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Spectroscopic Studies of Brooker's Merocyanine in Zeolite L

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Abstract

Zeolites are porous, crystalline substances that have very unique atomic organizations which allow for the formation of complex channels within the crystals. Each type of zeolite has a distinct shape and structure. To better understand the properties of zeolite channels, a dye molecule known as Brooker's merocyanine was inserted into Zeolite L. Maximum dye loading into the zeolite channels was achieved by altering different experimental variables, such as heat, solution concentration, stirring, cation exchange, and light exposure. X-ray diffraction was used to verify the synthesis of zeolites, the cation exchange process, and dye loading. UV-Vis spectroscopy was used to measure the amount of dye adsorbed by the zeolite. By using the UV-Vis absorbance values and Beer's Law, the concentration of dye in the zeolites was determined. The results showed that an increase of heat and stirring correlated to an increase of adsorption of dye by the zeolite. Due to the light sensitivity of Brooker's merocyanine, it was found that limiting the amount of light exposure of the dye solutions also resulted in higher dye adsorption by the zeolites. An increase of the concentration of the dye solution increased the rate of adsorption in the channels. However, exchanging the potassium ions found within the synthesized Zeolite L channels with smaller hydrogen ions did not have an affect on the adsorption of dye in the channels. Characterizing how to achieve a maximum of dye adsorption in the zeolites allows for a better understanding of how dye molecules interact within the zeolite channels.

Background

- 40 natural occurring and 150 synthetic zeolites
- Exploring new characteristics of zeolites (zeolite L) might help others to better optimize their adsorption properties
- Commercially used as a catalyst in the petroleum industry
- Another commercial use is as an absorbent:
  - Cat litter
  - Water softening salt
  - Laundry detergent

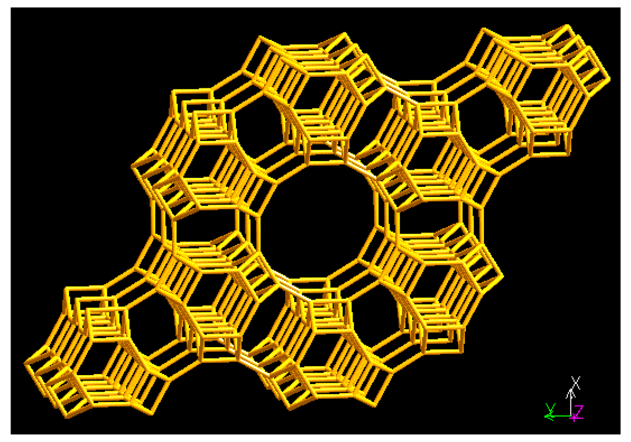

Figure 1: Microscopic view of zeolite L channels[1]

Zeolite L

- Composed of aluminum, silica, and oxygen
- Porous crystalline structure
- Has straight one-dimensional channels
- Easy to synthesize

Brooker's Merocyanine

- Model dye compound
  - Can be protonated and isomerized
- Various forms have different spectroscopic signals

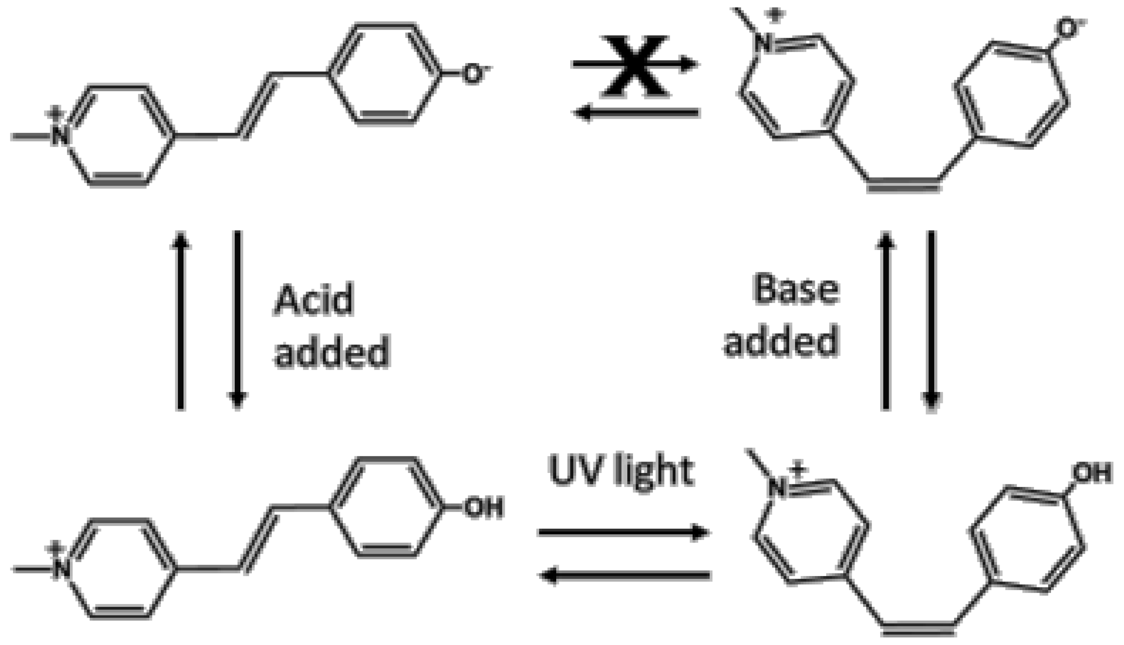

Figure 2: The isomerization cycle of Brooker's merocyanine

Synthesizing Zeolites

- Molar composition of 2.35 K_2O: Al_2O_3: 10 SiO_2 : 160 H_2O: trace amounts of $Mg(NO_3)_2$.
  - Solution 1: Mixed and boiled 5.0g H_2O, 3.0g KOH, and 15.82g alumina until clear.
  - Solution 2: Mixed 15.0g silica solution, 9.9g of water, and 1.4g of $Mg(NO_3)_2$ soln.
  - Mixed solutions 1 and 2 with 2.5g of water, inside the bomb calorimeter and heated to 175°C for 72 hours. [2]
- The crystals were filtered with 600mL of water and placed back into the oven to dry.
- X-ray diffraction ensured that zeolite L had been successfully synthesized.
  - The spectra that had been generated from the crystals was compared with the x-ray library spectra of zeolite L.

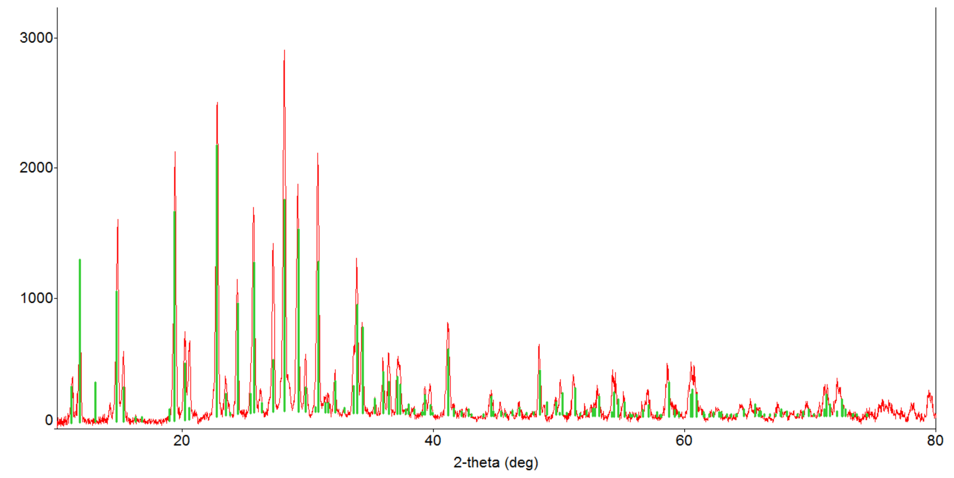

Figure 3: X-ray proved zeolite L had been synthesized. Red peaks indicate the zeolite crystals. Green peaks indicate the library spectra of zeolite L.

Cation Exchange

- K^+ ions reside in the channels once the crystals are produced
- Exchanging K^+ ions with smaller H^+ ions might allow for more dye to enter channels[3]
- HCl as hydrogen source→ destroyed crystals
- NH_4NO_3 as hydrogen source: $NH_4^+ \leftrightharpoons NH_3 + H^+$

Method:

- 300 mL of NH_4NO_3 solution per gram of zeolite
- Four soaking periods of 2 hrs each
- 500° C furnace overnight

Dye Loading

- Various amounts of zeolite were soaked in 10mL of dye solution.
- Samples were tested under different experimental conditions[4], such as heat, stirring, concentration, and light exposure.
- At regular intervals of time, small samples of the solution were taken and quantified using a UV-Vis spectrometer to collect an absorbance reading.
- A difference in the absorbance values from the beginning of the trial to the end of the trial shows that the crystals did adsorb the dye.
- Using the absorbance values and Beer's Law (A=εBC), the concentration of the dye solution was found, which can be used to find the molecules adsorbed per gram of zeolite.

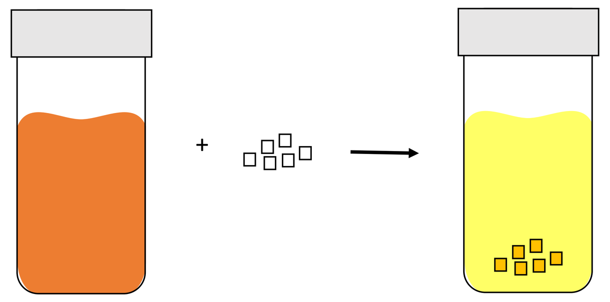

Figure 4: The dye begins as an orange color, but as it is adsorbed by the crystals turns to a yellow color. The color change in the zeolites from white to orange shows adsorption has occurred .

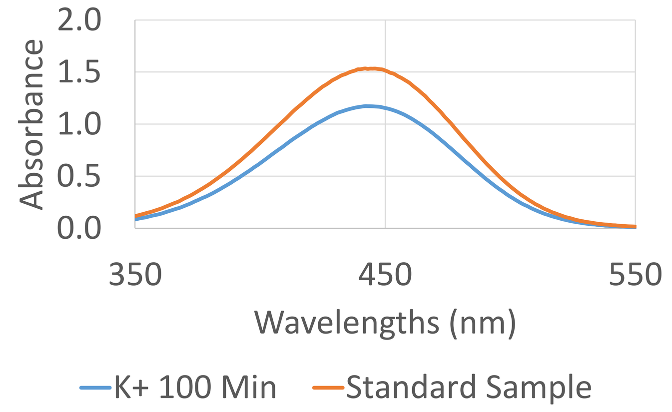

Figure 5: The difference between the two peaks at 445nm is proportional to the amount of dye adsorbed by zeolite L.

Results

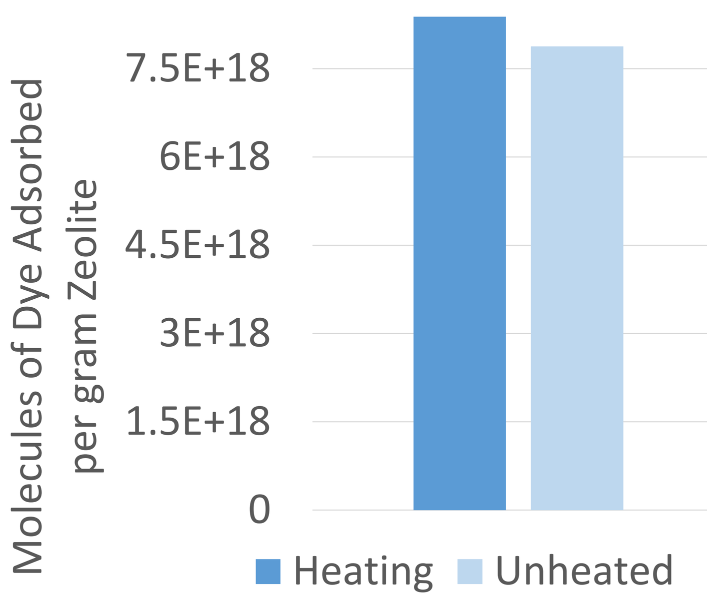

Figure 6: 0.5g of zeolite in 10mL dye heated to 50°C vs. no added heat

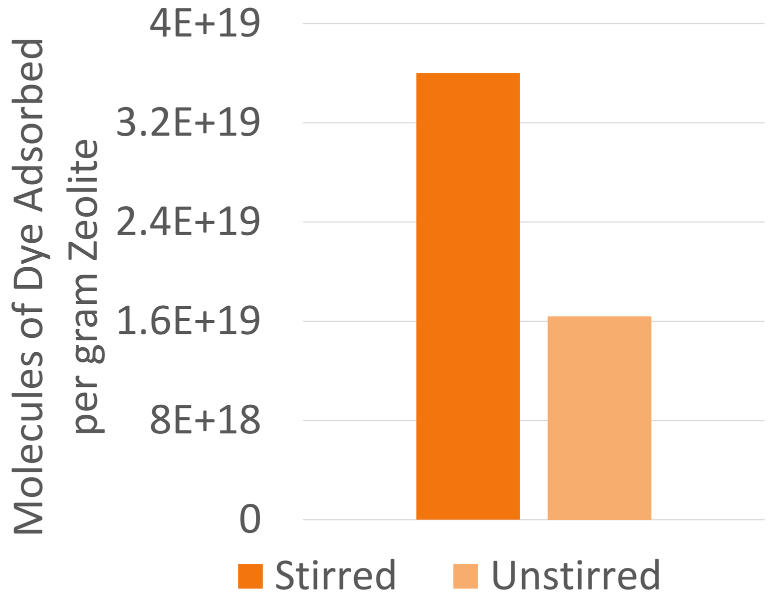

Figure 7: 0.2g of unstirred zeolite in 10 mL of dye after 2 hrs vs. stirred zeolite

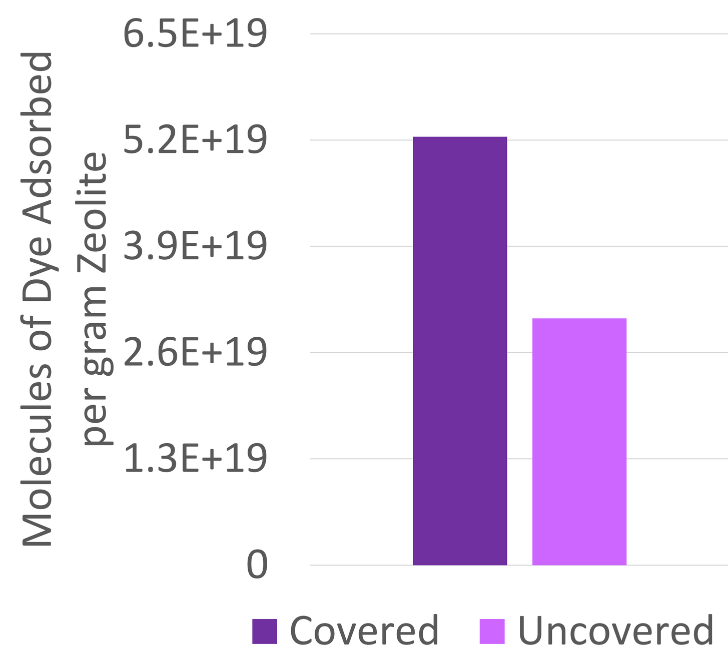

Figure 8: 0.2g of uncovered zeolites in 10mL of dye after 4 hrs vs. covered zeolite

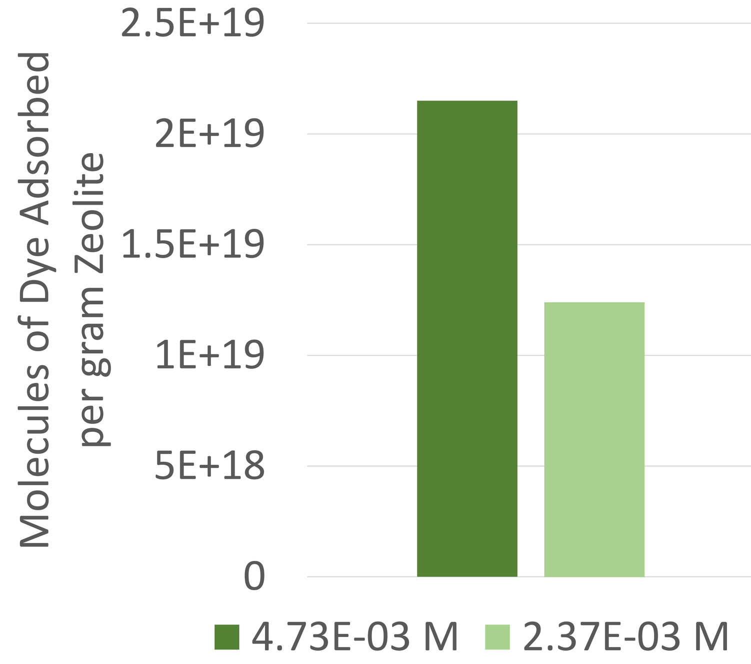

Figure 9: 0.5g of zeolite in 50mL of concentrated dye after 100 mins vs. less concentrated dye

Conclusion

- Heating, covering and stirring increased amount of dye adsorption in zeolite L
- More concentrated dye leads to faster rate of adsorption in zeolite L
- Preliminary results indicate that either cation will exchange with the dye molecule

Future Work

- Find the maximum amount of dye the zeolite can adsorb
- Potentially find better ways to synthesize zeolite L and use SEM to determine crystal size
- Attempt to produce optical properties from Brooker's merocyanine/zeolite L

References and Acknowledgements

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