A Novel Approach to Capturing CO2 Directly from the Air Using Metal-Organic Frameworks

Grant Proposal

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Executive Summary

Global warming causes many severe effects, such as rising sea levels, stronger storms, worsening droughts, and an overall increase in global temperatures. Global warming is caused by the greenhouse effect, which is driven by an abundance of greenhouse gases in the atmosphere absorbing heat that would have otherwise escaped into space. One notable gas is carbon dioxide, as CO2 levels in the atmosphere have been increasing drastically due to human activities. To prevent global warming from continuing its projected path until the conditions on Earth become unlivable for humans, the net carbon emissions have to be decreased, meaning that there is either a reduction in carbon emissions or carbon emissions are captured after being released into the atmosphere. One emerging material being studied for its potential to capture CO2 from the atmosphere is the metal-organic framework (MOF). MOFs are porous frameworks formed by metal ions or clusters connected by organic ligand linkers. Previous studies have shown that MOFs can selectively adsorb CO2 when presented with a mixture of gases released by power plants, a method of capture known as point-source capture. This selectivity for CO2 also be applied to the capture of CO2 directly from the air, which is known as direct air capture or DAC. Therefore, MOFs have the potential to aid in the development of a scalable DAC system. This project aims to design a cost-effective, energy efficient MOF optimized for DAC while considering synthesis and regeneration efficiency.

A Novel Approach to Capturing CO2 Directly from the Air Using Metal-Organic Frameworks

Global warming has many negative effects on the planet, including rising sea levels, worsening droughts, and stronger storms (NASA, n.d. b). One approach to reducing or potentially reversing these effects is to address the main cause of global warming: the abundance of heat-absorbing greenhouse gases in the atmosphere. The sun emits solar radiation, some of which the Earth absorbs and some of which the Earth radiates back into space in the form of heat; however, certain gases, termed greenhouse gases, absorb some of the Earth's heat radiation, causing heat to remain in the atmosphere (NASA, n.d. a). This effect, the greenhouse effect, is crucial to maintaining a temperature that supports life on Earth, but due to the excessive amount of greenhouse gases in the atmosphere, the Earth is retaining a lot more heat than it should be, causing an increase in temperature. If the amount of greenhouse gases in the atmosphere decreased, global warming could slow down or reverse (Herring & Lindsey, 2022), as there would be less heat absorbed and kept in the atmosphere.

Carbon Dioxide

There are many different greenhouse gases, including carbon dioxide, water vapor, methane, and nitrous oxide, but carbon dioxide tends to receive attention because it is the most abundant greenhouse gas released by human activity (NASA, n.d. a). The average concentration of carbon dioxide in 2019 was over 400ppm. The previous highest concentration was about 300ppm, over 300,000 years ago (Khan, 2021). This massive spike is the result of industries built upon the burning of fossil fuels and other human activities that contribute to carbon emissions. The most straightforward approach to reaching "net-zero" carbon emissions, where there is no overall addition of carbon dioxide into the atmosphere, is to decrease carbon emissions in general, but with the dependency of many industries on processes that emit carbon dioxide, simply reducing emissions may prove difficult. Additionally, in the long run, the overall concentration of carbon dioxide needs to be not only restricted from further increase but reduced to reverse the effects of global warming (Sanz-Pérez et al, 2016). As a result, many hope to develop efficient technology that can help remove carbon dioxide from the atmosphere to reach net-zero or net-negative carbon emissions (Brazzola et al, 2024).

Metal-Organic Frameworks

Many methods of carbon capture already exist, including the use of amine-based solvent systems and liquid sorbents, but more recently, there has been a less established method of carbon capture that is potentially more energy efficient and cost effective: metal-organic frameworks (MOFs) (Lin, J. et al., 2021). MOFs are porous nanomaterials formed by metal ions or clusters connected by organic ligands. They are versatile, varying in pore size and porosity. By changing the metal ions or organic ligands used to form the framework, the physical and chemical properties can be manipulated to get a higher selectivity for a specific chemical substance, meaning a certain molecule tends to be absorbed over another molecule when the MOF is presented with a mixture of the two (Safael et al., 2019).

Limitations of MOFs

Despite their promise, however, there are a few main drawbacks that need to be addressed. Firstly, MOFs can be developed in labs but might not be scalable in an actual market setting, in part because of costly or difficult synthesis procedures that could harm the environment, in energy consumption and in toxicity of byproducts (Zhang, Q. et al, 2023). Additionally, MOFs can adsorb molecules easily with limited energy use; however desorption may be more difficult or require a great deal of energy, undermining the purpose of using MOFs over a different method of carbon capture (Zhang, Q. et al, 2023).

Applications of MOFs in Carbon Capture

Pre-existing MOFs optimized for carbon capture tend to be designed for point-source capture rather than direct air capture (DAC) because of the relatively low concentration of CO2 in the atmosphere compared to flue gas (Lin, J. et al., 2021). Point-source capture, also known as post-combustion capture, refers to the capture of carbon dioxide directly from flue gas, power plant emissions that are a mixture of carbon dioxide and other gases such as water vapor and nitrogen (Lin, J. et al., 2021). Direct air capture refers to the capture of CO2 directly from air rather than from flue gas released from a power plant (Myers, J., 2020). DAC tends to be more difficult and costly since the concentration of CO2 in the atmosphere is so much lower than the concentration of CO2 in flue gas. Thus far, few MOFs have been optimized for DAC, posing the question of if it is feasible to design and optimize a cost-effective, energy-efficient DAC system using MOFs.

Section II: Specific Aims

This proposal’s objective is to design a cost effective and efficient metal-organic framework that can be used in the direct air capture of carbon. By implementing this framework into a DAC system, I hope to develop a product that can reduce the concentration of carbon dioxide in the atmosphere in the long-term, which would reduce and eventually reverse the effects of global warming.

Specific Aim 1: Cost-Effective and Energy Efficient Synthesis

Specific Aim 2: Selectivity for Carbon Dioxide and Regeneration Efficiency

The expected outcome of this work is a working prototype that fulfills each of the aforementioned criteria to some extent. Therefore, the prototype should not be too expensive or require too much energy to synthesize, as well as require a reduced amount of chemicals toxic to the environment than most MOFs. The most crucial goal would be CO2 selectivity over other gases found in the atmosphere, including water vapor and nitrogen gas, in conditions with a low concentration of CO2. A bonus would be the ability to easily regenerate, or desorb CO2, in an energy efficient manner, which would help to make this MOF even better for the environment, or “greener”.

Section III: Project Goals and Methodology

Relevance/Significance

This project is significant because it aims to address the pressing issue of global warming. If global warming is to continue on its projected path, then very soon, the conditions on Earth will no longer be able to support human life (NASA, n.d. b). For this reason, it is crucial that a sustainable way of slowing or even reversing global warming is discovered quickly, before it is too late, for the sake of the planet and all its inhabitants.

Innovation

The selective properties of MOFs have been widely studied, but most prior research is about the use of MOFs in point-source capture rather than in direct-air capture (Zhang, X. et al, 2023). The lack of research in this area is mostly because the concentration of carbon dioxide in the atmosphere is much smaller than the concentration of other gases, such as water vapor. Flue gas, gas emitted from power plants and other carbon emitting sites, has a much higher concentration of carbon dioxide, making it easier to capture more carbon through point-source capture; however, it may be inconvenient to employ point-source capture at every single site of carbon emissions, so the application of MOFs to direct air capture could be useful to reaching net-zero emissions in the future.

Methodology

Firstly, several types of MOFs will be synthesized at a lab at WPI and evaluated on the energy and cost efficiency of their synthesis. Then they will be exposed to the atmospheric air and their CO2 uptake will be monitored for the next 12 hours, when they will be regenerated to find out their total CO2 uptake and the efficiency of their regeneration. Each “step” or specific aim will be further explained and justified in their respective sections.

Specific Aim #1: Cost Effective and Energy Efficient Synthesis

The objective is to determine several MOFs that could be tested or optimized during this experiment. Many MOFs require extreme conditions during synthesis, which would require a lot of energy and may not be feasible in a laboratory setting. Therefore, as there is a lot of overlap between feasibility at the lab and this criterion, it would be easier to start off testing only a select few MOFs that can both be synthesized at the lab and fulfill the criterion of cost effectiveness and energy efficiency. The main approach would be to research different methods of MOF synthesis and different MOFs that tend to require less energy or fewer resources to synthesize. Ultimately, a few MOFs would be synthesized, then ranked against each other using quantifiable criteria.

Justification and Feasibility and Preliminary Data. This specific aim ensures that this experiment is feasible in regards to the lab, because the lab has synthesized MOFs before and has access to many materials needed for MOF synthesis, but it might not have all the necessary equipment to synthesize the more costly or high energy consuming MOFs. In addition, there are many different MOF synthesis methods, detailed in Figure 1. Using these methods, there is a wide variety of MOFs that can be synthesized and tested.

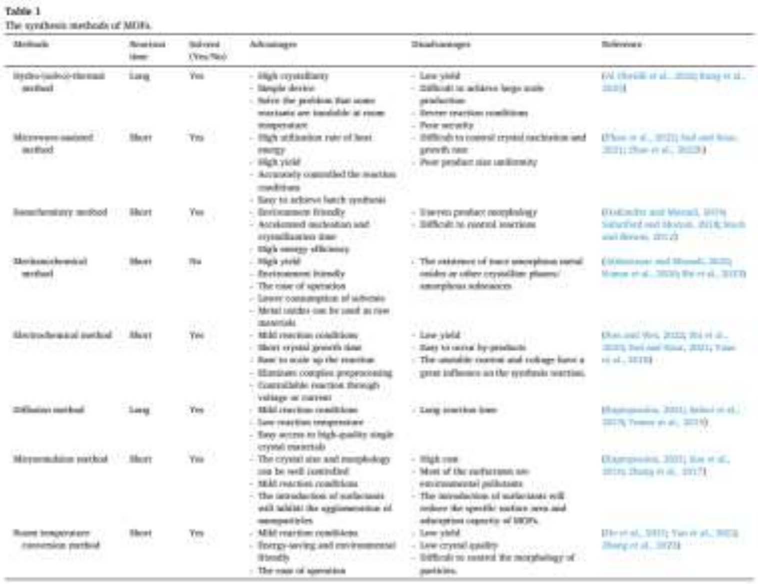


Figure 1: The advantages and disadvantages of a variety of methods of MOF synthesis, from a paper by Zhang (2023).

Expected Outcomes. The overall outcome of this aim is to determine what MOFs can be tested during this experiment based on their cost-effectiveness and their energy efficiency. This knowledge will be used to help decide which MOF would ultimately be a good fit for DAC but could also be used in the future to further improve MOF synthesis, which would reduce its environmental impacts and improve its scalability.

Potential Pitfalls and Alternative Strategies. Some of the synthesis strategies mentioned above still might not be feasible at the lab, which would limit the types of MOFs that can be synthesized and tested in this experiment. If the MOFs that can be synthesized are not sufficient, other MOFs that are known to have environmentally friendly synthesis processes could be bought and tested.

Specific Aim #2: Selectivity for Carbon Dioxide at a Low Concentration and Regenerability

The objective is to determine which of the selected MOFs performed the best when exposed to atmospheric air. They would be tested by exposing them to ambient air over a period of 12 hours and monitoring CO2 levels to see which MOF had the highest selectivity for CO2. Afterward, we would also take into account the energy or methods needed to desorb all of the CO2, or regenerate the MOF. In the end, the amount of CO2 taken by each MOF would be compared and the MOF that successfully adsorbed and desorbed the most CO2 would be decided.

Justification and Feasibility and Preliminary Data. This specific aim evaluates the selectivity of these MOFs and helps determine which MOF is the most effective, which can help lead to more refined knowledge about how to optimize a MOF for DAC. The following table (Figure 2) depicts a cumulation of different previously tested MOFs and their uptake capacity

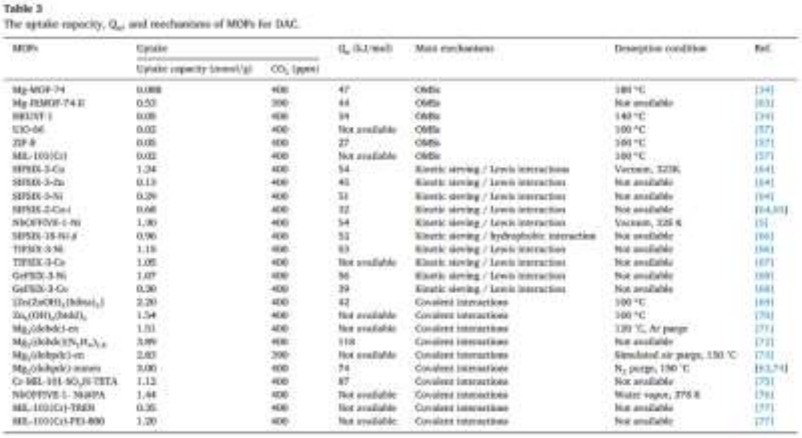


Figure 2: the uptake capacity of different MOFs exposed to ambient air from a paper by Zhang (2023).

for CO2, demonstrating the feasibility of testing and comparing different MOFs, though adsorption will be cut off at 12 hours.

Expected Outcomes. The overall outcome of this aim is to determine a MOF that effectively adsorbs and desorbs CO2. This knowledge not only reveals a potential candidate for future DAC methods, but it also demonstrates what characteristics of MOFs could be helpful in creating an even more optimized MOF in the future.

Potential Pitfalls and Alternative Strategies. A potential pitfall could be a significant underperformance of all MOFs tested, which could be addressed by looking into reasons for the underperformance and ways to prevent the issues that impeded the adsorption of CO2 or by retesting a different selection of MOFs that might not have been tested due to less cost efficiency.

Addendum

Due to unforeseen circumstances, rather than performing this experiment in a laboratory, it is being simulated using a simulation software named RASPA 2. RASPA 2 uses Monte Carlo simulations to calculate certain properties of frameworks and can be used to calculate the CO2 uptake of MOFs. Figure 3 displays a simulation of the adsorption of N2 into MIL-47 and was used as a proof of concept, as the run file was built into the RASPA 2 code as an example. The average absolute absorption of N2 is 0.3106058997 mol/kg of MOF.

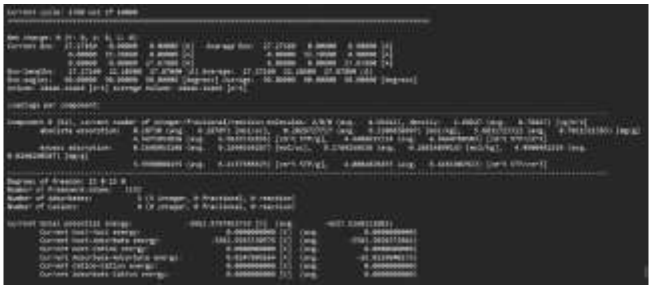
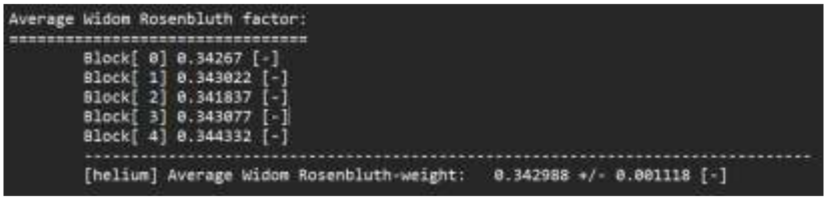


Figure 3:The simulation output of a simulation of the adsorption of N2 into MIL-47.

An additional proof of concept was the calculation of the helium void fraction of CALF-20 depicted in Figure 4. In a study by Lin et al in 2021, they calculated the helium void fraction of their experimental CALF-20 to be around 0.38. When simulated in RASPA 2 using a CIF file obtained from the Cambridge Crystallographic Data Centre, the calculated helium void fraction was 0.342988 +/- 0.001118, which has a 10% error compared to the experimental value.



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Average Widom Rosenbluth factor:
================================
        Block[ 0] 0.34267 [-]
        Block[ 1] 0.343022 [-]
        Block[ 2] 0.341837 [-]
        Block[ 3] 0.343077 [-]
        Block[ 4] 0.344332 [-]
        ------------------------------------------------------------------
        [helium] Average Widom Rosenbluth-weight:   0.342988 +/- 0.001118 [-]
```

Figure 4: The simulation output calculating the Widom Rosenbluth-weight, which also refers to the helium void fraction.

Section IV: Resources/Equipment

The equipment and materials needed for this experiment will be provided by the Burdette Lab at Worcester Polytechnic Institute, which includes both the equipment used to synthesize and regenerate the MOFs, as well as the materials that make up the framework.

Section V: Ethical Considerations

Protective gear will be worn when handling toxic or corrosive chemicals such as formaldehyde, though we hope to reduce our use of chemicals that are toxic to the environment so that the MOFs tested will be beneficial to the environment in the long run. Exposure to extreme conditions will also be avoided as much as possible, which relates to the energy efficiency and cost effectiveness of MOF synthesis.

Section VI: Timeline

November through December is focused on getting started in the lab, which includes lab training, collecting necessary preliminary data for the project, and brainstorming what MOFs might be tested and why. January will be mostly data collection and testing different MOFs, comparing their synthesis efficiency, selectivity for CO2, and regenerability. By February, I will have collected all the needed data and will either further integrate one of the MOFs into a DAC system and test or explore another route to optimization with other MOFs. Afterwards, I will analyze the results and work on my presentation for the science fairs.

Section VII: References

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