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Studies on Adsorbent Development for the Separation of Ca/Sc

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1. Introduction

A matched pair of radionuclides, ^{44}Sc and ^{47}Sc has received attention for PET imaging and radionuclide therapy because of the simplicity in the use of a labeling compound for both applications [1, 2]. Such isotopes can be produced by the irradiation of either protons or neutrons to the target materials. Calcium is a common element in the production of the isotopes as shown in the nuclear reactions below:

- Proton Irradiation: $^{44}Ca(p,n) \rightarrow {}^{43}Sc$
- Neutron Irradiation: $^{46}Ca(n,\gamma)^{47}Ca \rightarrow {}^{47}Sc$

In this study, silica-based adsorbents having two different ligands, sulfonic acid (SUL) or phosphonic acid (PSO) are synthesized by the sol-gel method and characterized for the extraction of calcium and scandium ions from aqueous solutions.

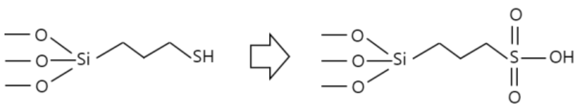
2. Methods and Results

In this section, the synthesis methods, characterization of the adsorbents, and results from extraction of scandium and calcium are described.

2.1 Synthesis of Adsorbents

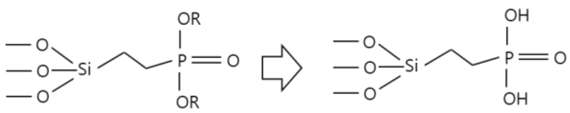
Both Silica-SUL and Silica-PSO adsorbents are synthesized by the sol-gel method similar to that is previously reported [3]. In both cases, parent adsorbents (Silica-Thiol and Silica-PSA) are synthesized and further modified to the desired ligand forms.

Silica-SUL
(Sol-Gel processing and then sulfonation reaction)



Silica-Thiol → Silica-SUL

Silica-PSO
(Sol-Gel processing and then esterification reaction)



Silica-PSA → Silica-PSO

In this study, both the parent adsorbents are synthesized to give the molar ratio of Si : S or P = 5 : 1. With this molar ratio, one can expect the ligand densities of the adsorbents about 2mmol/g. Through the sol-gel processing method, one can easily synthesize adsorbents with different ligand densities by the adjustment of molar ratio of silica to functional ligand.

2.2 Characterization of Adsorbents

Elemental Analysis has been performed to measure the ligand densities as shown in Table 1.

Table 1. Results of Elemental Analysis and Ligand Density of Adsorbents

Adsorbent	Element Weight %		Ligand Density (mmol/g)	
	C	S	EA*	Mole/Wt*
Silica-Thiol	10.2	6.7	2.1*1	1.9
Silica-SUL	9.0	6.1	1.9*1	N/A
Silica-PSA	14.9	N/A	2.1*2	2.0
Silica-PSO	6.4	N/A	1.8*2	N/A

* EA: Calculated from the results of elemental analysis for carbon (*1) and sulfur (*2)
* Mole/Wt: moles of the precursor / weight of resulting adsorbent

For both adsorbents, the secondary treatments (sulfonation or esterification) make approximately 10% loss of the ligand density. The losses are caused by the harsh conditions of the secondary reaction such as boiling in a concentrated hydrochloric acid.

FtIR analysis has been performed to verify the modification of the functional ligands as shown in Figure 1 and 2.

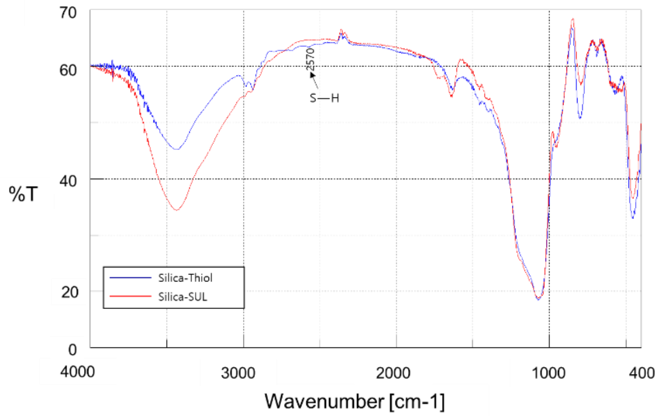


Figure 1. FtIR spectrum of Silica-Thiol and Silica-SUL

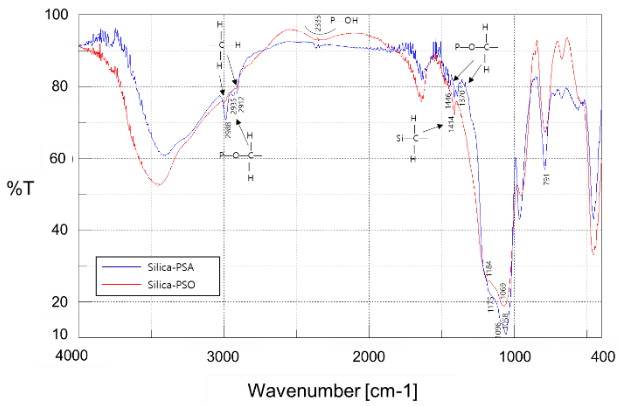


Figure 2. FtIR spectrum of Silica-PSA and Silica-PSO

The disappearance of the 2570 peak in the Figure 1, which represents thiol (SH) shows the thiol converted to sulfonic acid [4]. In the Figure 2, the disappearance of C-H bond on P-OR (Diethoxy phosphonate) are shown at 2912 and 2988. Also, Appearance of a broad vibration peak at 2335 shows the evidence of acidified P-OH [5].

2.3 Extraction of Scandium and Calcium

Calcium target in a form of calcium carbonate or calcium oxide can easily be dissolved with an acid such as hydrochloric acid or nitric acid. To establish separation protocols from a solution in which calcium ions exist predominantly with respect to the scandium ions, chemical speciation of scandium is analyzed by using a chemical speciation software, MINEQL®. Figure 3 shows the existing species of scandium at various solution pH values in an aqueous solution. In this study, the total amount of scandium in the solution is fixed to 0.02mol/L. As the pH becomes higher than 2.5, oxy scandium complexes appear that may affect to the adsorption chemistry with phosphonic acid or sulfonic acid. On the other hand, calcium exists only as Ca^{2+} under pH 7. Hence it is better to perform the separation of scandium and calcium at pH lower than 2 to achieve higher selectivity on scandium.

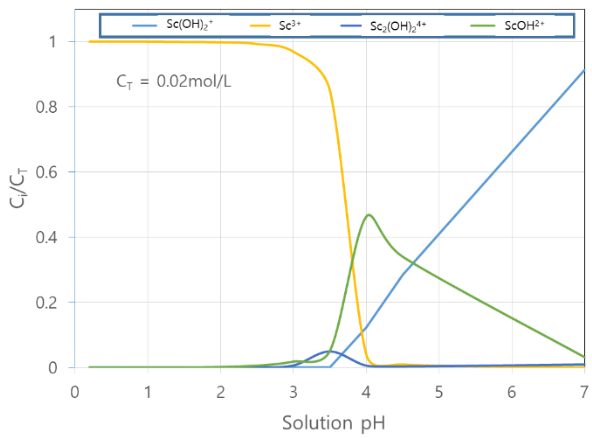


Figure 3. Chemical Speciation of Scandium in an Aqueous Solutions. Calculated by Using MINEQL®.

For the production of 10^{th} milli-Ci of Sc-47 at HANARO reactor, approximately 100mg of calcium carbonate (Ca-46 enrichment 4.9%) is required for the irradiation. When the target is dissolved in an acid solution, expected concentrations of calcium and scandium ions are 1,000mg/L and less than $1x10^{-3}$ mg/L, respectively. So the calcium concentration are more than a million times higher than the scandium concentration. Handling of such scandium concentrations is not easy in a conventional laboratory. Hence, the extraction experiments for calcium and scandium are performed in mg/L concentration ranges to show the performance of the synthesized adsorbents. A hot experiment in a micro-Ci level shall be performed as demonstration of the separation in near future.

Figure 4 and Figure 5 show the % adsorptions of scandium and calcium on Silica-SUL and Silica-PSO. Experimental Conditions are as follows; initial concentrations of Sc and Ca = 50mg/L each, Vol. of solution = 20mL each, amount of adsorbent = 0.2g each By comparing Figure 4 and 5, It is noticed that Silica-SUL has higher affinity on scandium than that of Silica-PSO in the range of HNO_3 concentration 0.1 ~ 2mol/L. Interestingly, SOL-PSO shows a consistent adsorption on both scandium and calcium in the HNO_3 concentration range between 0.5 and 3.0mol/L. It is necessary to do more adsorption experiments by varying the metal ion concentrations to see the affinity changes at low concentrations.

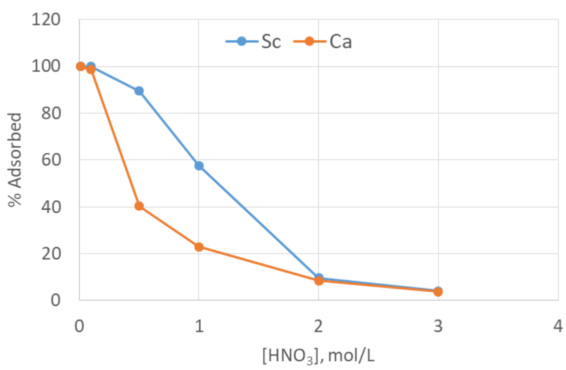


Figure 4. Adsorption of Scandium and Calcium with respect to the HNO_3 Concentrations by using Silica-SUL,

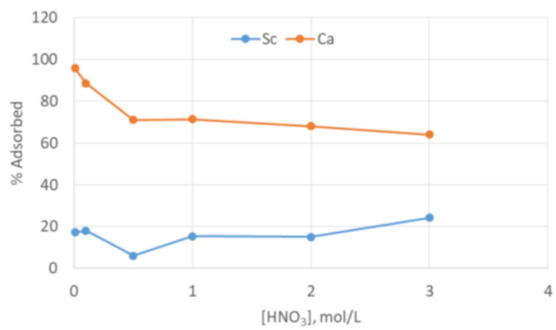


Figure 5. Adsorption of Scandium and Calcium with respect to the HNO_3 Concentrations by using Silica-PSO

3. Conclusions

Adsorbents with functional groups of sulfonic acid and phosphonic acid are synthesized and characterized to apply for the extraction of scandium and calcium. Even though the experimental study on this subject still going, Silica-SUL shows quite promising results for the separation of scandium from an acidic solution in which calcium exists predominantly. Isotherms by varying metal ion concentrations shall be further studied and be reported along with a data set of a demonstration experiment for the separation of Sc-47 and Ca-47.

4. Acknowledgements

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