Synthesis and Characterization of Cyclodextrin-Based Metal–Organic Frameworks: Laboratory Experiments Adaptable to High School Laboratories

Eddie Gaffny, Elise Hanley, Aylin Aykanat*
Department of Chemistry, University of New Hampshire, Durham, NH 03824

Introduction

- **What are Metal-Organic Frameworks (MOFs)?**

MOFs, or metal-organic frameworks, are porous materials composed of organic linkers connected by a metal ion, forming a highly ordered, crystalline structure.

MOFs have generated significant attention for their synthetic tunability, and exceptionally high porosity. Gamma-cyclodextrin can self-assemble into metal-organic frameworks when combined with KOH or RbOH, enabling applications in gas adsorption and environmental remediation. These crystalline CD-MOFs are synthesized via vapor diffusion, and their reversible adsorption of synthetic dyes is investigated through both qualitative and quantitative analyses. This experiment can be adapted for use in educational settings ranging from high school to advanced undergraduate laboratories, engaging students across various subfields of chemistry, including fundamental principles, advanced materials, and the broader societal impacts of chemistry.

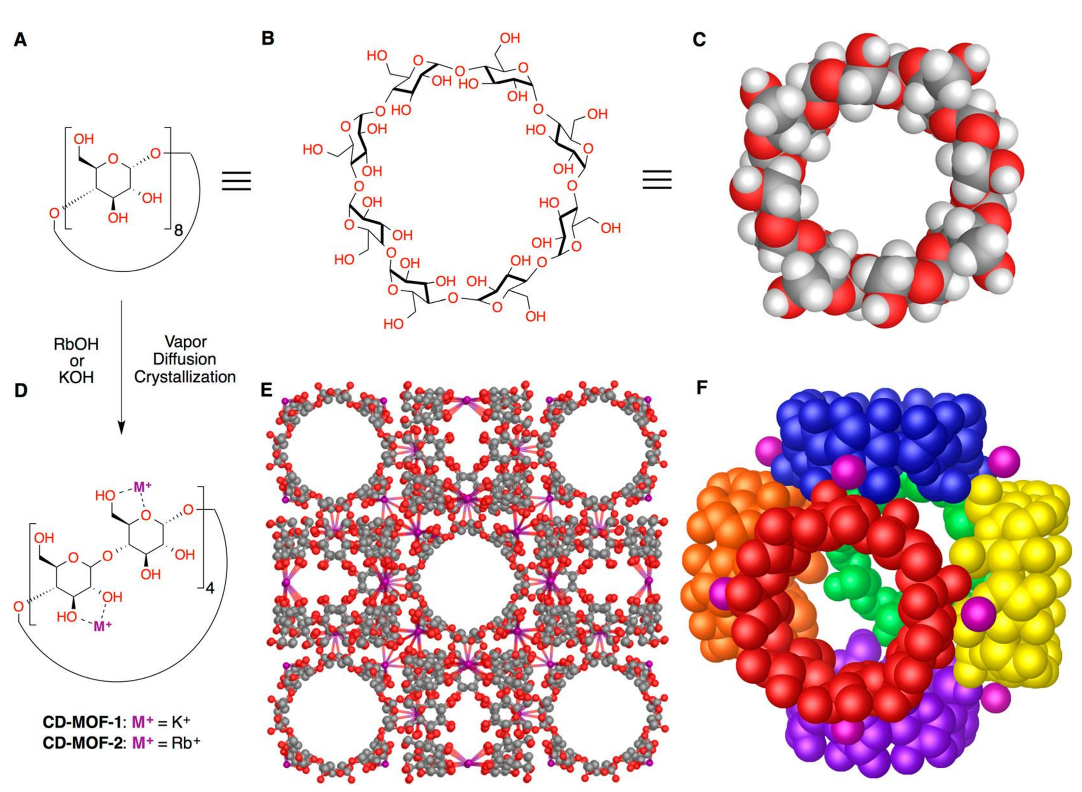


Figure 1. Three different representations of the chemical structure of γ-cyclodextrin: (A) condensed, (B) expanded, and (C) space-filling. (D) Crystallization of γ-cyclodextrin in the presence of RbOH or KOH results in coordination between the metal cations and γ-cyclodextrin, giving rise to porous metal–organic frameworks (CD–MOFs) as shown in (E) and (F). Metal cations are colored purple in (D–F). Individual γ-cyclodextrin macrocycles are colored in (F) to aid in visualizing their relative locations. J. Chem. Educ. 2015, 92, 2, 368-372

Methodology

The Method used for creating these crystals, was vapor diffusion. This technique is commonly used for crystal growth and holds the advantage of allowing us to manipulate the solvents used. One in which the compound is soluble and one in which it is poorly soluble or precipitates the compound (anti-solvent) causing the crystals to slowly form. In this instance, we used ethanol as the antisolvent to crash the crystals out of the water solution. This technique was used for both β-Cyclodextrin, and γ-Cyclodextrin.

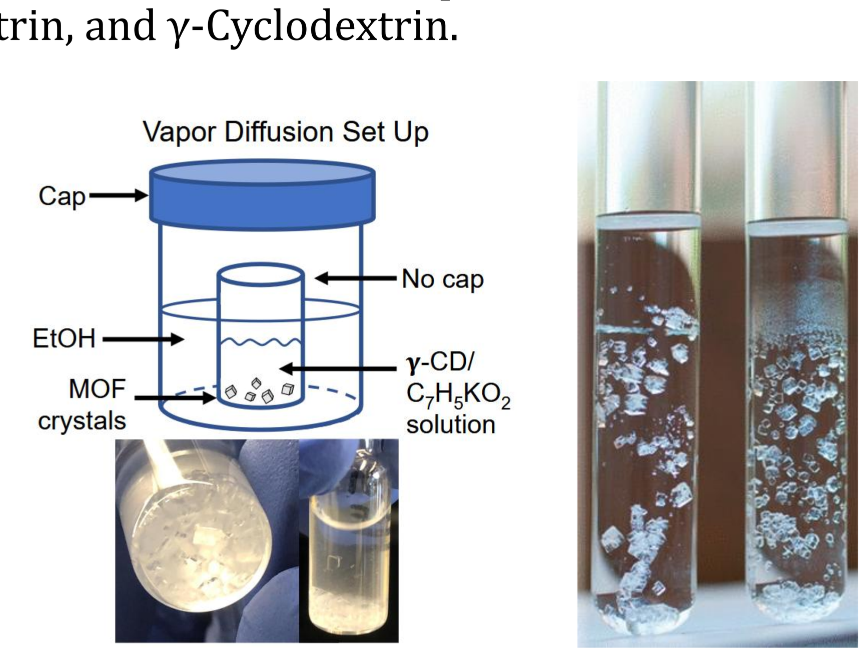
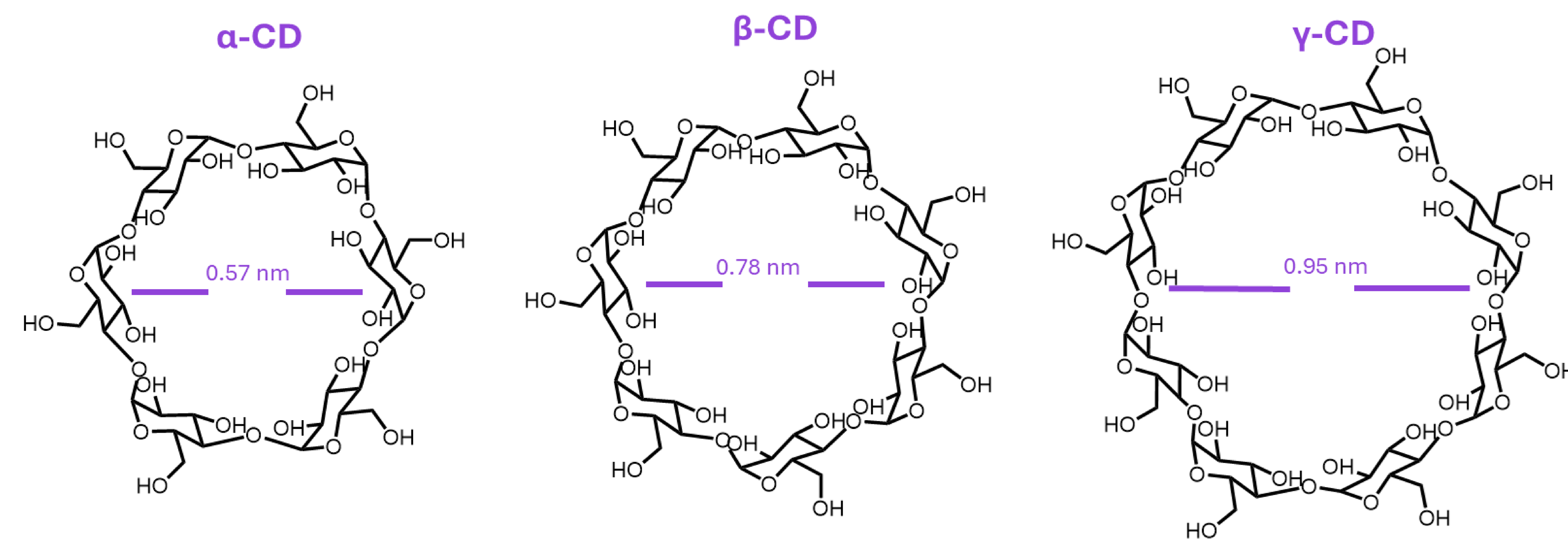
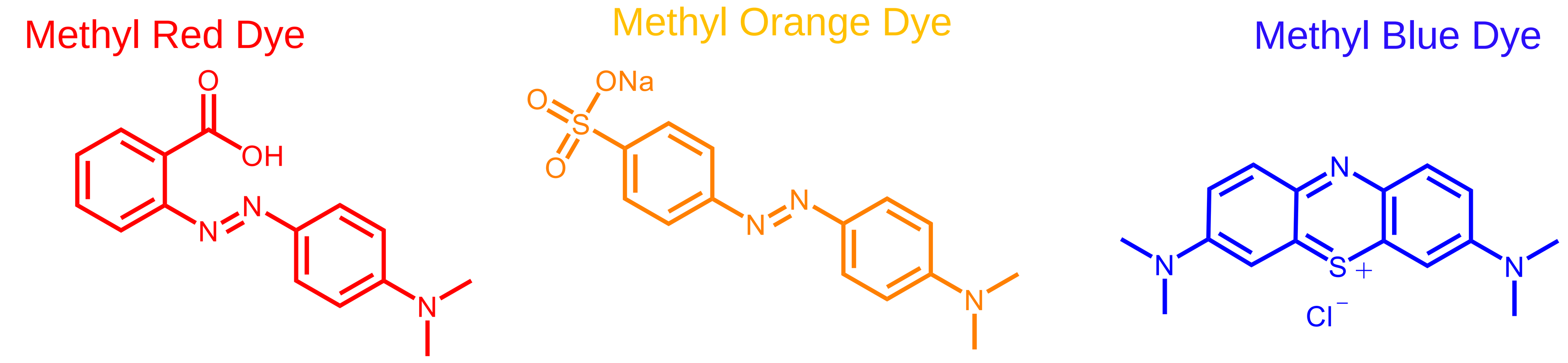


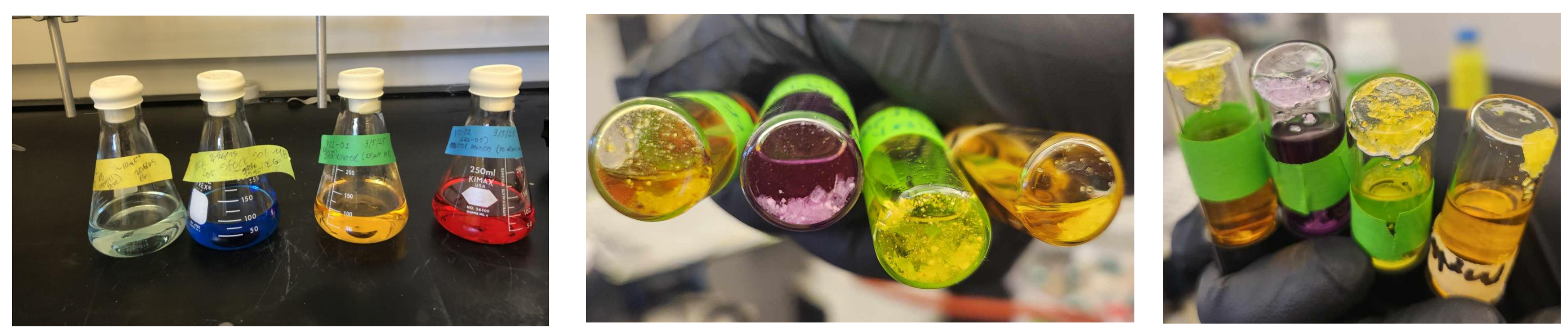
Figure 2: Vapor diffusion is a common technique used to grow crystals. A jar containing Cyclodextrin molecules are added to the vapor diffusion chamber containing Ethanol. J. Chem. Educ. 2015, 92, 2, 368–372

Experimental Design

Question 1: How does pore size affect dye adsorption?





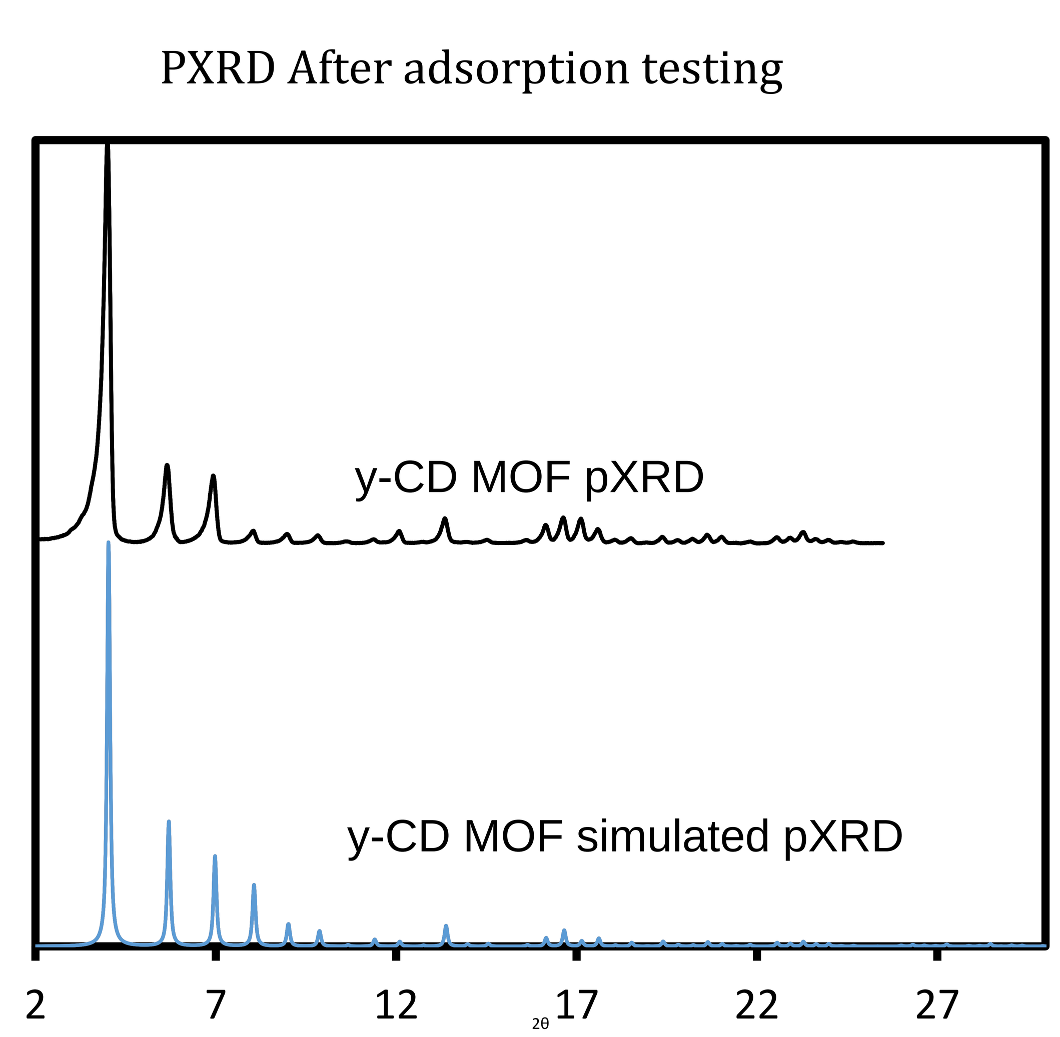


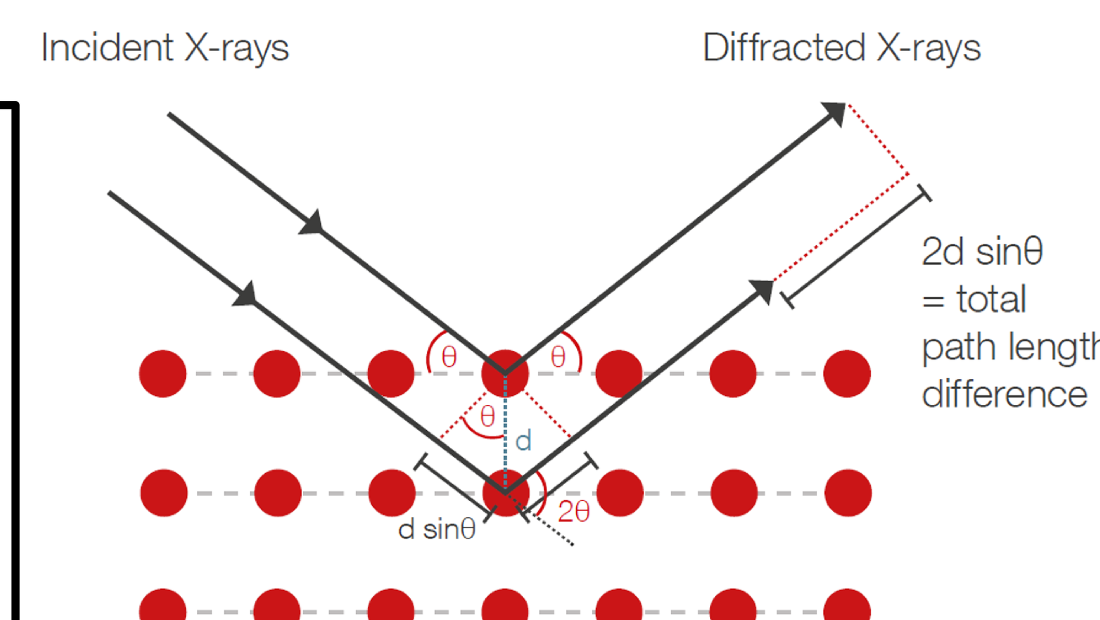
Procedural Description

In the first container is our dye solution, made up of our dye mixed in ethanol, at a concentration of ~25uL. In the next container, we have our β-Cyclodextrin, or γ-Cyclodextrin. In the third jar, we are combining the crystals and the dye solution, to show how the MOFs absorb the dye, resulting in a color change of the crystals. The final jar is our representation of the crystals fully absorbing the dye from the solution, giving a clear solution of ethanol, while the dye is completely enveloped by the crystals.

Powder X-Ray Diffraction and Infrared Spectroscopy

Question 2: How does morphology affect dye adsorption?





PXRD is the most frequently used XRD technique and is ideal for polycrystalline or powdered samples. Since the sample contains many randomly oriented crystallites, X-rays are diffracted in various directions, producing a pattern that can be analyzed for phase identification, quantification, and lattice parameter determination.

Optical and Scanning Electron Microscope

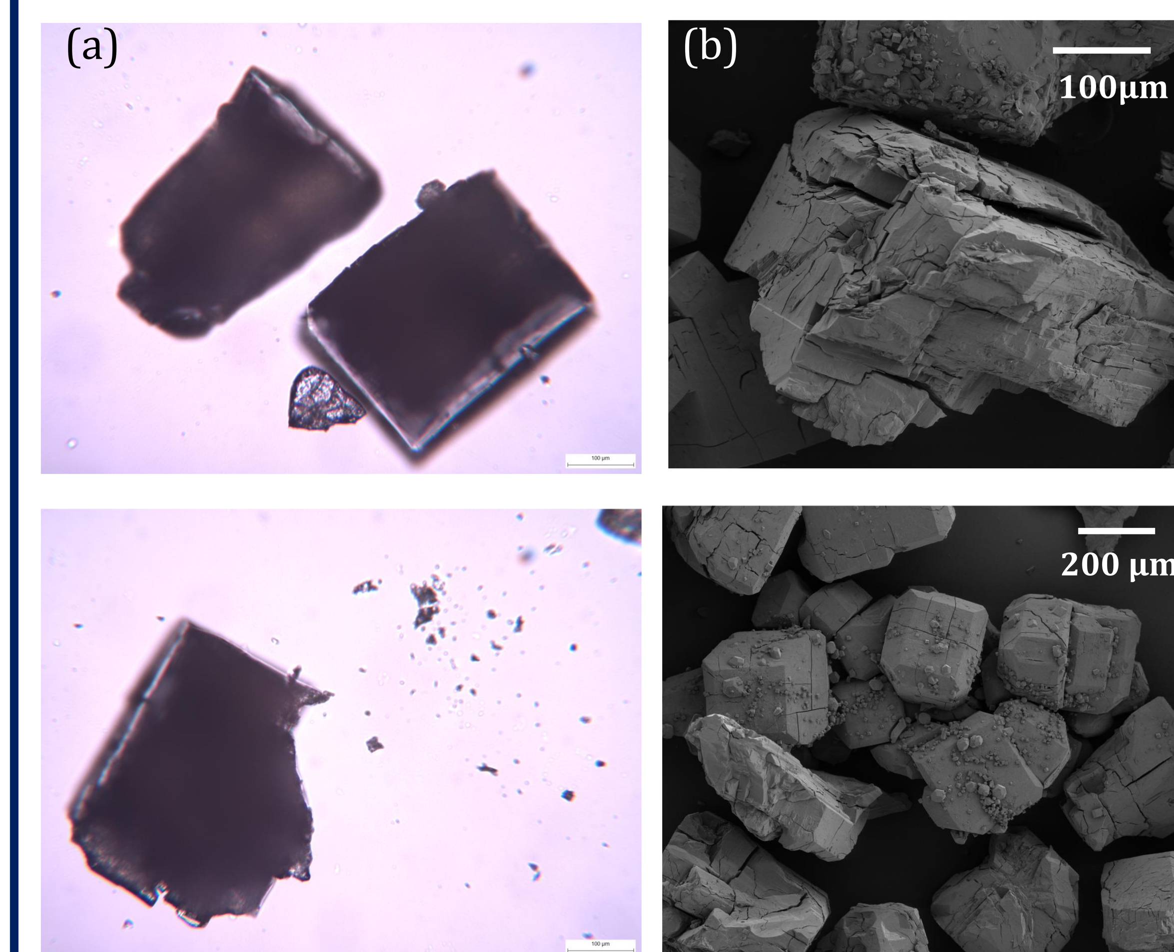
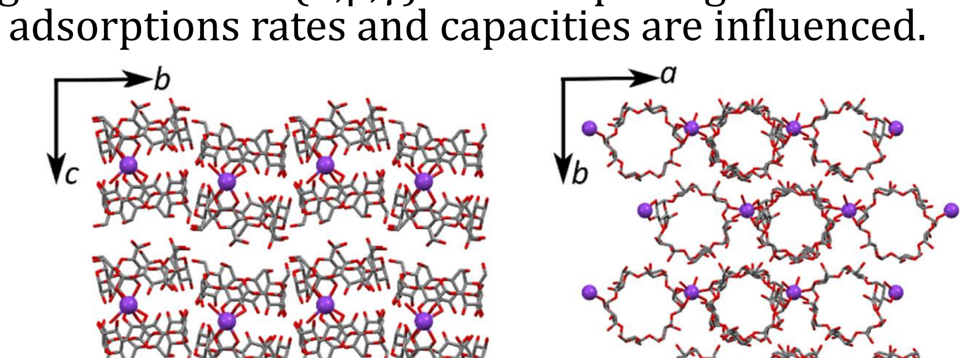


Figure 3: (a)High imaging Microscopes displaying square rigid crystallinity after dye absorption.(b) Scanning Electron Microscope imaging showing a retention of morphology on the microscale.

Future Work

We hypothesize that pore size and morphology can both affect dye absorption properties. Future work will entail using different CDs (α,β,γ) and morphologies to investigate how adsorptions rates and capacities are influenced.



This synthetic project will also be used to educate and inspire high school students to join the STEM field.

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