Exploration of Additive Controlled MIL-53(Al) Synthesis for Photocatalytic Applications

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Metal organic frameworks (MOFs) are crystalline coordination materials that are made up of metal-containing nodes connected by organic linkers.[1] MOFs have properties such as permanent porosity, stable framework, and large surface area, all of which make MOFs useful for applications in gas storage and separation, catalysis, biomedicine, and more.[2] This project focused on MIL-53(Al), an aluminum-containing MOF that has flexible porosity and is highly stable under varying thermal and moisture conditions, making it well suited for wastewater treatment applications.[3,4]

Previous work in the Ortoll-Bloch lab has shown that the addition of ionic liquids (viscous liquids composed completely of ions) to the synthesis of MIL-53(Al) has structure directing effects on the growth of the MOF, increasing its crystallinity and particle size when used up to a concentration of 0.50% by volume. This project aimed at exploring the application of these findings in the use of MIL-53(Al) for the removal of Rhodamine B, a toxic dye that is a common output of the textile industry, from wastewater.

Carrying out this project involved two main components. The first part involved synthesizing MIL-53(Al) with different concentrations of our ionic liquid, 1-methyl-3-octylimidazolium chloride, thus making MIL-53(Al) crystal samples of different sizes and crystallinities. These samples were analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to confirm that our syntheses followed the same pattern that was observed with previous work in the lab. The second part of the project involved testing the efficiency of the different MOF samples in the removal and photocatalytic degradation of Rhodamine B from water, all of which was quantified by UV-Vis Spectroscopy. Photocatalytic degradation of the dye by MIL-53(Al) was achieved by using a photocatalysis chamber that irradiated our samples with a specific amount of UV light.

We hypothesized that MIL-53(Al) crystals grown with an ionic liquid concentration of 0.50% by volume would be more efficient at removing Rhodamine B from solution than crystals grown with no ionic liquid or with higher ionic liquid concentrations because of their greater particle size and higher crystallinity. Although our results did show that MIL-53(Al) is indeed a good photocatalyst that is able to almost entirely degrade Rhodamine B from solution within 50 minutes, we also found that MIL-53(Al) grown without the addition of ionic liquid was the most effective photocatalyst for Rhodamine B.

These findings suggest that particle size plays a greater role in determining the photocatalytic efficiency of the MOF than its crystallinity, indicating that photocatalysis occurs primarily at the outer surface of the MOF crystals. Although the crystallinity of MIL-53(Al) grown without the addition of ionic liquid was lower, its greater surface area seemed to prevail over the effect of crystallinity. Moving forward, I hope to be able to isolate the effects of particle size and crystallinity to more definitively determine their individual impacts on the photocatalytic efficiency of MIL-53(Al). More broadly, I plan on continuing to explore additive controlled synthesis of MIL-53(Al) using a range of different ionic liquids.

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Citations:

(1) Sharmin, E.; Zafar, F. Introductory Chapter: Metal Organic Frameworks (MOFs). In *Metal-Organic Frameworks*; IntechOpen, **2016**. https://doi.org/10.5772/64797.

(2) Jiao, L.; Seow, J. Y. R.; Skinner, W. S.; Wang, Z. U.; Jiang, H.-L. Metal–Organic Frameworks: Structures and Functional Applications. *Materials Today* **2019**, *27*, 43–68. https://doi.org/10.1016/j.mattod.2018.10.038.

(3) Rehman, T. U.; Agnello, S.; Gelardi, F. M.; Calvino, M. M.; Lazzara, G.; Buscarino, G.; Cannas, M. Unveiling the MIL-53(Al) MOF: Tuning Photoluminescence and Structural Properties via Volatile Organic Compounds Interactions. *Nanomaterials* **2024**, *14* (5), 388. https://doi.org/10.3390/nano14050388.

(4) Ashling, C. W.; Johnstone, D. N.; Widmer, R. N.; Hou, J.; Collins, S. M.; Sapnik, A. F.; Bumstead, A. M.; Midgley, P. A.; Chater, P. A.; Keen, D. A.; Bennett, T. D. Synthesis and Properties of a Compositional Series of MIL-53(Al) Metal-Organic Framework Crystal-Glass Composites. *J Am Chem Soc* **2019**, *141* (39), 15641–15648. https://doi.org/10.1021/jacs.9b07557.