Mesoporous Alumina Affinities for Metals as a Function of pH

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ABSTRACT

One important application for mesoporous alumina is as the adsorbent for retaining Molybdenum-99m in the Molybdenum/Technetium generators used for medical imaging throughout the world. In 2016, Fujimi created a novel mesoporous alumina material that could retain 6x, by weight, the amount of molybdenum than other commercially available mesoporous aluminas.

Research has continued with several different mesoporous aluminas to study the affinity for different metal ions and how that affinity is affected by changes in pH. One commercially available mesoporous alumina, Brockmann, and two Fujimi prepared materials, MA2HS-B and MA C were used as the adsorbent materials. The following metal ions were studied: arsenic, calcium, cadmium, chromium, cobalt, copper, lead, lithium, nickel, magnesium, titanium, zinc, and zirconium. The pH range studied started as low as 1.5 and was increased to as high as 5.2 with dilute KOH.

At pH values less than 2.5, the stability of each of the aluminas was compromised and as a result retention was generally low for all of the materials. At pH levels of around 2.5, many of the metals showed a moderate affinity for each of the aluminas, with the exception of arsenic, titanium, and zirconium, which showed complete absorption for each of the aluminas tested. At a pH of around 5.0, most metals showed an increased absorption for each alumina. The exceptions are lithium and magnesium which had a fairly low retention for every test condition.

Fujimi's MA C material was shown to be superior at pH levels greater than 2.0 than the other tested materials in this study. None of the tested aluminas are suitable for use in conditions requiring a pH of less than 2.0.

Keywords: mesoporous, alumina, retention, metals, water

1 INTRODUCTION

Technetium-99m (^{99m}Tc) is one of the most commonly used materials for nuclear medical imaging, accounting for up to 85% of the procedures performed worldwide [1]. Our original research was aimed at maximizing the retention of molybdenum with mesoporous alumina [2]. We developed a material with 6 times better retention than other commercially available aluminas. As a result, the scope of research was extended to investigate if the retention of other environmentally significant materials could be improved with Fujimi developed mesoporous alumina.

There have been many headlines in recent years highlighting the importance of clean drinking water and contaminated water sources for municipalities. Additionally, research is currently on going to improve insecticide removal from the environment by using a mesoporous alumina [3].

2 EXPERIMENTAL SECTION

An HPLC style column was used to evaluate the performance of the different mesoporous aluminas for this study. The column body is 4.6 x 50mm made out of 316 stainless steel. In all cases, an HPLC pump was used to pass the solution through the column into a collection vessel. In all test conditions, the flow rate of the solution was 5mL/min and the tests were conducted for a total duration of 10 minutes for a total tested volume of 50mL. The resultant back pressure was monitored throughout the test duration.

The various metal ions were sourced from VWR as 1000ppm ICP standards stabilized in 2-3% dilute nitric acid. Samples were then diluted to 100ppm and the pH was raised accordingly with dilute potassium hydroxide. All solutions were stable up to a pH of about 5.0. With pH solutions higher than 5.0, some of the metals would precipitate out of solution. .

All solutions were analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES) to determine the amount of aluminum, being shed from the adsorbent, and metal ion in the solution before and after being passed through the column.

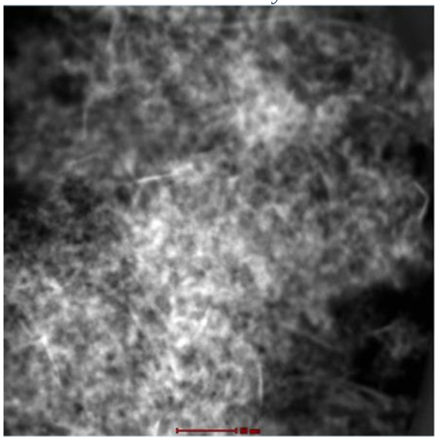
Initial efforts to synthesize mesoporous alumina followed the method provided by Xu et al. [4]. However, our group has learned how to produce higher performance mesoporous aluminas using a similar method but with pore formers other than glucose. Brockmann acidic alumina was obtained from Sigma Aldrich to use as baseline mesoporous alumina to compare the performance of our materials against.

The structure of the material was imaged with a scanning transmission electron microscope (STEM) and the porosity and surface area were determined with a Micromeritics TriStar II.

3 RESULTS AND DISCUSSION

3.1. Mesoporous Aluminas Structure

The structures as observed with an STEM and SEM of the aluminas used in this study are shown in



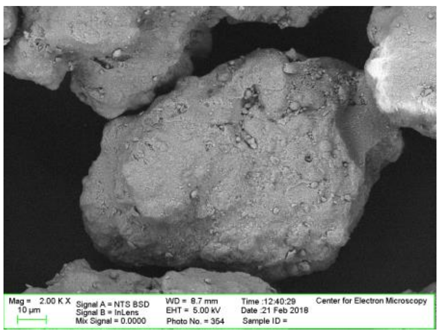
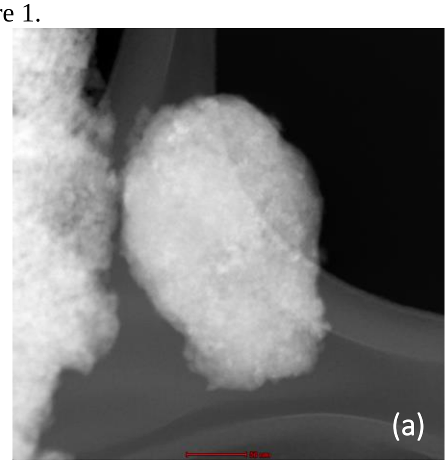


Figure 1.



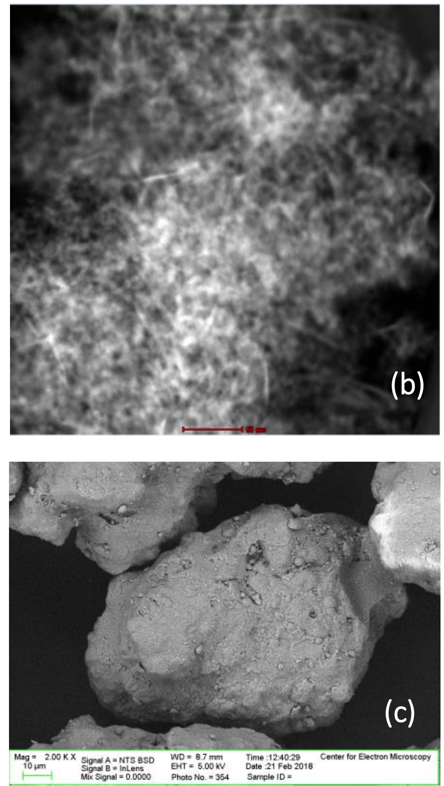


Figure 1: STEM images of (a) Brockmann acidic alumina, (b) Fujimi MA2HS-B. (c) SEM image of Fujimi MA C

Samples were then analyzed for pore size distribution and surface area and the results are shown in Figure 2 and Table 1. The material from Brockmann had the smallest surface area, pore volume, and average pore diameter. Meanwhile the Fujimi prepared MA2HS-B had the greatest surface area, pore volume, and average pore diameter. It can also be seen from Figure 2, that the MA2HS-B material has an appreciable number of pores greater than 500Å. As a result MA2HS-B has the lowest density of the materials used in this study.

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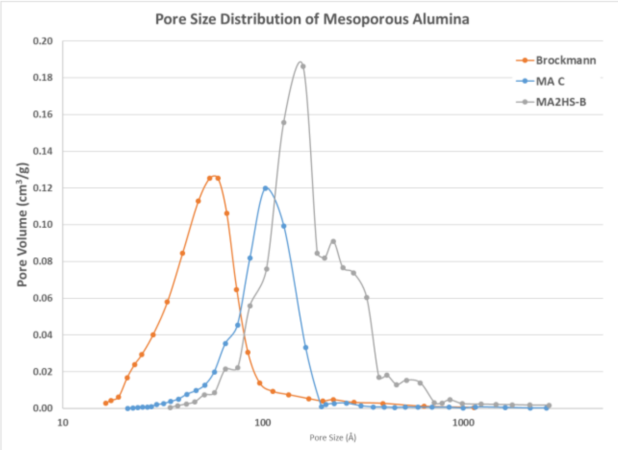

Figure 2: Pore size distribution as measured by BET for different mesoporous alumina samples

Material	Surface Area (m2/g)	Pore Volume (cc/g)	Avg. Pore Diameter (Å)
Brockmann	154	0.25	59.6
MA C	209	0.50	94.5
MA2HS-B	261	1.11	169.6

Table 1. Summary of the pore size and surface area for the different mesoporous alumina materials

3.2. Retention of various metals with mesoporous aluminas

The retention of the following elements were studied at pH=2.5 and pH=5.0: arsenic, calcium, cadmium, chromium, cobalt, copper, lead, lithium, nickel, magnesium, titanium, zinc, and zirconium.

The results for the retention performance at pH=2.5 are shown in Figure 3. The results are arranged in descending order to show which elements have the greatest affinity for alumina. Arsenic, zirconium, and titanium were totally absorbed for both the Brockmann and MA C aluminas. In general, the MA C material showed a greater affinity than the Brockmann alumina.

The results for the retention performance at pH=5.0 are shown in Figure 4. At a pH level of 5.0, many of the elements were completely absorbed by the MA C material. Also of note, is that magnesium and lithium showed a very low affinity for either alumina in any of the test conditions.

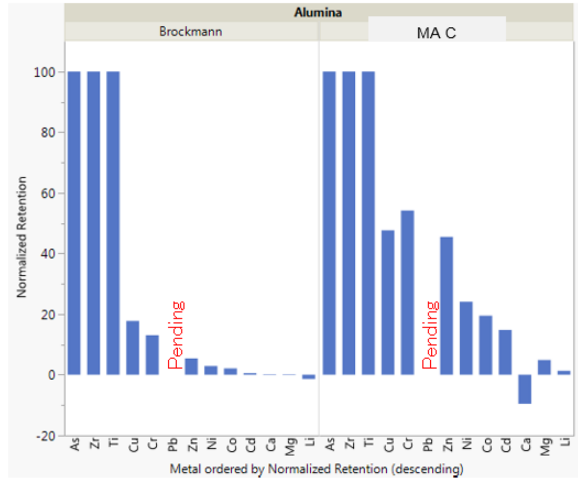

Figure 3: Retention of metals with mesoporous alumina at pH=2.5

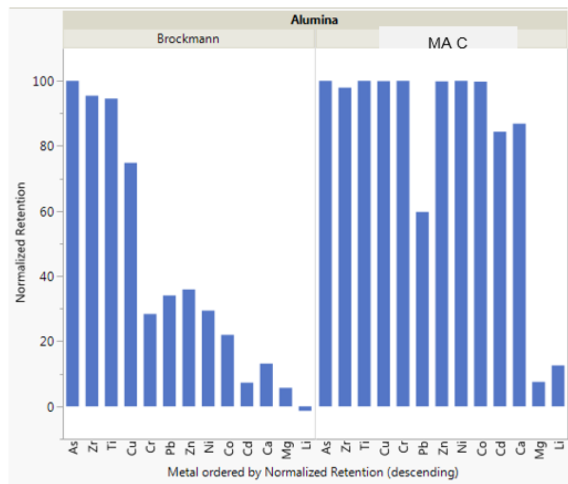

Figure 4: Retention of metals with mesoporous alumina at pH=5.0

The stability of the alumina in the column was also monitored for each test condition by measuring the amount of aluminum present after passage through the column. Figure 5 shows the amount of aluminum dissolved at pH < 2.5. Figures 6 and 7 show the amount of aluminum shed from the column at pH's of 2.5 and 5.0, respectively.

As the pH of the solution was increased the stability of the alumina got better for all of the materials tested. However, the MA C material proved to be the most robust at low pH levels. In fact, both of the Fujimi prepared mesoporous aluminas showed a greater stability than the commercially available Brockmann regardless of the solution's pH.

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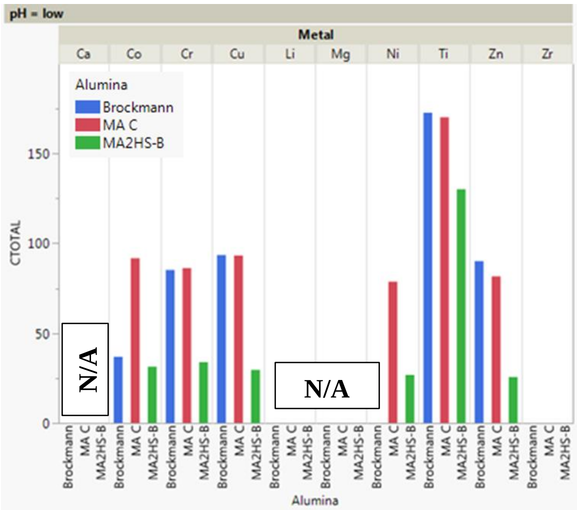

Figure 5: Amount of aluminum shed from the column after testing solutions with pH<2.5

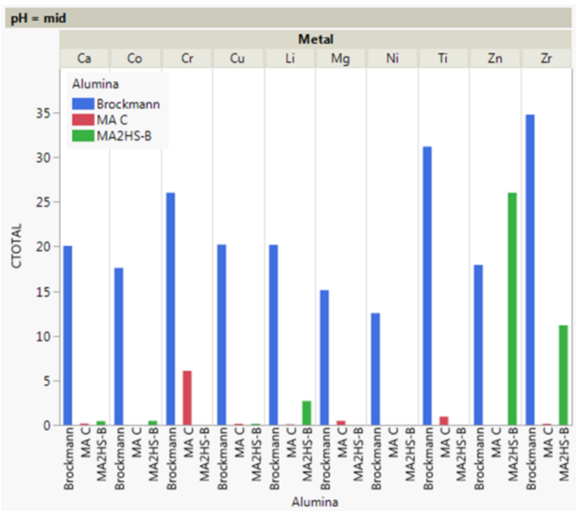

Figure 6: Amount of aluminum shed from the column after testing solutions with pH=2.5

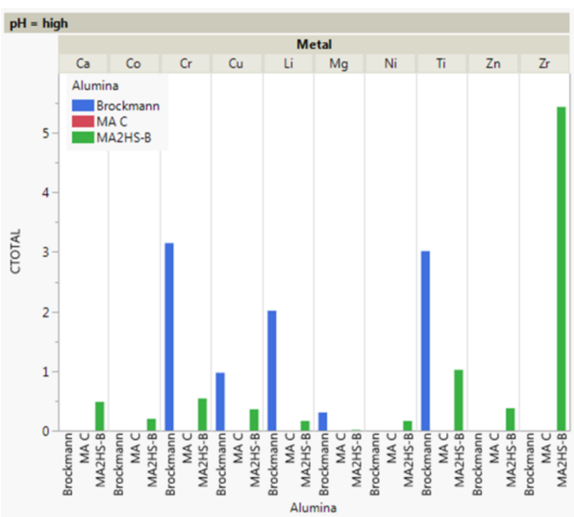

Figure 7: Amount of aluminum shed from the column after testing solutions with pH=5.0

4 CONCLUSIONS

In summary, Fujimi prepared mesoporous aluminas were shown to be more stable and have a greater affinity than a commercially available competitor for all of the metals tested in this study. There is on going research for the metals that had a great affinity for the alumina to determine how much more material can be retained by either increasing the concentration of the solution, or by increasing the volume of solution passed through the column.

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6 AUTHOR INFORMATION

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