THE DEVELOPMENT OF NATURAL SUSTAINABLE MATERIALS FOR CO_2 CAPTURE

Aoife Donohoe
Supervised by Prof Wolfgang Schmitt

School of Chemistry, Trinity College Dublin

Introduction

The use of CO_2 capture materials is a very exciting development in science today due to the need to drastically reduce the amount of greenhouse gases such as CO_2 in the atmosphere. However modest reductions of CO_2 emissions will only delay the increase of CO_2 levels in the atmosphere. Negative emission technologies are required to decrease these atmospheric CO_2 concentrations and meet the promises of the Paris Climate accord. Unfortunately, many proposed carbon capture technologies are not economically viable and are not sustainable and associated with large carbon footprints. The aim of this project was to aid the research into negative emission technologies through investigating if advanced porous organic frameworks with exceptional CO_2 capture abilities could be synthesised from natural organic materials.

Initial idea of project

Metal organic frameworks are known for their porosity and have been used for carbon capture and storage.[1] This project planned on making these porous frameworks from natural and sustainable materials. The material found to be most suitable for this was the naturally occurring sugar, chitosan. This sugar is found in the shells of shrimp and is a by-product of the seafood industry, making it highly sustainable. Chitosan has modified to become porous and has uses in a number of areas such as drug distribution.[2] In order to increase the carbon capture abilities of materials the nitrogen content must be increased.[3] The initial plan for this project was to increase the nitrogen content of chitosan and then bond the modified sugar to metal centres creating natural metal organic frameworks, MOFs, for carbon capture.

Problems encountered

Unfortunately, the project did not go to plan and the direction of the project had to be altered after the first synthesis. The natural sugar chitosan had been successfully modified to contain more amino group using a two step functionalisation reaction.[4] The modified sugar was reacted with the metal salts, nickel(II) nitrate hexahydrate, manganese(II) nitrate tetrahydrate, copper(II) acetate monohydrate, copper(II) nitrate trihydrate, and zinc(II) nitrate hexahydrate, appearing to bond with them as the colours of the metals were absorbed into the sugar. These metal compounds were not found to be porous when tested using a volumetric gas adsorption studies. This meant that metal organic frameworks could not be formed with the sugar chitosan.

Modifications

The project was then modified to make porous materials from chitosan without bonding to metals to make MOFs. The porosity was instead formed by crosslinking the sugar with tetraethyl orthosilicate, TEOS. TEOS has been used to successfully make chitosan porous. [5] For this method beads of chitosan were synthesised through dissolving the sugar in acetic acid and dropping the solution into concentrated sodium hydroxide base. The TEOS was then added in a number of different ways in varying concentrations. Sometimes the TEOS was added before the beads were formed, sometimes with double or half the concentrations of chitosan or TEOS. 14 different types of beads were formed in total. All of these were tested for their porosity and the porous compounds then underwent gas absorption testing to determine their carbon dioxide capture abilities.

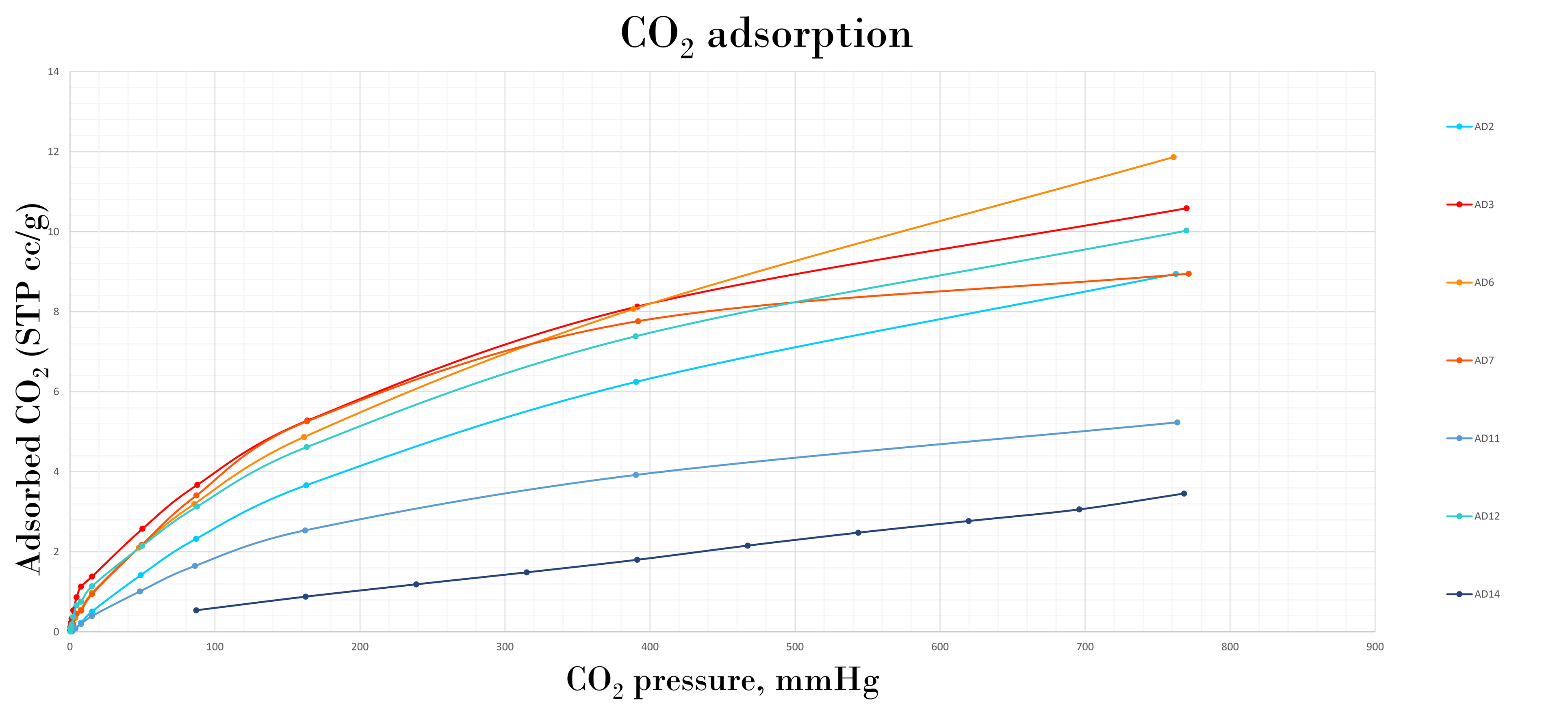

Figure 1: The results of the CO_2 absorption tests run on the different compounds synthesised.

Results

Seven of the fourteen types of beads formed during the course of the project were found to be porous after gas absorption tests. These tests also determined the pore sizes, the surface area, and the void volume present in the compounds. The porous compounds were further tested in 'breakthrough' studies, which involved passing CO_2 through a column of the beads to determine the carbon capture abilities of the different compounds. Figure 1 shows that the compound known as AD 6 was found to be the most successful in adsorbing CO_2. This compound was synthesised by forming the chitosan beads and then reacting these with a solution of TEOS acidified with hydrochloric acid. It absorbed a maximum of 11.8649 cubic centimetre of carbon dioxide per gram of compound at a carbon dioxide pressure of 761.1367 mmHg. This unfortunately is not a very effective as the pressure of carbon dioxide in our atmosphere normally is just over 0.3 mmHg. At this pressure there was not adequate adsorption of carbon dioxide for any of the compounds, for them to be considered for large scale carbon capture.

Data on compound AD6

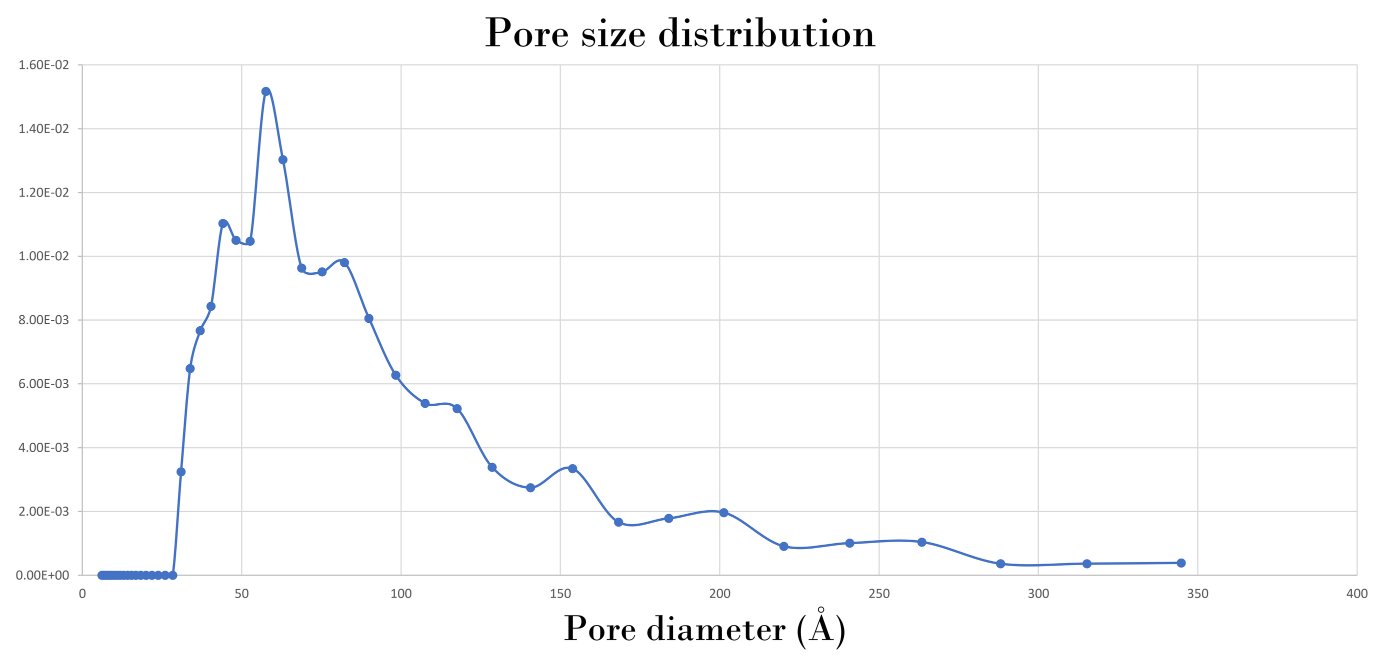

Figure 2: The distribution of the pore sizes in the AD 6 compound

Figure 2 shows that majority of the pores in the compound are around 40 – 80 Å in diameter. This is a very good result as for capturing small molecules like CO_2 the smaller the pores the better.

The surface area was found using the BET (Brunauer, Emmett and Teller) theory and N_2 gas adsorption. The total surface area = 136.02 m^2/g

The pore volume was also calculated from the N_2 gas adsorption data. The void volume of the pores = 0.233 cm^3/g

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Conclusion

The synthesis of metal organic frameworks from the naturally occurring sugar, chitosan, was not successful. However porous beads were able to be synthesised from this highly abundant and sustainable compound using the crosslinking technique with the compound TEOS. While these compounds were not overly promising in their carbon capture abilities, further research and development could bring about brighter results for theses materials in the future.

References

1. Salma Ehab Mohamed Elhenawy, Majeda Khraisheh, Fares AlMomani and Gavin Walker, 2020. Metal-Organic Frameworks as a Platform for CO2 Capture and Chemical Processes: Adsorption, Membrane Separation, Catalytic-Conversion, and Electrochemical Reduction of CO2, Catalysts 2020, 10, 1293
2. F L Mi, S S Shyu, C T Chen, J Y Schoung, 1999. Porous chitosan microsphere for controlling the antigen release of Newcastle disease vaccine: preparation of antigen-adsorbed microsphere and in vitro release. Biomaterials 1999
3. Eloy S. Sanz-Perez,́ Christopher R. Murdock, Stephanie A. Didas, and Christopher W. Jones, 2016. Direct Capture of CO2 from Ambient Air. Chem. Rev. 2016, 116, 11840−11876
4. Shao, K., Han, B.Q., Gao, J.N., Song, F.L., Yang, Y., Liu, W.S., 2015. Synthesis and characterization of a hydroxyethyl derivative of chitosan and evaluation of its biosafety. Journal of Ocean University of China 14, 703-709.

Peng, Y.F., Han, B.Q., Liu, W.S., Xu, X.J., 2005. Preparation and antimicrobial activity of hydroxypropyl chitosan. Carbohydrate Research 340, 1846-1851. Jing Zhong, Hui-Lian Huang, Jing Li, Fu-Chu Qian, Li-Qin Li, Ping-Ping Niu, and Li-Cheng Dai, 2015. Development of hybrid-type modified chitosan derivative nanoparticles for the intracellular delivery of midkine-siRNA in hepatocellular carcinoma cells. Hepatobiliary Pancreat Dis Int, Vol 14, No 1, 82-89

5. Guillermo J. Copello, Marıa E. Villanueva, Joaquın A. Gonzalez, Sofia Lopez Egues, Luis E. Diaz, 2014. TEOS as an Improved Alternative for Chitosan Beads Cross-Linking: A Comparative Adsorption Study. J. APPL. POLYM. SCI.

Thomas Y. A. Essel , Albert Koomson , Marie-Pearl O. Seniagya , Grace P. Cobbold ,Samuel K. Kwofie , Bernard O. Asimeng , Patrick K. Arthur , Gordon Awandare, and Elvis K. Tiburu, 2018. Chitosan Composites Synthesized Using Acetic Acid and Tetraethylorthosilicate Respond Differently to Methylene Blue Adsorption. Polymers 2018, 10, 466.