Optimizing Mordenite and Brooker's Merocyanine

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Zeolites are a class of materials that are composed of oxygen, silicon, and aluminum with channels embedded in the crystalline structure. Zeolites have many applications, some of which include water purification, biomass conversion, or as molecular sieves. The zeolite's crystal structure allows them to act as a host for smaller guest molecules without chemical bonding between the host and guest molecules. An example of a guest dye molecule is Brooker's Merocyanine. Brooker's Merocyanine is zwitterionic, where there are opposite charges on each end, and is a unique property that could be used to enhance the dye organization within the channel. By combining the host zeolite with the guest molecule Brooker's Merocyanine, the dye is expected to go into the zeolite channels by a cation exchange process, based on previous work. This project focused on a zeolite known as Mordenite, chosen due to this lab's previous work with other similar zeolites studied with Brooker's Merocyanine that included LTL and ZSM-5. The purpose of this project was to optimize the combination of the Mordenite and Brooker's Merocyanine. We used UV-Visible spectroscopy to confirm the dye is interacting with the zeolite. Dye loading Mordenite was most successful when refluxing the sample in acidic aqueous dye solution in the dark overnight with stirring. Through these experiments, we found that Mordenite can interact with Brooker's Merocyanine more than LTL or ZSM-5.

Zeolites

Zeolites are a crystalline composite of silicon, oxygen, and aluminum that can vary in ratios and structures depending on the growing conditions, including time, temperature, and pressure. Zeolites can act as a host for smaller guest molecules. These host-guest properties allow for zeolites to have uses in:

- Water purification
- Gas purification
- Carbon dioxide capture
- Molecular sieves

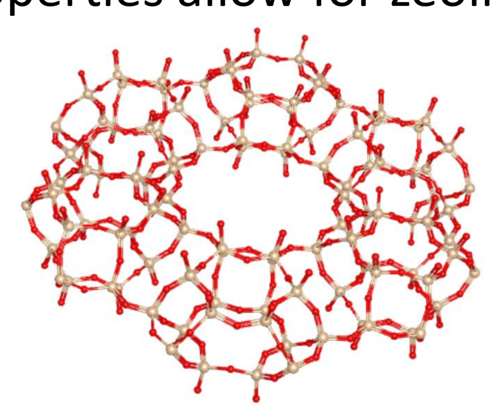


Figure 1 (above). Ball and stick structure showing the channels of a zeolite.

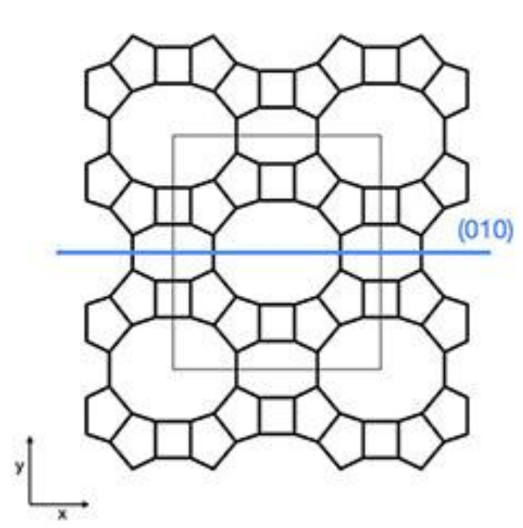


Figure 2 (left). Line structure of Mordenite, a type of zeolite.[1]

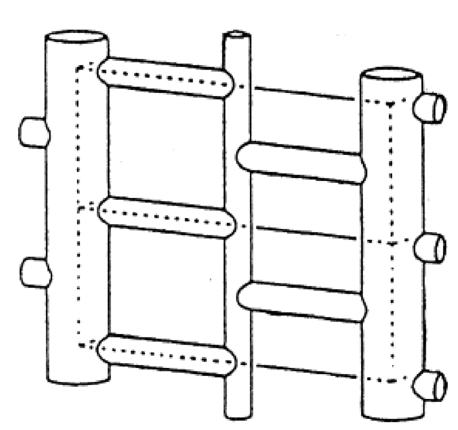


Figure 3 (right). Mordenite is represented in terms of one plane of channels. The large tubes are 12-ring channels and the small tubes are 8-ring channels.[2]

Zeolites are a host material due to their charge and channels, which allows them to easily capture small molecules.

Brooker's Merocyanine (BM)

- BM is a zwitterion that can form chains of molecules due to the partially charged ends.
- These molecules can exhibit second harmonic generation when aligned.

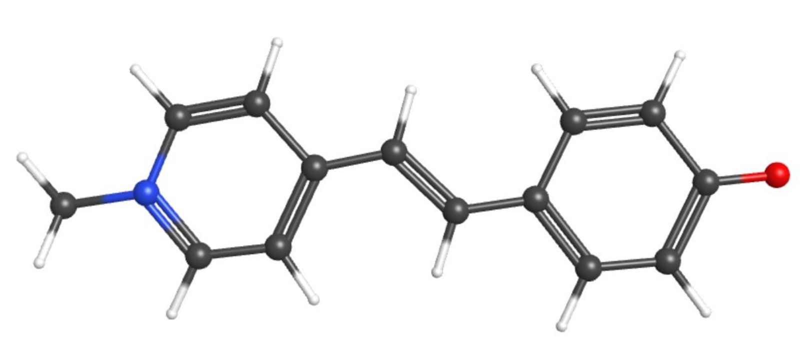


Figure 4. Brooker's Merocyanine in its charged form.

When the zeolite and dye are combined, the dye should enter the channels in a process called dye-loading.

Mordenite

We chose Mordenite due to this lab's previous work with other similar zeolites studied with Brooker's Merocyanine, which includes LTL and ZSM-5.

	LTL	MOR	ZSM-5
Channel size (# member channel)	round 12	oval 12	round 10
Accessible diameter of sphere(A)	7.1	7.0 x 6.5	5.5 x 5.1
SiO_2/Al_2O_3 ratio	10*	13.1	18

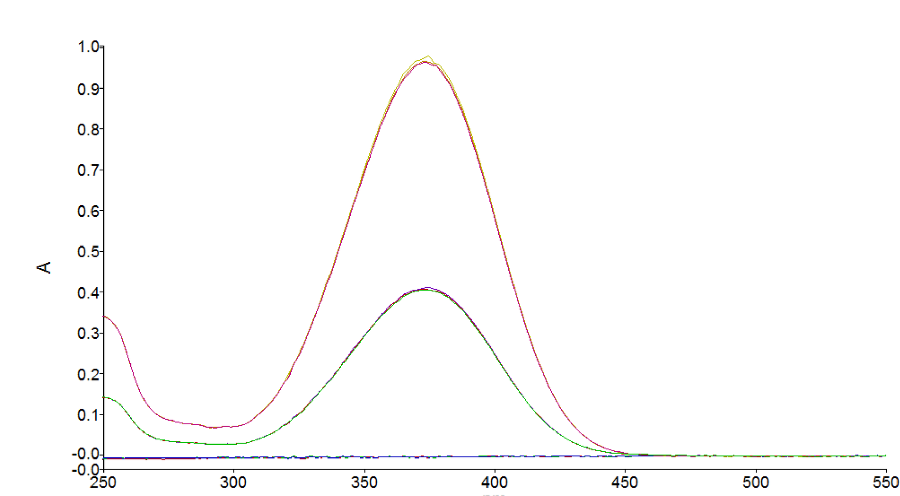
Table 1. Comparison of Mordenite to other zeolites, LTL and ZSM-5.[1]

One aspect of this project was to synthesize Mordenite to control the growing conditions to change the size of the crystal, which was unsuccessful so far. We purchased Mordenite from Fisher Scientific with a 38 nm crystal size and confirmed the crystal structure using XRD.

UV-Visible Spectroscopy

To see how much dye the zeolite adsorbed, each experiment required two samples. Equal amounts of aqueous solution of BM was used to make a reference and sample, and the sample contained MOR. After letting it stir, the MOR was filtered out and the solutions of both samples were analyzed by UV-Vis. UV-Visible Spectroscopy can be used to determine the amount of dye loading in Mordenite.

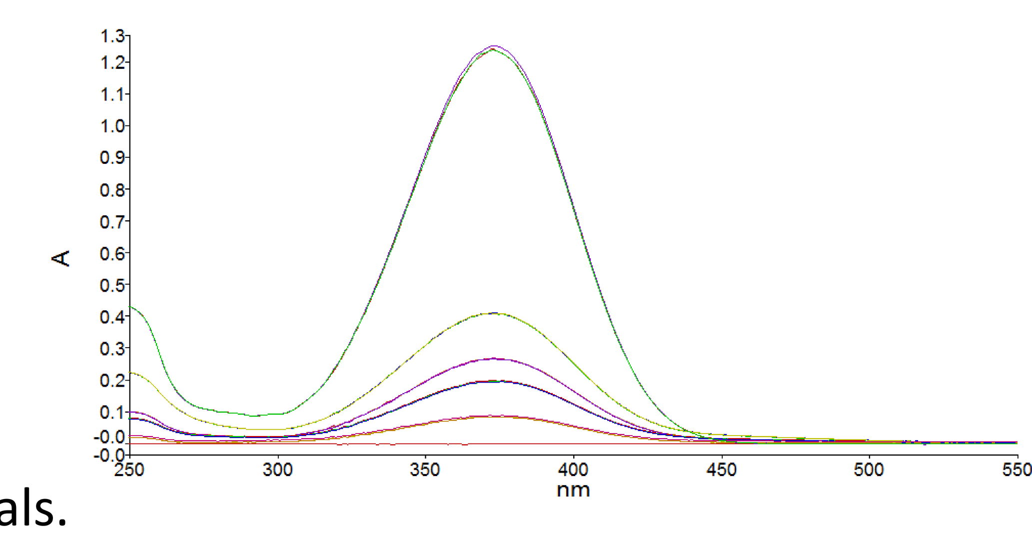
Figure 5. UV-Vis spectra. The top line is the reference dye solution while the bottom is dye loaded sample. The bottom decreases due to dye lost from solution to MOR.



A large part of the project was optimizing the dye-loading. Many factors were tested, some of which include pH, level of light, and heat. Our best conditions were found to be acidic, no light, stirring for hours under reflux in water.

A significant factor seemed to be amount of time for dye loading. Dye loading to low absorbance at room temperature took place over 24 hours while elevated temperatures reduced the time to 2-3 hours.

Figure 6. Sample spectra from UV-Vis that shows more dye adsorbing with longer time intervals.



Conclusions

- We were able to optimize the conditions for dye-loading
- Based on optimized conditions, MOR appears to interact with BM more than LTL or ZSM-5
- Our next step is to determine if the dye is adsorbed to the surface or the inside of the channels

References

1. *Framework Type*, america.iza-structure.org/IZA-SC/framework.php?ID=152. Accessed 16 July 2024.

2. Larry Kevan. "Microporous Materials: Zeolites, Clays, and Aluminophosphates." Encyclopedia of Physical Science and Technology (Third Edition), Academic Press, 17 June 2004, www.sciencedirect.com/science/article/abs/pii/B0122274105004427.

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