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Baker/Koob Final Report Template

Final reports will be published on the Cal Poly Digital Commons website(http://digitalcommons.calpoly.edu).

Title of Project:

Development of Polyethylenimine-Modified γ–Cyclodextrin Metal Organic Frameworks for Enhanced Post-Combustion CO2 Capture

Project Completion Date:

This specific portion of the project was completed on March 25th 2022.

Student Names and Majors:

Corinne Watson, Environmental Engineering

Faculty Advisor and Department:

Dr. Amro El Badawy, Civil and Environmental Engineering

Cooperating Industry, Agency, Non-Profit, or University Organization(s):

N/A

Executive Summary:

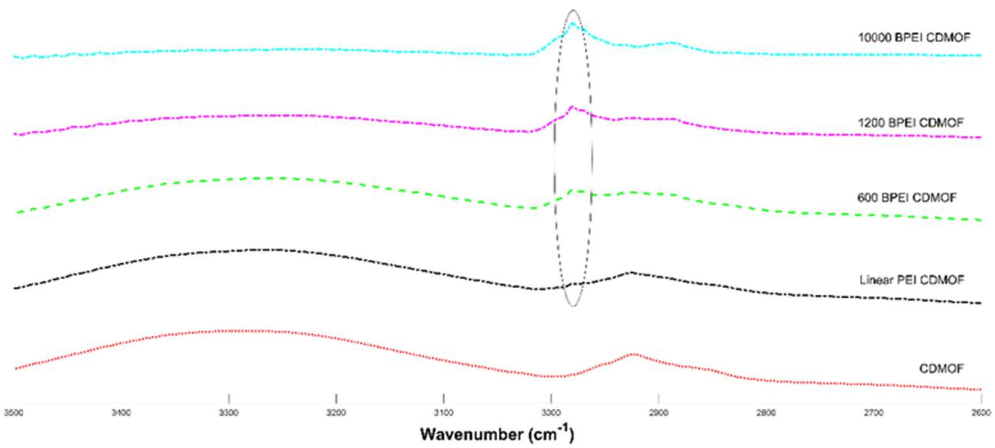
PEI-γ-CD-MOF Synthesis

γ-CD-MOFs were synthesized according to Ton Kar Yan's et. al 2016 method. The prepared MOFs were impregnated with linear PEI, 600 bPEI, 1,200 bPEI, and 10,000 bPEI according to Xian's et. al 2015 method.

PEI-γ-CD-MOF Characterization

Fourier-transform infrared spectroscopy (FTIR) (Figure 1.a) and thermogravimetic analysis (TGA) (Figure 1.b) were performed on all synthesized PEI-γ-CD-MOFs. The FTIR analysis showed a distinct peak at ~2980 cm^{-1} for all PEI-impregnated γ-CD MOFs compared to the control (Figure 1.a). As reported by Xin et al. (2015), PEI exhibits distinct peaks within the 2800-3500 cm^{-1} range that corresponds to n(NH) and n(CH) groups. Therefore, the ~2980 cm^{-1} peak in Figure 1.a could be attributed to the presence of the PEI on the surface of the MOFs. These FTIR results suggest that all types of PEI tested herein had some degree of interactions with the γ-CD-MOFs. The TGA data presented in Figure 1.b quantifies the PEI-γ-CD-MOF interactions with respect to the mass of PEI loaded onto the γ-CD-MOFs. The control-, 1,200 bPEI-, and 10,000bPEI-γ-CD-MOFs exhibited a total weight loss of ~72% within the tested temperature range (0-600°C) (Figure 1.b). On the other hand, the 600 bPEI γ-CD MOF had a total weight loss of ~85%, which means the PEI loaded was ~13% (Figure 1.b). The second highest loading achieved was ~6% in the case of linear PEI γ-CD MOFs (Figure 1.b).

a)



b)

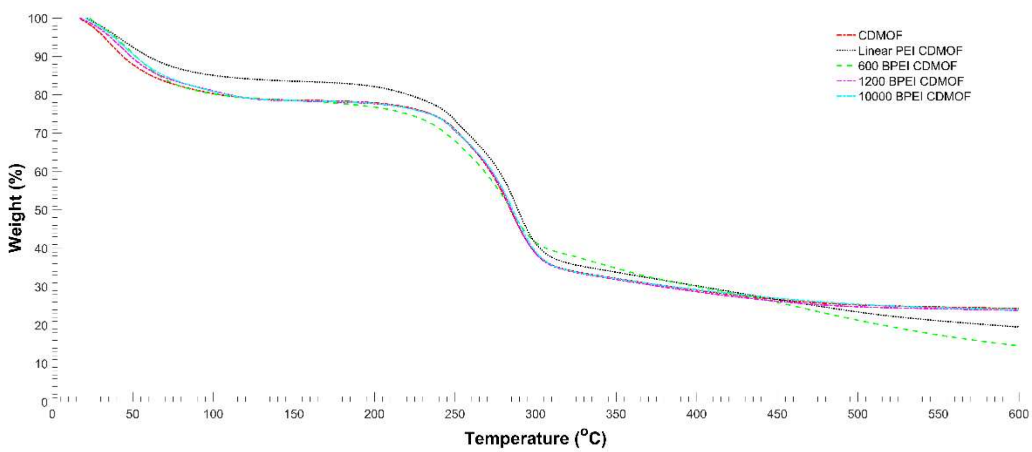


Figure 1. Characterization of control γ-CD-MOFs and PEI loaded γ-CD-MOFs with a) FTIR spectra and b) TGA

<u>QCM CO_2 Sorption Testing Apparatus</u>

The CO_2 sorption capacity was determined using a custom-built quartz crystal microbalance (QCM) assembly (Figure 2). This assembly was a modified design of the apparatus developed by Hesketh et al. and consists of a front load single sensor, loaded with quartz crystals (6MHz, gold electrode). The QCM is housed within a vacuum chamber, attached to a vacuum outlet and CO_2 gas inlet (Figure 2). Through measuring changes in frequency, the mass of MOF deposited and CO_2 sorbed can be calculated using the Sauerbrey Equation.

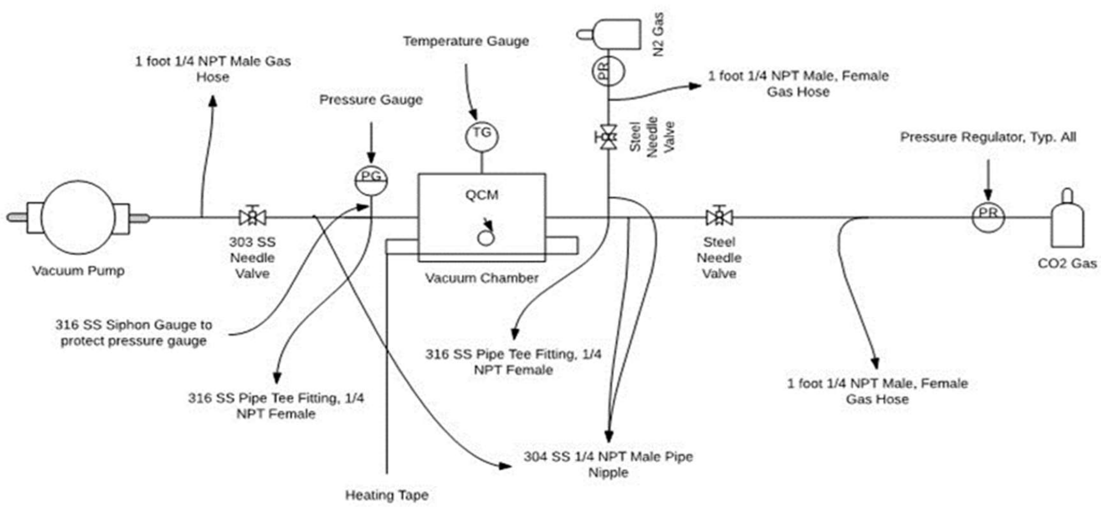


Figure 2. Quartz crystal microbalance assembly for testing CO_2 sorption

<u>PEI-γ-CD-MOFs CO_2 Sorption</u>
Figure 3 presents the amount of CO_2 sorbed (mmol/g) as a function of influent CO_2 partial pressure for γ-CD MOFs impregnated with different PEI arrangements and molecular weights. The γ-CD-MOF impregnated with 600bPEI sorbed the highest amount of CO_2 (.90 mmol/g) as compared to the other PEI impregnated γ-CD-MOFs.

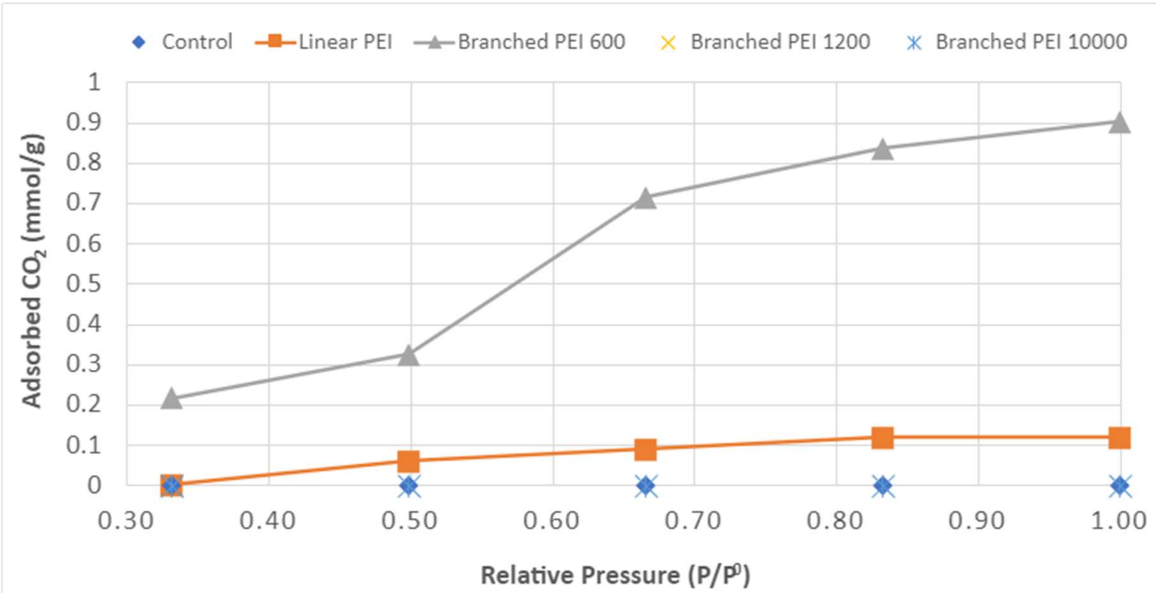


Figure 3. Impact of PEI arrangements and molecular weights on CO_2 sorption behavior of γ-CD MOFs

<u>QCM Testing Apparatus Improvements</u>

Upon receiving the Baker/Koob Endowment Grant, several improvements were made to the existing CO_2 sorption testing apparatus. The QCM crystals and CO_2 were restocked and refilled, respectively. The acquistion of these materials will lead to more experimental sorption analysis and further research regarding enhancing the capaicty and selectivity of PEI-γ-CD-MOFs for CO_2 soprtion. Furthermore, the previous 27.5 Hg rated vacuum pump was exchanged for the SERIES-9B 29.9 Hg vacuum from US Vacuum. The addition of this vacuum allows for testing lower CO_2 partial pressures within the system, which represents more environmentally relevant testing conditions to better simulate CO_2 partial pressures in flu gas stream.

<u>Conclusions</u>

The objectives of this work were to 1) identify the optimal PEI molecular weight and arrangement to enable the eco-friendly γ-CD-MOFs for CO_2 capture applications, 2) improve the CO_2 sorption testing apparatus by installing a 29.9 Hg vacuum, and 3) refill and restock the CO_2 gas cylinder and QCM crystals needed for conducting further research. The PEI tested were linear PEI, 600 bPEI, 1,200 bPEI, and 10,000 bPEI. Due to the large pore size, the control γ-CD-MOFs expectedly did not show measurable CO2 sorption. Also, impregnation of the γ-CD-MOFs with 1,200 bPEI or 10,000 bPEI did not achieve detectable CO2 sorption likely because of their relatively large molecular weight that caused pore blockage as demonstrated by the molecular docking simulation results. On the other hand, impregnation with the linear or 600 bPEI unlocked the potential for CO2 capture by γ-CD-MOFs. The sorption capacities were 0.12 mmol/g and 0.90

mmol/g for linear PEI- γ-CD-MOFs and 600bPEI- γ-CD-MOFs, respectively. The higher CO2 sorption achieved by the 600bPEI-γ-CD-MOFs, compared to linear PEI-γ-CD-MOFs, could be explained by the higher loading percentage (13% for 600bPEI and 6% for linear PEI) and the larger PEI molecular size in the case of 600 bPEI. Thus, among the polymers tested herein, the 600bPEI was the ideal candidate for impregnation of γ-CD-MOFs for CO_2 capture applications. Furthermore, the testing apparatus system was improved through the addition of the 29.9 Hg vacuum to simulated flue-like conditions. Future work is warranted to improve the 600bPEI loading percentage so that the γ-CD-MOFs will achieve higher CO_2 sorption capacities.

Major Accomplishments:

<u>Drafting of Journal Paper</u>

A draft journal paper is completed and is curnetly being reveiwd internallly before submision for publication (Watson, Lee, El Badawy, Kivy, Kathuria 2022).

<u>Conference Presentation of Findings</u>

Watson, C.; Lee, D., El Badawy, A. (2021). Development of Polyethylenimine-Modified Ɣ-Cyclodextrin Metal Organic Frameworks for Enhanced Post-Combustion CO2 Capture. Oral Presentation at the Climate Change 2021: *The Push to Carbon Neutrality, Adaptation, and Resiliency Virtual Conference, Air and Waste Management Association*, December 1-2, 2021.

<u>Accepted Abstract for Poster Presentaton</u>

Watson, C.; Lee, D., El Badawy, A.; Kivy, M.; Kathuria, A. (2022). Impact of Polyethylenimine Characteristics on the CO2 Sorption Capacity of γ–cyclodextrin Metal Organic Frameworks. Accepted for Poster Presentation at the Air and Waste Management Association’s 115th Annual Conference & Exposition, San Francisco, CA June 27-30, 2022

Expenditure of Funds:

Item	**Relation to Project**	**Total Cost**
29.9 Hg Series-9B Vacuum Pump	In order to similate flue gas-like conditions, a 29.9 Hg vacuum pump was necessary to create realistics CO_2 partial pressures.	$1064.51
CO_2 Gas Tank Refill	A refill of the CO_2 tank was necessary to continue operating the CO_2 sorption testing apparatus.	$14.81

QCM Crystals (6MHz, Gold)	A restock of the QCM crystals were necessary to continue testing and improving MOF sorption.	$247.71

Impact on Student Learning:

I am incredibly grateful for the skills and experience I gained from this project. As an undergraduate, this project was my first full imersion into the scientific research process. I gained several skills including technical laboratory skills that I could not find in a class setting. Dr. Kathuria allowed me to sit-in on his lectures on FTIR and TGA analysis. Through coupling my in-person synthesis of the MOFs and learning the characterization process, I was able to understand the concepts behind the research at a deeper level. Additionally, I was fortunate enough to gain knowledge on system design, specifically the CO_2 sorption testing apparatus. The original creator of the apparatus, Dustin Lee, was a graduate student in 2019, and he maintained contact with me over email to further understand and adjust the system. Furthermore, I was given the opportunity to improve my public speaking and communication skills through presenting at the Air and Waste Management Conference on carbon nuetrality. Finally, I gained experience in technical writing and data reporting. I plan to continue this research with Dr. El Badawy, and I am very fortunate to have had this experience in my future career field. Dr. El Badawy is a wonderful advisor and mentor, and I will continue to be thankful for his knowledge and teachings!