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Impregnation and Adsorption of Rare Earth Elements on Amberlite XAD-7

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by

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Summary:

Beads were washed then impregnated with an organophosphorous extractant D2EHPA. The washing process, as well as factors in the impregnation process were studied. Water was deemed sufficient to prewash the beads before use over small and large amounts of acid with acetone. The impregnation of beads at an Amberlite D2EHPA ratio of 1:1 was determined to be best. Absorption isotherms of Neodymium were the first to be studied. By testing different concentrations, Amberlite was determined to absorb the max amount at 4000 ppm. The pH values from 2-7 were determined to have no effect on the amount of Neodymium absorbed by Amberlite. The pH values 0 and 1 were not able to be measured by the ICP; possibly due to the large number of ions in the solution. The shaking time of Amberlite to adsorb Neodymium was determined to be over 15 hours. It is recommended to shake Amberlite with the Rare Earth solution overnight. The adsorption isotherm of Lanthanum was also tested and determined to be similar to Neodymium. When a Lanthanum and Neodymium solution was created, the isotherm showed that Neodymium adsorbed much better than Lanthanum. The elution of Neodymium from Amberlite was also achieved and the Amberlite was reloaded successfully with Neodymium.

Characterization of Beads:

The particle size distribution and surface area were measured for a variety of Amberlite samples. It was determined that surface area decreased dramatically from 401.9 m2/g in the Unimpregnated beads to 18 m2/g in the 1:1 D2EHPA Amberlite Impregnated beads (Table 1). The particle size distribution can be seen in Figure 1. The graph shows most beads fall in the 500-1000 micrometer range. The size distribution of Amberlite was determined using Quick Pic Technology. While the particle size distribution falls under the known values for Amberlite, the numbers may be subject to error due to bead swelling during measurement.

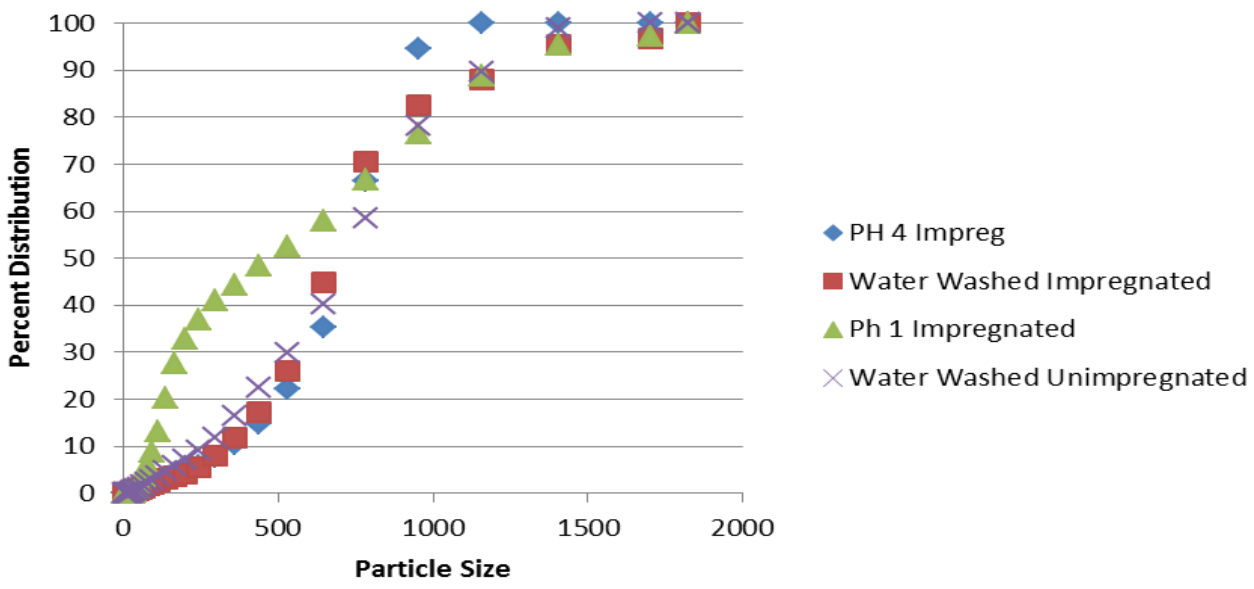

Figure 1: Particle Size Distribution (micrometers)

Washing of beads:

Amberlite XAD-7 is packaged with ions in order to insure shelf life. These ions must be removed before the impregnation process. First, the beads were washed with 65% HNO_3 acid unsuccessfully. The beads were destroyed by the acid and had no ability to retain the D2EHPA. Beads were next washed with a variety substances including 2M HNO_3, acetone, a combination of both varying the pH, and water. Each method removed the ions but using acid gave the beads a slight yellow hue and it was determined that water was best for removing the packaging agents from Amberlite XAD-7. It is recommended to use a conductivity meter to insure complete removal of ions when washing with water. Per 100 grams of Amberlite, 5 liters of water was used.

Impregnation process:

The impregnation process is based off work done by Juang 1998. First, a set amount of D2EHPA is diluted in roughly three times the amount of acetone. The liquid is then stirred with the prepared Amberlite under reduced pressure for 30 minutes. After stirring, the beads are then placed in a rotary evaporator for removal of acetone. In order to insure full removal of acetone, the beads are placed in a drying chamber overnight at 50 degrees Celsius. Finally, the beads are weighed in order to determine impregnation success.

Summary of Absorption Isotherms Process:

In this paper ICP-OES analysis was used in combination with different concentrations of Neodymium. The process steps were as follows: measure out .1000 grams of selected Amberlite, create a “mother liquid” solution of Neodymium to be measured by the ICP as a known concentration, add different amounts of mother liquid and water for desired concentration, shake the Neodymium solution with the beads for 24 hours, and separate beads and liquid for measurement with the ICP machine. The parameters tested in this paper were concentration, pH, adsorption of different elements, and shake time of beads.

Adsorption Isotherms of Various Impregnation Methods:

In order to determine best method of impregnation, ICP-OES analysis was used to determine amount of Neodymium adsorbed for beads impregnated differently. Figure 1 shows the results. Figure 1 shows the Amberlite to D2EHPA ratio of 1:1 is the best for extracting Neodymium. Adding less D2EHPA resulted in a lower adsorption. In addition to Figure 1, an Amberlite D2EHPA ratio of 1:2 was also studied. The 1:2 Amberlite became very adhesive and were difficult to dry. The beads were deemed unsuitable for extracting Neodymium. As a control un-impregnated Amberlite was also tested. As expected, the un-impregnated Amberlite had an adsorption of zero. Hexane was used in substitute of acetone for the dilution process. The isotherm shows that acetone provides a better means of impregnation than hexane.

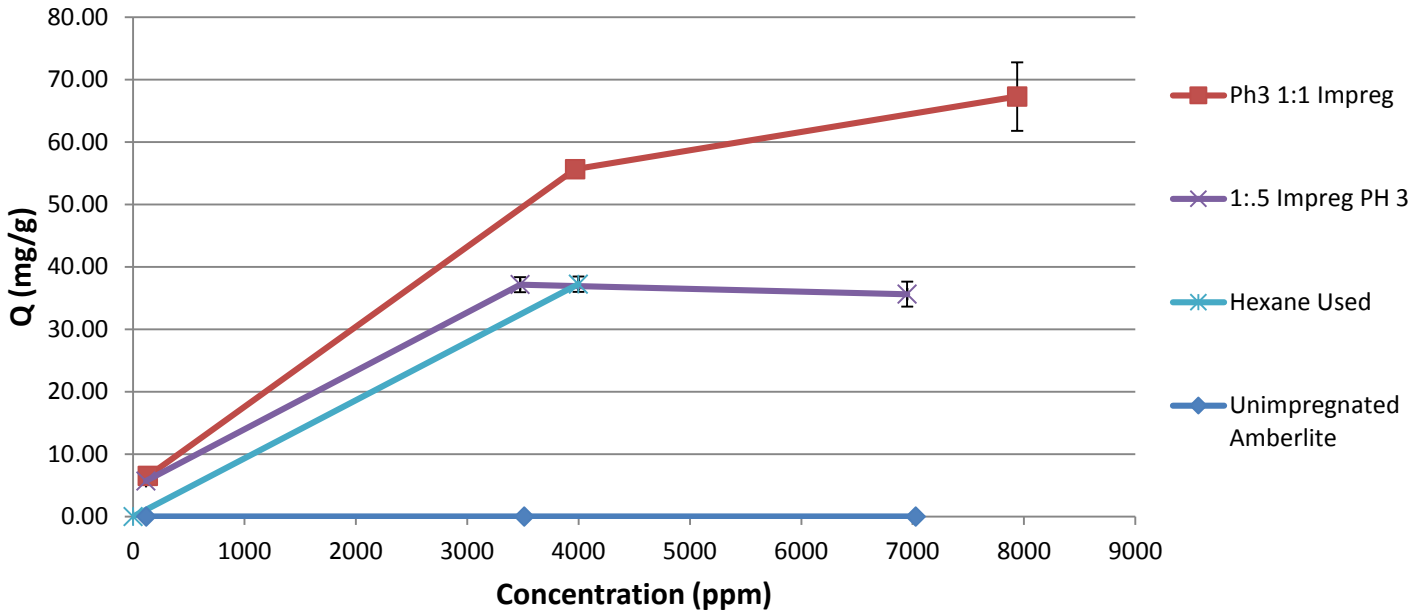

Figure 2: ICP-OES Results for Different Methods of Impregnation with Neodymium

Ultraviolet–visible spectroscopy vs. ICP OES:

When using ICP-OES analysis to measure adsorption of Rare Earth Elements many problems arise. After shaking, each sample must be individually separated and diluted to a known value in order to fall in to a measureable range for the ICP machine. The dilutions require very small amounts of the sample which causes for very time consuming sensitive results. Ultraviolet–visible spectroscopy was used as an alternative for ICP. Ultraviolet–visible spectroscopy was much faster and required no dilution of samples, but could not measure low concentrations or Lanthanum results. Also, Ultraviolet–visible spectroscopy was shown to have larger standard deviations than ICP. Figure 2 shows ICP results vs. the same samples measured with Ultraviolet–visible spectroscopy. The point that is most important on the graph is where the slope decreases sharply. This point is the max amount of target element the Amberlite can adsorb.The charts show that the ideal concentration for extracting Neodymium with Amberlite is around 4000 ppm.

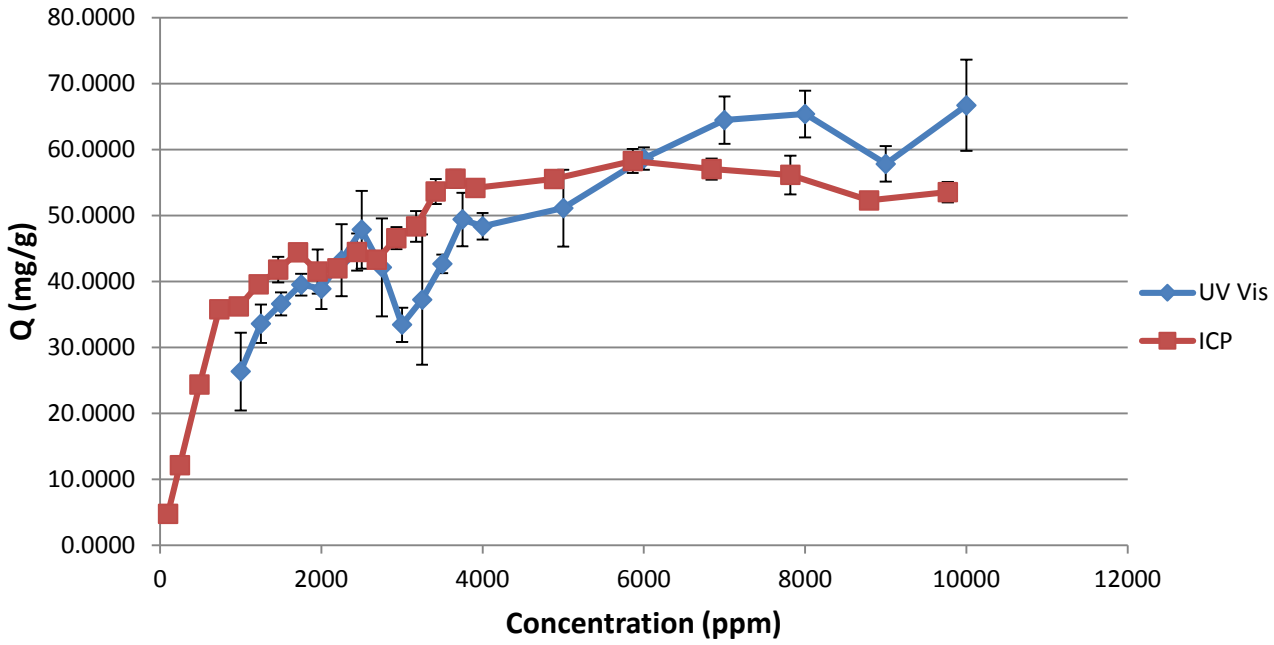

Figure 3: ICP-OES vs. UV-Vis for Adsorption of Nd with Amberlite XAD-7

Effect of pH on extracting Neodymium:

Figure 3 shows the results of Neodymium and Lanthanum extracted by impregnated Amberlite at various pH levels. The standard deviation for pH values zero and one for Nd suggests that they were not able to be measured with the ICP machine. This is possibly due to large amounts of ions due to the addition of acids. The graph shows that for pH values from 2-7 is not a factor for extracting Neodymium. The Lanthanum graph shows a higher tendency towards adsorption at a few pH values. However, these values do not take into account slight variations of original concentrations measured in the individual mother liquids. Further equations need to be developed in order to account for this factor.

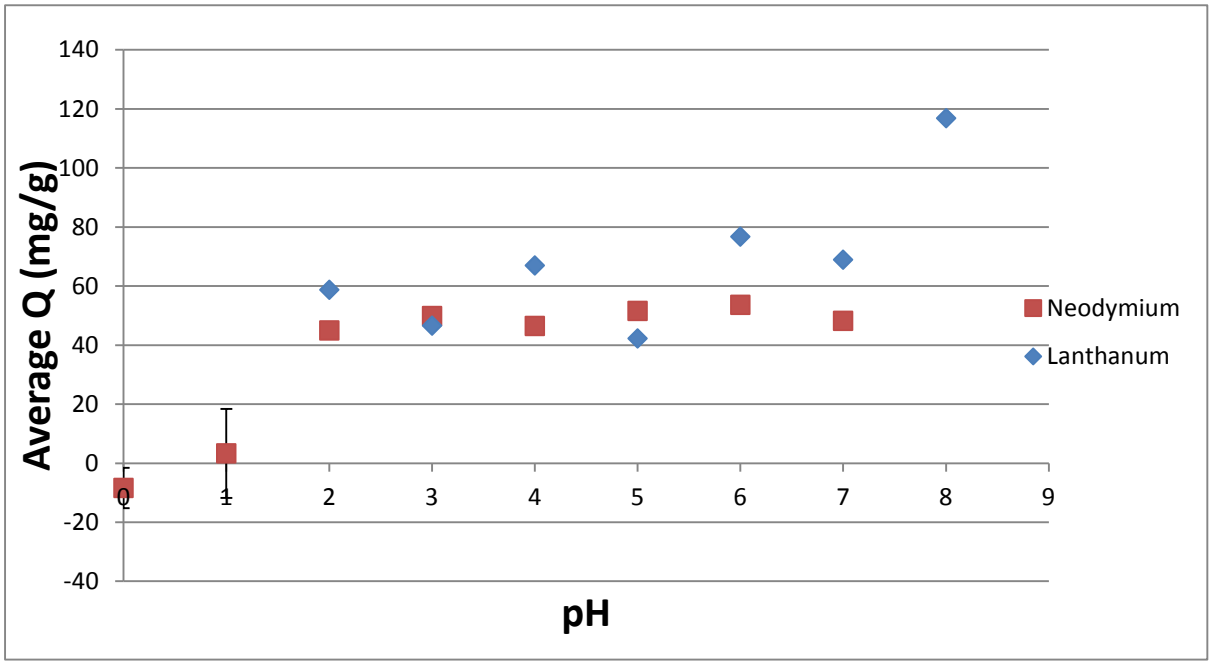

Figure 4: Effect of pH on Adsorption on Nd and La

Comparison of Adsorption of Erbium, Neodymium, and Lanthanum:

The adsorption capability of Amberlite with Erbium, Neodymium, and Lanthanum was studied. It is important to note that Neodymium and Lanthanum came in a nitride salt whereas Erbium was a chloride salt. In order for consistency in ICP measurements, the ions added to retain pH values must be consistent. For this experiment a pH of around 3 was used. This pH was chosen because it coincides with the normal pH for La and Nd solutions and in order to insure Erbium Chloride to fully dissolve. Figure 4 shows the results. Lanthanum and Neodymium show similar trends for adsorption. This is to be expected due to the similar properties of Rare Earth Elements close to each other on the periodic table. Erbium shows a slightly lower absorption which may be due to the increase of molecular weight. Some discrepancies on the graph include inconsistency of amount of points and a relatively high standard deviation for Erbium. These problems can be alleviated by repeating concentrations and by adding more concentration points. By repeating concentration tests, outliers can be detected easily. Adding more concentrations allows for a complete view of the adsorption of an element.

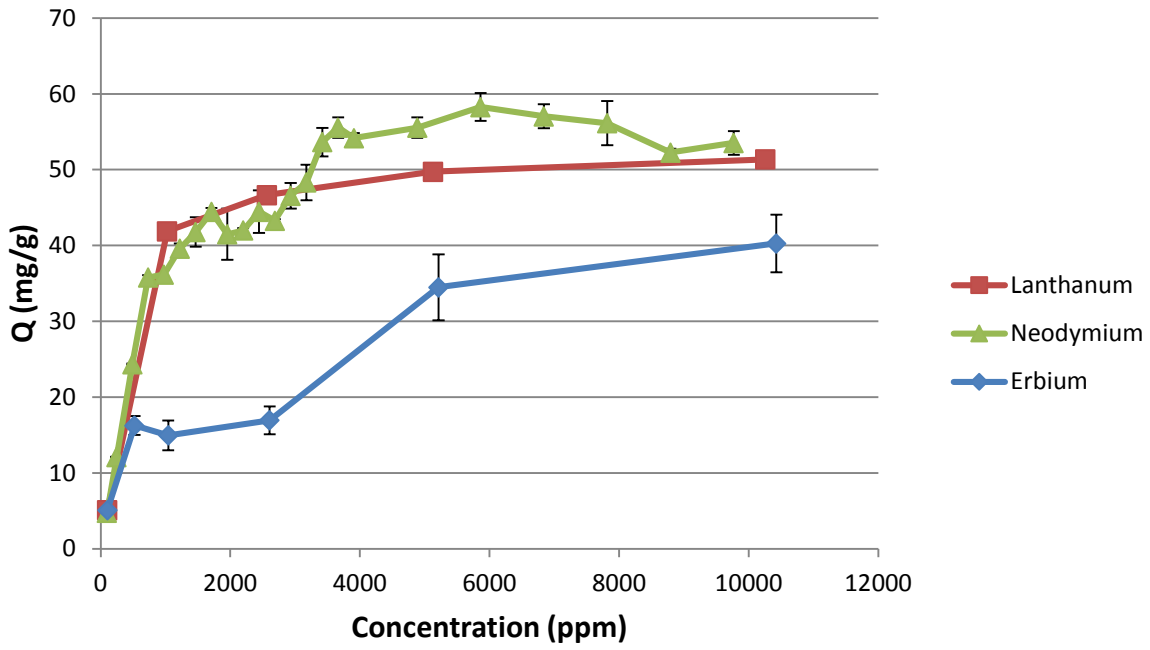

Figure 5: Effect of pH on Adsorption of Nd

Determining Shake Time Required for Amberlite XAD-7:

Samples consisting of Amberlite and Nd at the same concentration were prepared. The samples were the shaken at the same intensity for various times to determine the amount of time needed in order to allow full adsorption of target element on Amberlite. Figure 5 shows the results. The graph shows that the amount of Nd attached to the Amberlite is increasing past 15 hours. Therefore it is recommended to shake the beads overnight in order to show full attachment.

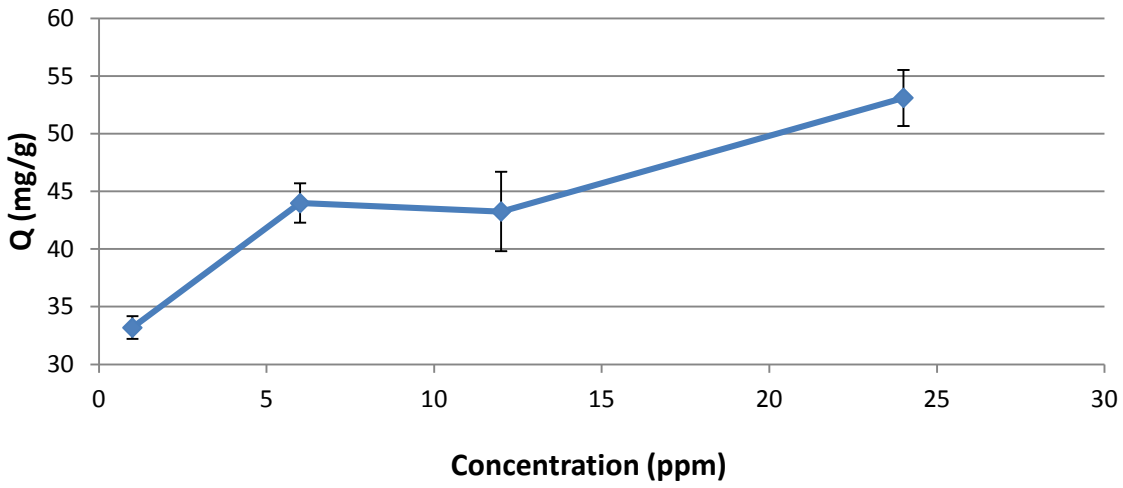

Figure 6: Effect of Shake Time on Nd Adsorption

Effect of Amberlite particle size on Adsorption:

Impregnated Amberlite particles were sieved post impregnated into three categories: particles smaller than 0.315 mm, particles between 0.315 mm and 0.630 mm, and particles larger than 0.63 mm. By mass the particles larger than 0.63 mm made up around 50%, particles with size between 0.315 mm and 0.630 mm accounted for around 40% by mass. The smallest 10% were destroyed beads that were in the form of a fine powder. Figure 6 shows that the smaller beads are more efficient in adsorbing Nd. This is as expected because of the better ratio of surface are to volume seen in smaller particles.

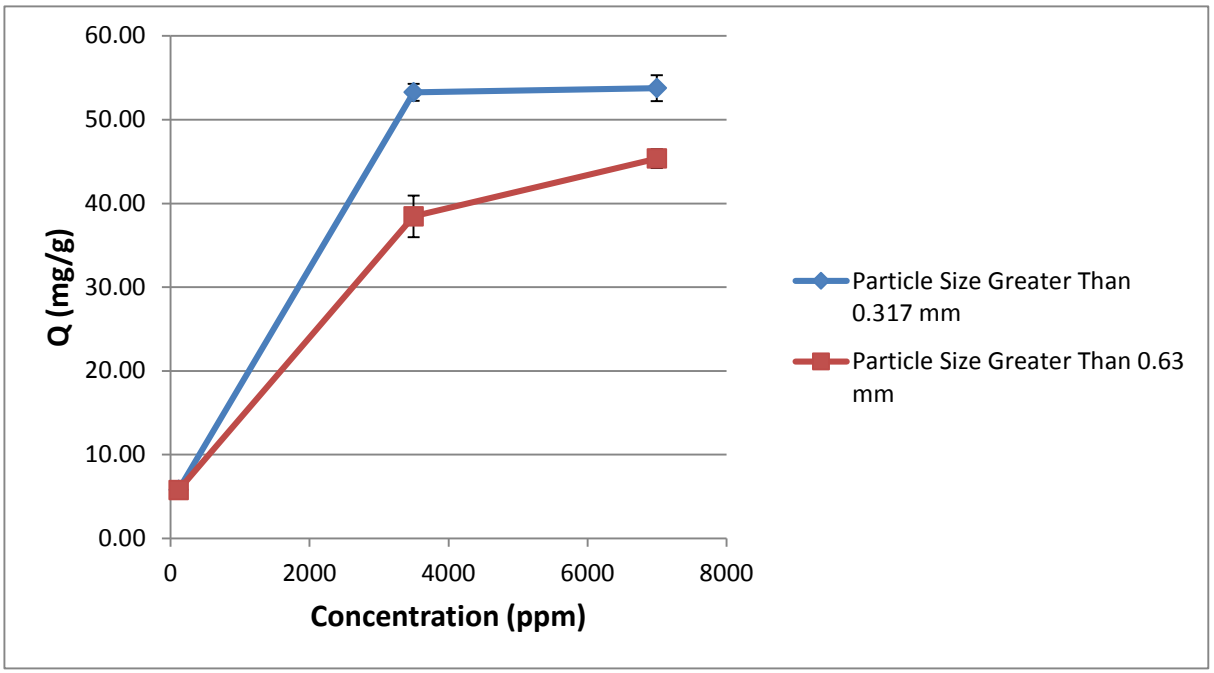

Figure 7: Effect of Particle Size on Nd Adsorption

Recovery and Reuse of Amberlite:

The process of loading Amberlite was repeated for three concentrations. The absorption isotherm was measured as shown in Figure 7. The loaded Amberlite was than shaken with 2M HCl overnight in order to remove the Neodymium. The absorption isotherm proved the elution of Neodymium from Amberlite to be to be 100%. The Amberlite was then reloaded successfully with Neodymium at a point of 4000 ppm to prove Amberlite impregnated with D2EHPA can be reused in the extraction of Rare Earth Elements.

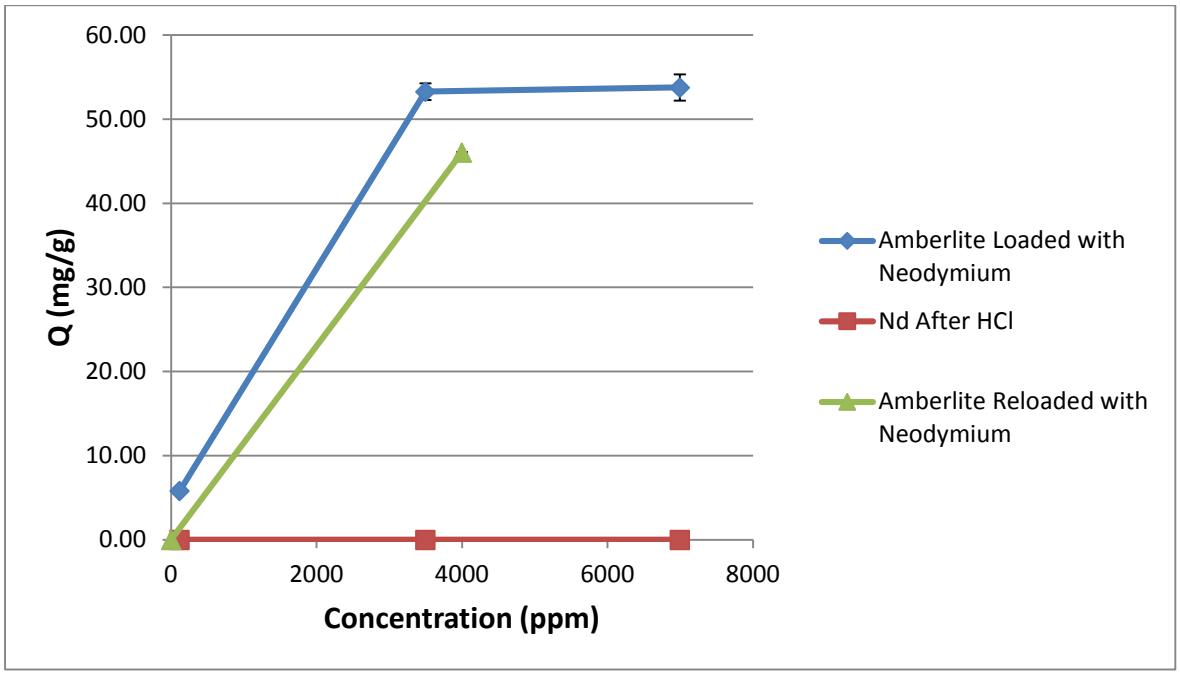

Figure 8: Recovery of Neodymium and Reuse of Impregnated Amberlite XAD-7.

Tables

Amberlite	Surface Weight (Grams of D2EHPA)	Surface Sm (m^2/g)
Unimpreg. Water Washed	0	401.9
Impreg (1:1) Water Washed	5	18.13
65 % HNO3 Washed Impreg	5	0.17
1:.5 Impregnated	2.5	79.85
1:2 Impregnated	10	0.24
PH 1 Wash Impreg	5	10.21
PH 4 Wash Impreg. (HNO3 and much Acetone)	5	19.18

Table 1: Measured Surface Weight and Surface Area

Material Used	Provider	Product Number
Amberlite XAD-7	Rohm and Haas France SAS	Code 63290
Acetone greater than 99.5 Synthese (Dichte 0.79)	Roth	5025.3
Hexane	Sigma Aldrich	270504-1L
D2EHPA	Merck	814181
Hydrochloric Acid (37%)	Roth	9277.2
Nitric Acid 65%	Merck	1.00456.1000
Sodium Hydroxide	Roth	6711.1
Neodymium(III) nitrate hexahydrate	Aldrich	
Lanthanum (III) nitrate hexa-hydrate	Aldrich	
Erbium Chloride		

Table 2: Materials Used

Works Cited

Juang, Ruey-Shin. *Prepatation,Properties and Sorption Behavior of Impregnated Resins Containing Acidic Organophosphorus Extractants*. Chungli, Taiwan: Department of Chemical Engineering Yuan Ze University, 1998.

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