides were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA). All batch experiments were performed in triplicates and the averaged values were reported.

2.4. Sorption capacity

The sorption capacity of each material for lanthanides was measured in the same fashion as with the K_d , but only a single element was used and its concentration was varied in the solution until maximum sorption capacity was obtained. This was accomplished by using a large excess of the lanthanide to the number of binding sites on the sorbent materials (e.g. 0.1–5 mg/L of lanthanides at L/S of 100,000).

2.5. Sorption kinetics

The kinetics of lanthanide sorption was performed in the same fashion as with the equilibrium studies except that 1 mL of well-mixed aliquot was removed and filtered at 1, 2, 5, 10, 30, 60 min, 1, 8, and 24 h and the initial sample volume was increased to 50 mL to minimize the change in L/S.

2.6. Regeneration

Six cycles of Gd adsorption and desorption on Prop-Phos-SAMMS were performed to assess its ability to be regenerated and its effectiveness after the regeneration. For the adsorption step, 10 mL of 230 $\mu\text{g/L}$ of Gd in dialysate was passed through the bed of 0.01 g Prop-Phos-SAMMS at the flow rate of 2 mL/min and the filtrate was collected for Gd and Si analysis. For the regeneration step, 40 mL of 0.5 M HCl was passed thru the same bed at 4 mL/min and the filtrate was collected for Gd and Si analysis. The cycles were repeated for six times.

3. Results and discussion

The adsorption of lanthanides by sorbent materials was evaluated as follows.

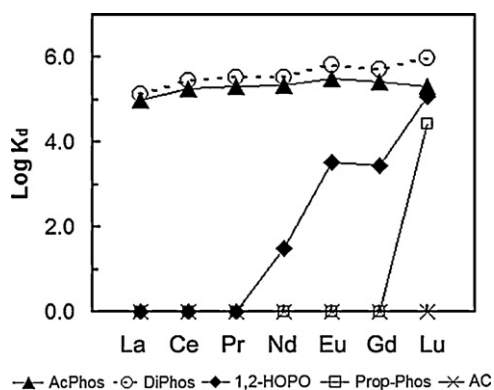


Fig. 2. Distribution coefficients (K_d) of lanthanides on various sorbents measured in 0.1 M $\text{HNO}_3/\text{NaNO}_3$ (pH 1.82), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

3.1. Adsorption affinity

The affinity of a sorbent for a target species was frequently represented with the distribution coefficient (K_d) (in the unit of mL/g throughout), which is simply a mass-weighted partition coefficient between the solid phase and the liquid supernatant phase as follows:

$$K_d = \frac{C_0 - C_f}{C_f} \times \frac{V}{M} \quad (1)$$

where C_0 and C_f are the initial and final concentrations in the solution of the target species determined by ICP-MS, V is the solution volume in mL, and M is the mass in gram of the sorbent. In general, K_d values of $\sim 10^3$ mL/g are considered good and those above 5×10^4 mL/g are outstanding [47]. Higher affinities (K_d values) are absolutely keys for the capture of trace level constituents. Dynamic affinities (large differences in K_d with changing analyte or conditions) are the basis for selective separations.

Figs. 2–7 show the distribution coefficients of lanthanides on various sorbent materials, measured in 0.1 M NO_3^- (pH 1.82), 0.1 M Cl^- (pH 2.42), filtered river water, filtered ground water, filtered sea water, and dialysate, respectively. The specific behavior of SAMMS in various matrices can be explained as follows.

3.2. K_d in acid solutions

Industrially, lanthanides are commonly processed and handled in acid solutions, and so we started off by studying these sorbents in acidic solutions to address any effluents (or waste) arising from these process streams. In both acidic nitrate and chloride systems,

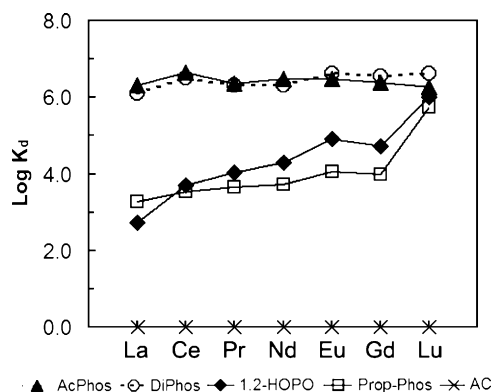


Fig. 3. Distribution coefficients (K_d) of lanthanides on various sorbents measured in 0.1 M HCl/NaCl (pH 2.42), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

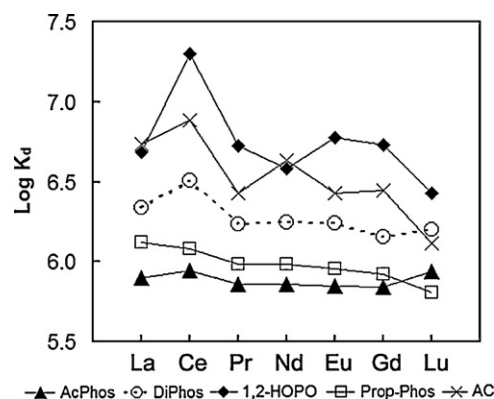


Fig. 4. Distribution coefficients (K_d) of lanthanides on various sorbents measured in river water (pH 7.98), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

the AcPhos-SAMMS and DiPhos-SAMMS outperformed 1,2-HOPO-SAMMS and Prop-Phos-SAMMS due to the higher acidity of the AcPhos and DiPhos ligands. Both materials can effectively bind all lanthanides ($K_d \sim 10^5$ to 10^6) covering the entire range of ionic radii from La to Lu. On the other hand, phenols and carboxylic acids (the two main classes of ligands in activated carbon, AC) are fully protonated in the acid solutions, resulting in virtually no affinity ($K_d \sim 0$) of AC for all lanthanides. Being weaker ligands in acid solutions, the 1,2-HOPO and Prop-Phos ligands may also be affected by competing anions in the solutions. This is evidenced with nitrates which form stronger complexes with lighter lanthanides (La to Gd) than the heavier lanthanides like Lu [54], and bind less favorably to SAMMS.

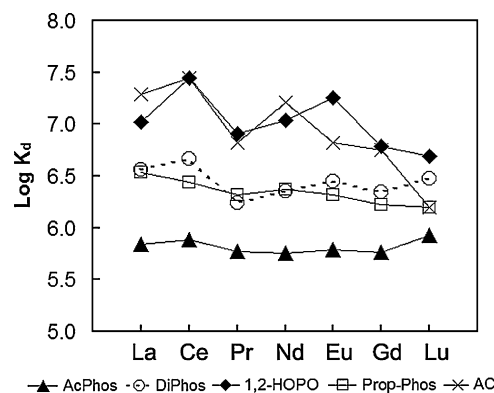


Fig. 5. Distribution coefficients (K_d) of lanthanides on various sorbents measured in ground water (pH 8.07), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

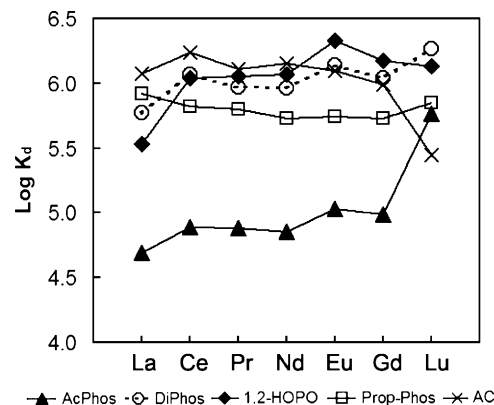


Fig. 6. Distribution coefficients (K_d) of lanthanides on various sorbents measured in sea water (pH 7.68), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

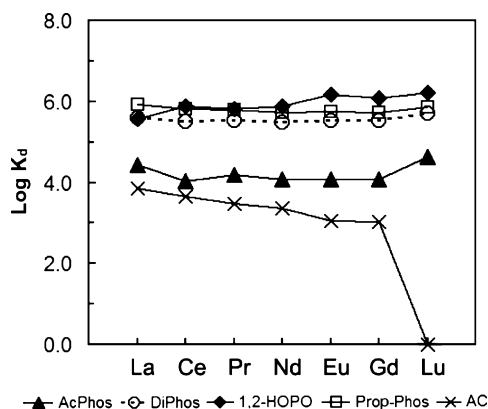


Fig. 7. Distribution coefficients (K_d) of lanthanides on various sorbents measured in dialysate (pH 8.33), initial [lanthanide] of ~ 50 ppb (each), L/S of 5000 mL/g.

As a result, the K_d of lanthanides on 1,2-HOPO-SAMMS and Prop-Phos-SAMMS increased along the lanthanide series and was highest with Lu which forms the weakest complexes with nitrates (Fig. 2). The same holds true with chloride system (Fig. 3) but to a lesser extent since chloride is a much weaker ligand for lanthanides than is nitrate. The differing affinity (K_d) for differing lanthanides of 1,2-HOPO-SAMMS and Prop-Phos-SAMMS suggests that they can be used to chromatographically separate lanthanides for both analytical and larger scale lanthanide separation processes.

3.3. K_d in natural waters

All sorbents (SAMMS and AC) offer large K_d values ($>50,000$) for all lanthanides, suggesting that they are outstanding for capture of lanthanides from natural waters. Note that the K_d in natural waters was measured in filtered waters. When river waters are not filtered, the humic substances often present in river waters are readily bound to activated carbon [55] and may cause fouling. As a result, the activated carbon will become less effective metal binder. On the other hand, fouling of SAMMS materials have not been observed even in protein-rich samples like human plasma and blood (unpublished data).

For light lanthanides (La to Gd), in filtered river water (FRW) the order of binding affinity is 1,2-HOPO \sim AC $>$ DiPhos $>$ Prop-Phos $>$ AcPhos (see the data in Fig. 4); in filtered ground water (FGW) the order is 1,2-HOPO \sim AC $>$ DiPhos \sim Prop-Phos $>$ AcPhos (see Fig. 5); and in filtered seawater (FSW) the observed binding affinity is 1,2-HOPO \sim AC \sim DiPhos \sim Prop-Phos $>$ AcPhos (as summarized in Fig. 6). In these “natural” aqueous environments the affinities of the lighter lanthanides clearly show a significant dependence upon the sorbent ligand chemistry. For the heavy lanthanide Lu, the K_d of the five sorbents are similar with 1,2-HOPO- and DiPhos-SAMMS having the highest K_d . For all sorbents, K_d values in the three natural waters decreases as follows: river water \sim ground water $>$ sea water, clearly showing the negative effect of ionic strength (which is highest in sea water) on the sorption properties of the materials.

3.4. K_d in dialysate

In light of severe lanthanide toxicity from the recent studies [24,25], in addition to their potential use for limiting lanthanide exposure (by removal of lanthanides from acidic streams and natural waters), SAMMS materials having high affinity and selectivity for lanthanides may be used in sorbent dialysis for treatment of lanthanide poisoning. In conventional hemodialysis, the removal rate of a toxin is determined by the concentration gradient of the toxin as well as its diffusion coefficient. The normal dialysis duration is 3 h.

If the dialyzer is used with sorbent to remove the toxins that have been cleared into the dialysate, the dialysate can be recycled, which is an important step toward developing of personal and portable dialysis devices. The current state-of-the-art sorbent dialyzers still rely on activated carbon for cation removals, which is not yet optimal for lanthanide clearance. We have found that in dialysate (pH 8.33), the affinity of lanthanides for sorbents decreased as follows: 1,2-HOPO \sim Prop-Phos \sim DiPhos $>$ AcPhos $>$ AC. In carbonate-rich dialysate (pH 8.33), lanthanides (noted as HLn for heavy lanthanides and LLn for light lanthanides) are likely to be present as follows [56]: $\text{HLn}(\text{CO}_3)_2^- > \text{LLn}(\text{CO}_3)_2^- > \text{LLnCO}_3^+ > \text{HLnCO}_3^+ \gg \text{Ln}^{3+}$. Unlike ligands on SAMMS, which bind to lanthanides via strong multidentate chelation reaction, the ligands of the activated carbon (e.g. carboxylates, phenols, etc.) undergo a less ordered, more random coordination with anionic lanthanide-carbonate complexes. When compared with filtered seawater (Fig. 6), which also has as high an ionic strength as the dialysate, the bicarbonate, lactate and glucose components of the dialysate did not significantly affect the binding of all lanthanides on the 1,2-HOPO-, Prop-Phos- and DiPhos-SAMMS: the $K_d \sim 10^6$ in both FSW and dialysate. However, for AC, the K_d drops from 10^6 to $10^{3.5}$ for light Lanthanides and to 0 for Lu. This drop in binding affinity is felt to be due to less effective binding of the lanthanide-carbonate complexes by AC, especially for Lu which forms stronger dicarbonato complexes than the lighter lanthanides [56,57].

In short, the greatest advantage of SAMMS over activated carbon is in challenging matrices such as in acidic streams (e.g. industrial waste effluents, nuclear wastes, and mine waters), in high-organic-content natural waters where fouling of AC is severe, and in high carbonate solutions (e.g. dialysate). We further explore the properties of SAMMS including adsorption kinetics and capacity in the challenging matrices.

3.5. Adsorption kinetics

Fast sorption kinetics is highly beneficial for deployment of sorbent materials both in large-scale water treatment and sorbent dialysis devices. Fig. 8 shows the sorption kinetics of Gd in dialysate measured on Prop-Phos-SAMMS and activated carbon. Even in a dialysate containing high concentration of chloride, carbonate, glucose and lactate, over 95% of 100 ppb Gd was removed by the Prop-Phos-SAMMS after 1 min (and 99% after 10 min). The fast kinetics is similar to what previously reported for plutonium in carbonate-free matrices on Prop-Phos-SAMMS [47] and 1,2-HOPO-SAMMS [48]. This rapid sorption rate is owed to rigid structure and suitable pore sizes of the SAMMS, which allow easy access of Gd (likely present as Gd-carbonate complexes) to the binding sites inside the pores. From 4 to 24 h of contact, the extent of sorption

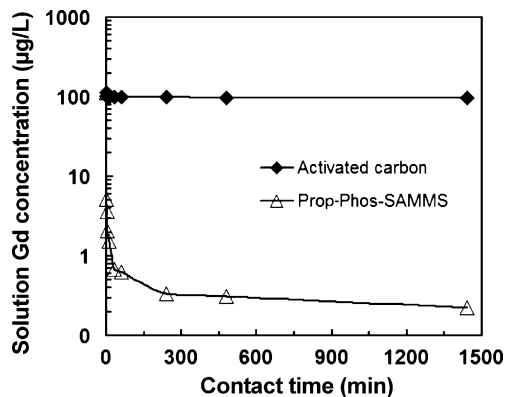


Fig. 8. Adsorption kinetics of Gd on SAMMS and activated carbon in dialysate (pH 8.33), initial [Gd] of ~ 100 ppb, L/S of ~ 5000 mL/g.

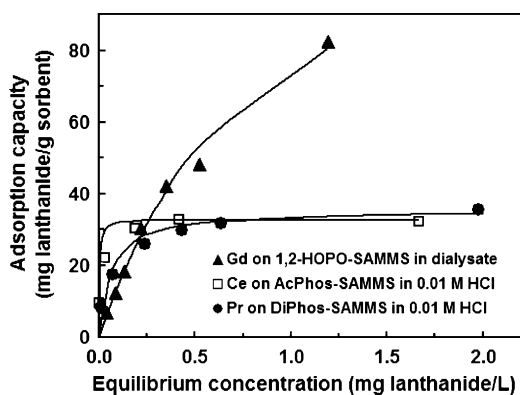


Fig. 9. Adsorption isotherms of Ce, Pr, and Gd on SAMMS materials measured in 0.01 M HCl for Ce and Pr and dialysate for Gd at L/S of 10^5 mL/g.

remains steady, suggesting no significant degradation of the materials in the dialysate. Note that due to the limited affinity of activated carbon for Gd in dialysate (Fig. 7), only ~15% of Gd could be removed by the activated carbon after 24 h.

3.6. Adsorption capacity

Fig. 9 shows the adsorption isotherms of Ce and Pr in 0.01 M HCl (pH 2.4) measured on AcPhos-SAMMS and DiPhos-SAMMS, respectively. Also shown is the adsorption isotherm of Gd on 1,2-HOPO-SAMMS in dialysate. These materials were selected for the isotherm measurements because of their high affinity (K_d) for the lanthanides in these matrices. All isotherms were measured at L/S of 10^5 mL/g. All three data sets are represented well by Langmuir adsorption model ($R^2 > 0.99$) suggesting monolayer adsorption without precipitation of the lanthanides out of the solutions at these conditions. The Langmuir model estimates the maximum sorption capacity in 0.01 M HCl to be 35.5 mg Pr/g DiPhos-SAMMS, 33.0 mg Ce/g AcPhos-SAMMS, and in dialysate to be 135 mg Gd/g 1,2-HOPO-SAMMS.

3.7. Regeneration

After capturing lanthanides, the ability to release lanthanides and regenerate the sorbent materials is important for many reasons: it allows the cost-effective use of the materials either in field applications or devices (e.g. in sorbent dialyzers) and it enables the preconcentration of lanthanides from large sample volume into a small specimen prior to analytical instruments in order to improve the detection limits or the separation of the lanthanide species. The smaller K_d values in acidic solutions compared to in neutral solutions suggest that SAMMS can be regenerated by a pH swing (i.e. an acid wash). We tested the hypothesis by passing 0.5 M HCl to strip Gd adsorbed on Prop-Phos-SAMMS and then re-exposing the SAMMS to fresh Gd in dialysate and measuring the adsorption and

Table 1
Adsorption and desorption of Gd on Prop-Phos-SAMMS.

Cycle	mg Gd adsorbed/g ^a	mg Gd desorbed/g ^b	Recovery (%)
1	0.227	0.195	86.0
2	0.227	0.207	91.2
3	0.230	0.194	84.7
4	0.229	0.213	93.2
5	0.230	0.199	86.1
6	0.228	0.191	83.5

^a 10 mL of 230 ppb Gd³⁺ in dialysate (pH 8.33) passing through 0.01 g SAMMS at 2 mL/min.

^b 40 mL of 0.5 M HCl passing through 0.01 g SAMMS at 4 mL/min.

desorption of Gd per gram of SAMMS. Results shown in Table 1 suggest that rapid acid washing with 0.5 M HCl (at 4 mL/min on 0.01 g bed) could remove from 84 to 93% of adsorbed Gd. Longer contact time between the acid and SAMMS should result in near-complete desorption. Repeating the cycle 6 times revealed no loss in binding affinity and the extent of Gd sorption remained the same. This easy and efficient regeneration could make Prop-Phos-SAMMS a viable strategy for many types of selective lanthanide separation needs, ranging from industrial processing to medical dialysis.

4. Conclusion

This work investigates lanthanide binding ability of nanoporous silica materials which may potentially lead to various applications associated with lanthanide management strategies from reducing their environmental exposure levels, their monitoring, to the treatment of acute lanthanide poisoning. AcPhos- and DiPhos-SAMMS not only can remove lanthanides in acidic streams (where they were originally designed to operate), but they are also very effective in alkaline solutions consisting of complexing anions (e.g. natural waters). This allows flexible use of the materials in systems where the pH may fluctuate (e.g. chemical process and mining effluents). Phos-Phos- and 1,2-HOPO-SAMMS have differing affinities along the lanthanide series, thus they may be used for chromatographic lanthanide separation (e.g. for collection of valuable lanthanides or for their preconcentration prior to analytical devices). The two SAMMS materials are also ideal for regenerative sorbent dialysis since they offer high affinity for lanthanides in dialysate, while allowing regeneration of the materials using acid wash.

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