TESTING VIABILITY OF SOLID AMINE-BASED ADSOIRPTION METHODS FOR CARBON SCRUBBING ON SPACE HABITATS

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Acknowledgements

I want to thank my graduate mentor Daniel Lobree for aiding me in designing this project's experimental procedures. He was also a tremendous help in synthesizing the aerogel sorbents and gathering data for each sorbent sample. I also want to thank Keelin Craige for aid on the aerogel synthesis. Credit to former undergraduate students Bradon Tapia and Tiffany Fung for providing previous research data. Also, Dr. Stephen Martin and the whole Martin Research Lab are fantastic to work with this semester. Finally, I wish to thank the Virginia Space Grant Consortium for giving me the opportunity to conduct this research through their undergraduate research scholarship.

Abstract

Carbon capture is critical for use in space habitats like the International Space Station (ISS) to regulate CO_2 concentrations. Currently, this process relies on 5A zeolite molecular sieves, which are safe and selective on CO_2. Properties like humidity resistance and low desorption temperature make guanidinium a viable alternative to zeolite sorbents. To test the effectiveness of guanidinium for carbon scrubbing, the sorption capacity of synthesized guanidinium sorbents was compared to 5A zeolite molecular sieves. Two solid guanidinium sorbents were synthesized: one using 15wt% guanidinium carbonate (Gn_2CO_3) and another using 15wt% guanidinium isophthalate (Gn_2Isp), both complexed with activated carbon. Their capacities were evaluated by placing each material inside an adsorption column and running CO_2 mixture. To maintain design principles, the guanidinium sorbents were made into solid beads by encasing guanidinium sorbent powder into an aerogel bead structure. The sorbent with the highest sorption capacity is 15wt% Gn_2CO_3 powder. Both synthesized aerogel sorbents have slightly smaller sorption capacities than zeolite. Increasing CO_2 concentration in sorption column generally increases the sorption capacity of sorbents.

Research Motivation

Carbon scrubbing is a crucial process for maintaining habitability on space habitats. The purpose of this process is to regulate CO_2 levels inside of space habitats by capturing excess CO_2 molecules from the air for maintaining habitable conditions inside of space habitats like the International Space Station[5]. In the International Space Station, CO_2 is captured through selective adsorption, where CO_2 is trapped into a certain material[6]. Innovations in carbon-capture methods would be important to NASA as it plays a significant role in providing habitability for closed space environments. Typically, the material used for carbon capture is a version of Zeolite with pore sizes around 5 angstroms. A recent article by Sherif and Knox highlights issues that have surfaced over the usage of this material[6]. The article highlights problems such as accidental release of solid sorbent dust, which results in increased maintenance for carbon scrubbing systems. Another problem is the material's high desorption temperature which results in massive energy expenditure for the sorbent when recycling the material[7]. Other problems include frequent maintenance and low adsorption capacities[7].

This research aims to evaluate the viability for solid guanidinium-based materials as sorbents for carbon-scrubbing in space habitats. Guanidinium is a cation of the molecule guanidine, which contains 3 partially protonated primary amine groups. These sorbents have the potential to improve on the current method of CO_2 scrubbing on the ISS, as they can be regenerated easily by heating the sorbent and it requires a significantly lower desorption temperature compared to Zeolite[3]. Furthermore, as guanidinium sorbents are solid, there would be no concern over the volatility of the sorbent, as is the case for some liquid amine-based sorbents used in CO2 capture[8].

Previous Research

Amine Based Carbon Adsorption

Solid amine-based sorbents show a promising path for further carbon sorption research due to their high selectivity for CO_2 and their economic viability[3]. Primary and secondary amine groups can adsorb CO_2 through a chemisorptive process where the CO_2 molecule bonds to a nitrogen atom with the aid of a base, creating a zwitterionic system[3]. The proposed mechanism for this process is shown in figure 1. Typically, this base is water, which leads to amine sorption functioning especially well under humid conditions, which is contrary to most solid sorbents[3].

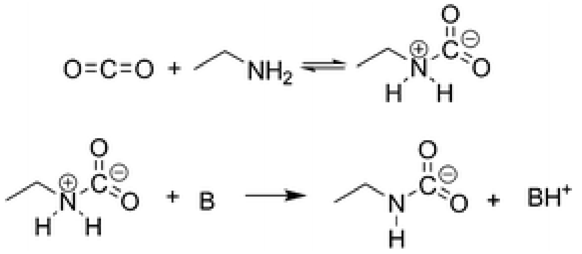

Figure 1. “Zwitterion mechanism for CO_2 capture (valid for primary, secondary, and sterically hindered amines) in solution[3]”.

The amine sorbents are compatible with both temperature and vacuum swing adsorption methods[3]. During temperature swing, the temperature of the sorbent is increased as inert gas is flown through it[3]. In this lab, the sorbent is heated to 120°C and flushed with purge gas. These sorbents are typically run with a porous support to serve as composite materials for the amines[3]. Previous research in the lab by Brandon Tapia has measured the CO_2 adsorptive capacity of the guanidinium-based sorbent guanidinium carbonate (Gn_2CO_3) compared it to activated carbon (AC), PGSS, and a 10wt% addition of Gn_2CO_3 to activated carbon. The results demonstrated guanidinium has an adsorptive capability greater than activated carbon (AC) as shown in figure 2. More importantly, mixing the two sorbents creates a sorbent with significantly higher sorption capacity, as activated carbon provides a porous support for the guanidinium sorbent.

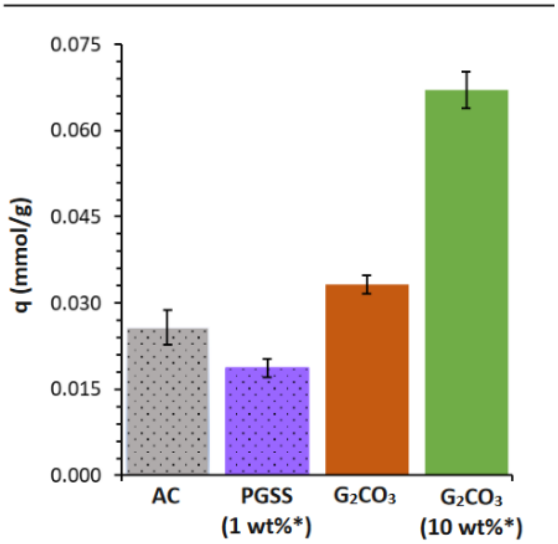

Figure 2. CO_2 Sorption capacity of different sorbents measured by Brandon Tapia – AC, PGSS (poly(guanidine styrene sulfonate)), Gn_2CO_3, and AC mixed with 10wt% Gn_2CO_3.

Guanidinium Sorbent Sorption Capacity

Previous research by in this lab Tiffany Fung sought to determine the sorption capacity of additional guanidinium compounds to determine the effects of crystal lattice shape on the sorption capacity of guanidinium based sorbents. In figure 3, the measured sorption capacity of guanidinium terephthalate (Gn_2BDC) was compared to Gn_2CO_3. The greater sorption capacity of Gn_2CO_3 was attributed to special 2D hydrogen bonded networks observed in guanidinium dicarboxylates as outlined in an article by Videnova-Adrabinska et al[4].

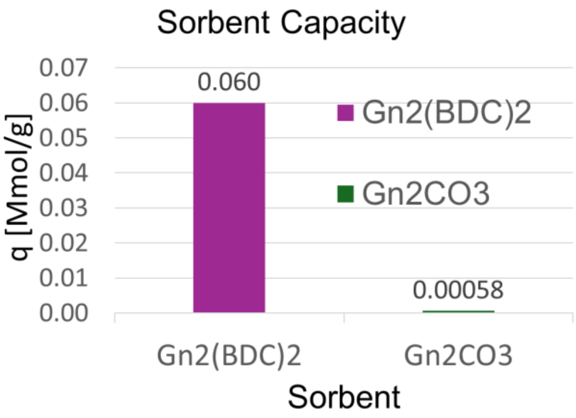

Figure 3. Sorbent capacity of Guanidinium Terephthalate and Gn_2CO_3 measured by Tiffany Fung.

To further observe the possible relationships between crystal lattice structure and sorption capacity, other guanidinium sorbents were synthesized using different carboxylic acids. These acids included guanidinium isophthalate (Gn_2Isp), guanidinium benzoate (GnBnz), and guanidinium trimesate (Gn_3TMA), each with a unique crystal structure. Previous research then involved creating sorbents from these crystals by complexing them with activated carbon and measuring their sorption capacities in dry room conditions. The results for these experiments are shown in figures 4 and 5. Data from Gn_2BDC on figure 4 was borrowed from Tiffany Fung with permission and Gn_2CO_3 data in figure 5 was borrowed from graduate advisor Xakin Ramizez Isunza with permission. The results demosntrate that there is minor difference in sorption capacity across different guanidinium carboxylate sorbents. As a result, it was concluded that crystal lattice structure does not have a significant impact on the sorption capacity of guanidinium sorbents. However, the sorption capacity of Gn_2CO_3 both seemed to overperform the guanidinium carboxylate sorbents in figure 5 and underperform in figure 4.

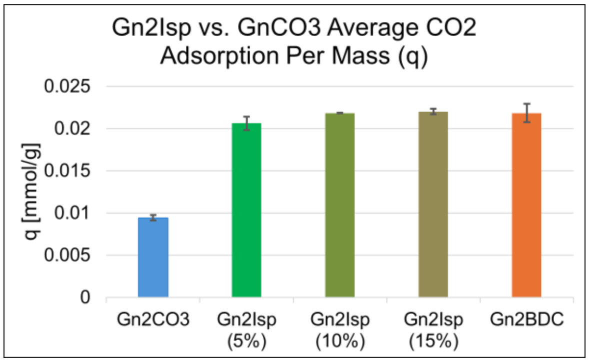

Figure 4: Average sorption capacity (q) of each wt% sorbent compared to Gn_2CO_3 and Gn_2BDC data

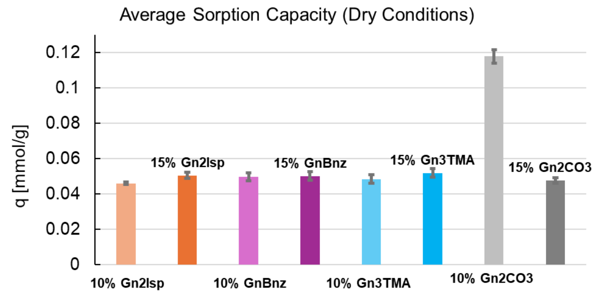

Figure 5. Average sorption capacity data for each synthesized sorbent compared to AC-Gn_2CO_3 data collected by Xakin Ramirez Isunza. Error bars are 95% confidence intervals.

Experimental Design

The purpose of this research is to determine the viability of using solid guanidinium based sorbents for the purposes of carbon scrubbing. To determine this, the sorption capacity of select guanidinium sorbents is compared to the sorption capacity of the zeolite used in the International Space Station. Guanidine carbonate (Gn_2CO_3) and guanidinium isophthalate (Gn_2Isp) were selected to be compared to zeolite sorbent. For this project, 5A 8-12 mesh zeolite is used. This zeolite is similar to the zeolites that were typically used in the ISS. Zeolites in the ISS typically took a spherical or cylindrical (pellet) shape and ranged from 2.19 – 3.53mm[2]. The zeolite pore size for adsorbing CO_2 is 5 angstroms which are shortened to 5A for identification[2]. Each sorbent will be evaluated in both atmospheric and raised CO_2 (~2500ppm) condition to determine the effect of raised CO_2 concentration on sorption capacity. This is since the CO_2 concentrations on the International Space Station are significantly higher than typical atmospheric concentrations - ~400ppm and 2500ppm respectively[1]. This project also aims to find out if the structure of the sorbent has any effect on sorption capacity. The solid guanidinium sorbents used in the lab typically take the form of a powder. However, using a powder as a sorbent for a carbon scrubber is unfeasible, as it would result in high pressure drops and frequent dust formation. As a result, this project also aims to find a way to create solid beads out of the guanidinium sorbents, to follow design principles for carbon scrubbing. The way this is done is by encasing the guanidinium powder inside of aerogel beads. Aerogels are light and very porous materials formed from removing fluids from hydrogels. The solid nature of aerogels helps create a solid bead shape where guanidinium powder can be inserted inside. Meanwhile, the porous nature of an aerogel allows air to flow through it and interact with the guanidinium sorbents for adsorption. As zeolite already takes the shape of a bead, it does not need to be placed inside aerogel beads. However, zeolite beads were crushed to compare the sorption capacity of the guanidinium sorption powders. From these experimental goals, a matrix can be created showing the different tests necessary to show the effect from all variations. The matrices are shown below in figure 6; this includes the type of sorbent, concentration of CO_2, and sorbent structure.

15% Gn_2CO_3-AC Atmospheric Conc. Powder	**15% Gn_2Isp-AC Atmospheric Conc. Powder**	**Zeolite Atmospheric Conc. Powder**
15% Gn_2CO_3-AC Raised Conc. Powder	**15% Gn_2Isp-AC Raised Conc. Powder**	**Zeolite Raised Conc. Powder**

15% Gn_2CO_3-AC Atmospheric Conc. Aerogel	**15% Gn_2Isp-AC Atmospheric Conc. Aerogel**	**Zeolite Atmospheric Conc. Bead**
15% Gn_2CO_3-AC Raised Conc. Aerogel	**15% Gn_2Isp-AC Raised Conc. Aerogel**	**Zeolite Raised Conc. Bead**

Figure 6. Matrix of possible experiments. Sorbent variation includes 15wt% Gn_2CO_3, 15wt% Gn_2Isp, and 5A 8-12 mesh Zeolite. Atmosphere variation includes atmospheric CO_2 concentration (~400ppm) and raised atmospheric concentration closer to ISS levels (~2500ppm). Structure concentration includes powder and beads.

Experimental Procedures

Bulk Guanidinium Crystal Synthesis

While Gn_2CO_3 already comes in bulk, Gn_2Isp needs to be synthesized. To begin synthesizing the sorbent, weigh out 0.50 grams of guanidinium carbonate using a scale. This compound will be dissolved and mixed with isophthalic acid to get the desired guanidinium crystal. A simple ion exchange reaction is assumed to occur, leading to the production of a guanidinium isophthalate crystal plus carbonic acid (which decomposes into H_2O and CO_2). Using this reaction, dimensional analysis was conducted to determine the mass of carboxylic acid needed for synthesis as seen in equation 1 and 2. Weigh out the calculated mass of the desired carboxylic acid.

For Isophthalic Acid

$$Gn_2CO_3 + H_2Isp \rightarrow Gn_2Isp + H_2CO_3 \quad (1)$$

$$\frac{0.50g\ Gn_2CO_3}{1} * \frac{1mol\ Gn_2CO_3}{180.17g\ Gn_2CO_3} * \frac{1mol\ H_2Isp}{1mol\ Gn_2CO_3} * \frac{166.132g\ H_2Isp}{1\ mol\ H_2Isp} = 0.4610g\ H_2Isp \quad (2)$$

Add ~60mL of methanol inside a 250mL beaker. Place that filled beaker on a heated stir plate connected to a thermocouple. Place the thermocouple inside the methanol and heat the beaker to ~40°C. Add the guanidinium carbonate and desired carboxylic acid measured previously and leave the mixture to stir for 60 minutes, once finished, turn off the stir and heat. Leave the beaker in a fume hood to fully evaporate in ~24 hours. Once fully evaporated, gather all the leftover guanidinium isophthalate into a sample jar.

Complexing with Activated Carbon

To synthesize the sorbent, measure 0.15g of the desired guanidinium crystal (Gn_2CO_3 or Gn_2Isp). Fill in a 250mL beaker with ~20mL of solvent and place it on a stir plate. This solvent depends on the solubility of the guanidinium crystal. For this case, water should be used for Gn_2CO_3, and methanol should be used for Gn_2Isp to ensure best solubility. For this experiment, a 15wt% ratio of guanidinium crystal and activated carbon is used for the final sorbent composition. Measure 1.13g of activated carbon. Then, add it and the weighed out guanidinium crystal into the methanol beaker and leave it to stir for ~30min without heating the mixture. Afterwards, leave the beaker inside a fume hood to evaporate for ~24hours. Gather the sorbent mix into a sample jar.

Synthesis of Aerogels

Aerogel synthesis begins with the synthesis of hydrogels. For this experiment, a 6wt% aqueous solution of the respective sorbent was mixed with a 6wt% aqueous solution of alginate. Using a syringe, this mixture was dripped in a solution of 0.2M calcium chloride ($CaCl_2$) which immediately transforms the drops into small hydrogel alginate beads. These hydrogels are then stored in 6-dram vials. The sorbent-alginate solution was dripped using a 30mL glass syringe and extruded through an 18G needle to ensure a similar bead diameter to the 5A zeolite beads. Afterwards, the hydrogels are soaked in deionized water for 24 hours in preparation for solvent exchange. In solvent exchange, the fluid inside the hydrogel structure is gradually changed to another solvent. For this case, the water inside the aerogel is gradually changed into ethanol (EtOH). Beginning with pure water, the solvent is exchanged with 15mL of a new stock solution containing 10% greater concentration of EtOH than the previous solvent. The aerogels are left to soak for 24 hours after which the process is repeated until 100% EtOH is reached. Once pure ethanol makes up the hydrogel, it is replaced with supercritical CO_2 through a drying process. This process freezes the hydrogel structure in place, leaving only the dry alginate structure behind. After this drying process, the aerogels are taken out and stored in vials. The final products for both the 15wt% Gn_2CO_3 and 15wt% Gn_2Isp aerogels are shown in figure 7.

Figure 7. Image of synthesized 15wt% Gn_2CO_3-AC and 15wt% Gn_2Isp-AC aerogels. Image from Daniel Lobree.

Adsorption Column Runs

To begin measuring sorption capacity, prepare a blank column by adding two pieces of glass wool to a thin glass column made for the column system, a schematic of which appears on figure 9. Then Place the column in the measuring system and run the system's MATLAB program: new_column_20251027. Use the following settings: Number of runs: 10, number of blanks 3, Time of adsorption run (min): 25, Temperature of adsorption run (C): 21, Time of desorption period (min): 15, Temperature of desorption period (C): 120, N2 flow [sccm] (range: 0 – 3000): 300, N2 flow [sccm] (rang: 0 – 1000): 225. Mark 1 to start blanks. These runs are meant to simulate dry room conditions. Once the blank runs are done, remove the column and add ~40mg of sorbent between the 2 pieces of glass wool. The column should look something similar to figure 8. Then, place the column back in the measuring system and attach the thermocouple to the side of the column using heating tape. Wrap the column around with an insulator, type the mass used in the MATLAB program, and continue the program. 10 runs typically last a full day. Once the runs finish, the column should be cleaned, and the system should be turned off. Data collected from the program was extracted and analyzed.

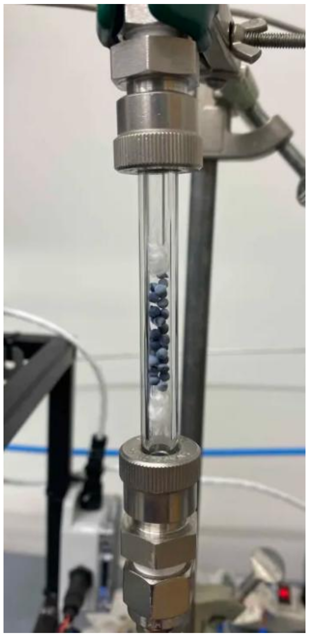

Figure 8. Image of sorption column with aerogel sorbent placed inside **before the addition of the thermocouple and heating tape**. Image from Daniel Lobree.

The blank time from the data collected from the blank runs before calculating for sorption capacity, a graph of which is presented in Figure 9. This was done by calculating the standard deviation of the CO_2 concentration (CO2PPM) when it reaches a steady state, locating the time at which CO2PPM values exceeded 5 times this standard deviation, and then taking the average of the 3 times calculated from the 3 blanks as the blank time. The sorption capacity was calculated by integrating the area above the CO2 concentration curve and below the average CO_2 concentration once the breakthrough curve reaches steady state. Sorption capacity was then calculated from this value, the column flow rate of the column, and the mass of the sorbent added.

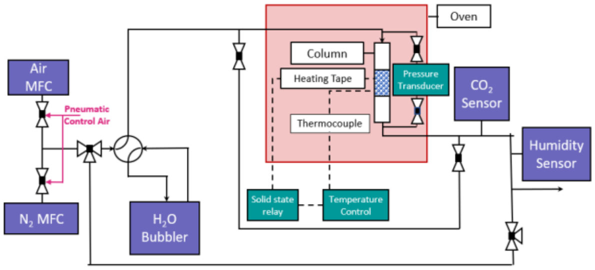

Figure 9. Model schematic of adsorption column mechanism used for sorption testing.

Results

Each sorbent was run through the adsorption column to measure and calculate their sorption capacity. A total of 12 runs were conducted including: 15wt% Gn_2Isp powder and aerogel, 15wt% Gn_2CO_3 powder and aerogel, 5A zeolite powder and beads, all under room CO_2 concentrations and elevated CO_2 concentrations. The average sorption capacity for each sorbent is graphed in figure 10. From this graph, the 15wt% Gn_2CO_3 sorbent has the highest sorption capacity at 0.180mmol CO_2/g sorbent. Then, the zeolite beads, zeolite powder, and both aerogel sorbents all have a similar sorption capacity of 0.03-0.04 mmol CO_2/g sorbent, though the aerogel beads have slightly lower sorption capacities on average. The Gn_2Isp powder has the lowest sorption capacity at ~0.017mmol CO_2/g sorbent. This figure shows that changing the structure of zeolite sorbent from bead to powder does not change its sorption capacity. However, placing guanidinium sorbent inside aerogels does significantly affect its sorption capacity. Increasing CO_2 concentrations in sorption gas appears to universally increase the sorption capacity of every sorbent. Strangely, the 15wt% Gn_2CO_3 powder had a significantly higher sorption capacity than under atmospheric conditions than under elevated. Additionally, creating aerogel beads for Gn_2Isp significantly increased its sorption capacity. One explanation for Gn_2Isp aerogels' higher sorption capacity is that this is a result of guanidinium crystal dissolving off from the final product. Since part of the synthesis process for aerogels requires using polar solvents like water or ethanol, it is possible that the guanidinium crystals in the sorbent dissolved out of the material. However, this would imply that removing the Gn_2Isp crystal from its respective sorbent is beneficial to the sorbent's sorption capacity. It is also possible that the atmospheric runs for 15wt% Gn_2CO_3 powder were performed under more humid conditions, which is known to increase sorption capacity for the material. Future research should re-test this run. Ultimately, the graph demonstrates that current methods of creating guanidinium-based bead sorbents result in comparable sorption capacities to 5A zeolite. However, it seems it is possible to increase the sorption capacity of these guanidinium beads by improving synthesis methods. Future work should determine improvements to sorbent synthesis to increase guanidium retention in sorbent. TGA characterization was conducted on each sorbent and their components to determine their guanidinium crystal compositions. TGA data demonstrated that significant portion of guanidinium crystal material was not retained during sorbent and aerogel syntheses. Future research should attempt to revise synthesis methods so more guanidinium crystal is retained in the final product..

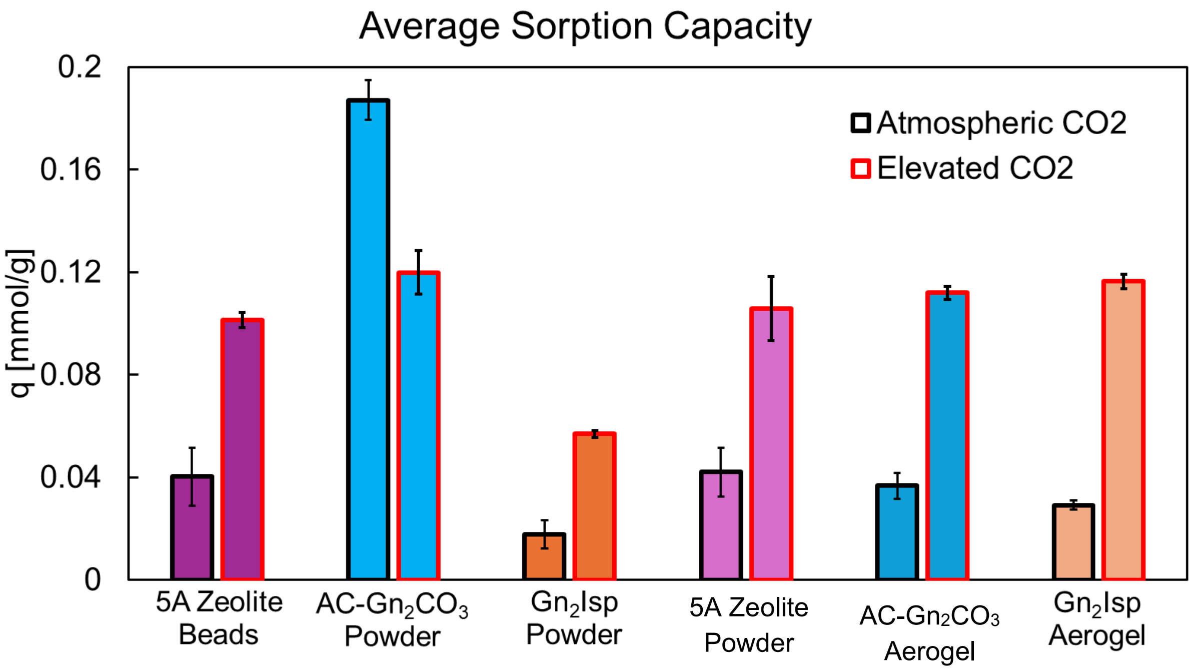

Figure 10. Average sorption capacity data for each synthesized sorbent.

Discussion/Conclusion

The purpose of this research was to evaluate the viability of using guanidinium based sorbents as an alternative to zeolite for carbon scrubbing on space habitats. To evaluate this, the sorption capacity of Zeolite was compared to 2 different guanidinium based sorbents – 15wt% Gn_2CO_3-AC and 15wt% Gn_2Isp-AC sorbents complexed with activated carbon. Gn_2Isp crystal was synthesized by dissolving and recrystallizing Gn_2CO_3 and H_2Isp. The sorption capacity of each sorbent was measured using an adsorption column which runs air through the sorbent under dry conditions. The output concentration of CO_2 was measured over time to create a breakthrough curve. The sorption capacity of a sorbent is then calculated by integrating the area between the breakthrough curve and the steady state CO_2 concentration in the column. The average sorption capacity of each sorbent was calculated and compared to each other. In this experiment, the structure of each sorbent was also varied between bead and powder sorbents. The zeolite was turned into a sorbent through crushing of zeolite beads while the guanidinium sorbents were turned to beads by encasing them in alginate based aerogels. TGA analysis was conducted for each sorbent to determine degradation behavior and to calculate the actual wt% of guanidinium crystal in the guanidinium-based sorbents. TGA analysis showed significant decreases in actual guanidinium crystal wt% compared to theoretical amounts. Ultimately, current methods for synthesizing guanidinium based sorbents for carbon scrubbing do not show a significant improvement in sorption capacity over zeolite sorbents. Both Gn_2CO_3 and Gn_2Isp aerogel sorbents, intended for use in carbon scrubbers, have comparable but slightly lower sorption capacities than the capacity measured for both zeolite beads and powder all of which sit ~0.03-0.04mmol CO_2/g sorbent. Furthermore, increasing the CO_2 concentrations of each sorption run increased the sorption capacity of every sorbent by similar amounts. The only exception are the runs for 15wt% Gn_2CO_3-AC powder. However, there were likely instrument errors present during this measurement. Furthermore, it is assumed that some guanidinium crystal was lost during the aerogel synthesis process, leading to a decrease in sorption capacity for the Gn_2CO_3 aerogel compared to its powder form. Future research should attempt to improve the synthesis process of the Gn_2CO3 based aerogel sorbents through close monitoring of the amount of guanidinium present during synthesis, and modification of synthesis methods to increase guanidinium retention. Other limitations include loss of guanidinium during complexing with activated carbon and addition of solvent into the crystal lattice structure of the synthesized Gn_2Isp. Ultimately, the comparable sorption capacities between the zeolite and guanidinium sorbents in both atmospheric and elevated conditions support the idea that guanidinium material could serve as sorbents for future carbon scrubbing operations. Future work should attempt to vary the aerogel morphology to determine if it is a significant barrier for CO_2 adsorption. Furthermore, it would also be useful to revise the synthesis methods for guanidinium sorbents and aerogels to preserve more guanidinium crystal in the final product.

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