The 2018 Partnership in Research and Education in Materials
Research Experience for Undergraduates

Synthesis and Characterization of Metal-Organic Framework Hydrogel Composites

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What are MOF hydrogel composites?

Metal-organic frameworks (MOFs) are an emergent class of porous crystalline materials with a wide range of applications due to their high surface area and tunable structures. However, lack of stimuli responsiveness and macroscopic ordering of MOFs pose issues in integrating them into functional devices. To mediate these limitations, MOF hybrid materials are of special interest. One class of hybrids are MOF hydrogel composites which utilize the large scale structuring and responsive nature of hydrogels to improve MOF functionality.

In this study, we synthesized a Zr-trimesic acid (BTC)-alginate (Alg) hydrogel composite modeled after MOF 808.

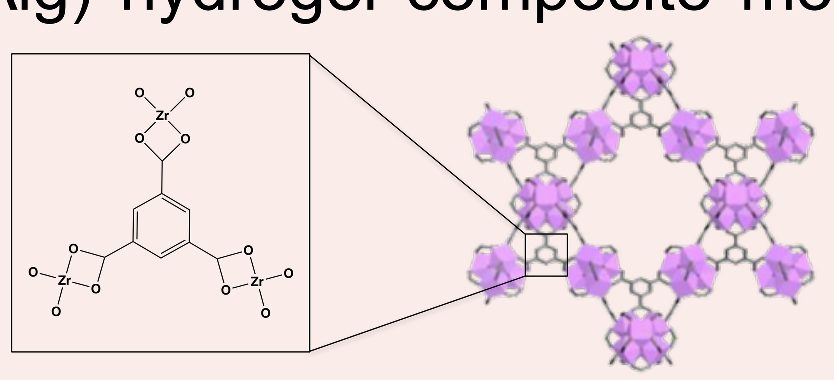

Figure 1. Crystal structure of MOF 808 as modified from reference 1.

Gel Synthesis

Zr-BTC-Alg gels made using a one-pot synthesis method.

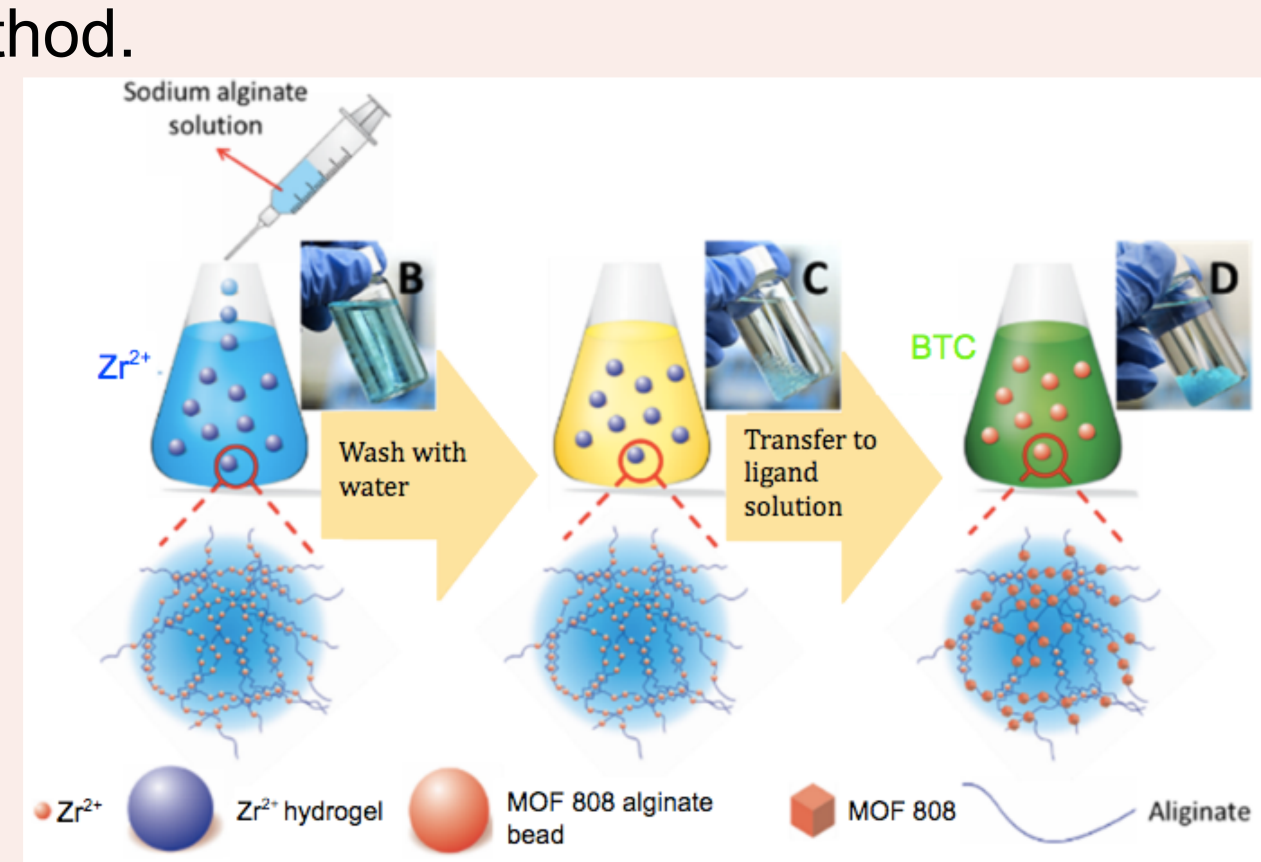

Figure 2. Synthetic procedure for MOF alginate gel beads as modified from reference 2.

Bonding Configurations

Using the procedure outlined in Figure 2, there are a couple of possible bonding arrangements which could be present in the product. Most likely, the synthesized product is a combination of these.

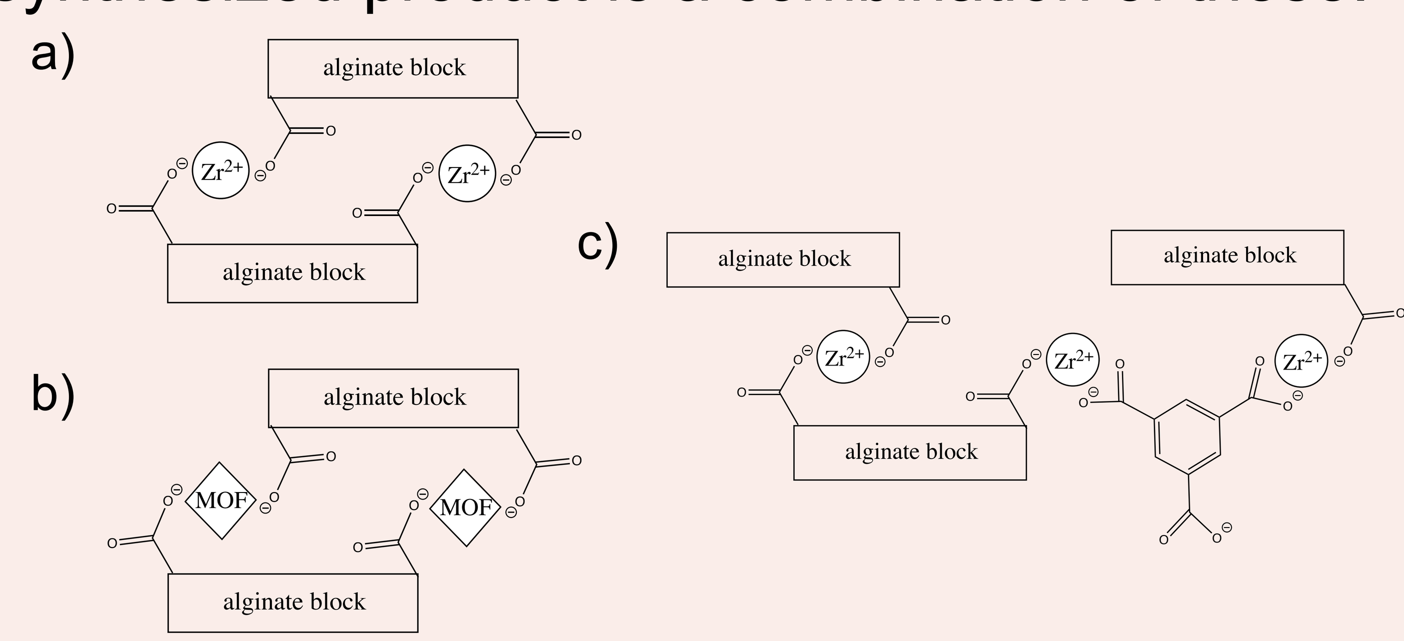

Figure 3. Alginate cross linked by zirconium ions (a), MOF particles (b), and an interpenetrating network of MOF ions and linkers (c).

Results

- FTIR used to determine incorporation of zirconium ions and BTC linker into gel

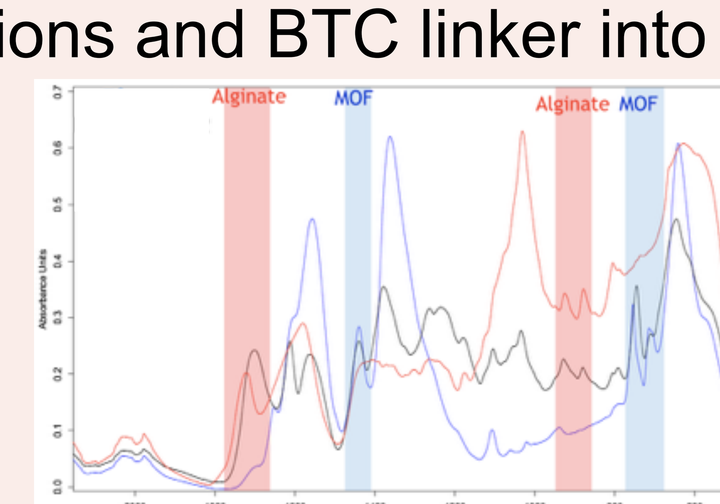

Figure 4. Compiled FTIR of MOF 808 (blue), zirconium ion cross linked alginate (red), and the MOF 808 alginate composite (black).

- Particle formation within gel analyzed by PXRD of dried gel and uptake of methylene blue dye

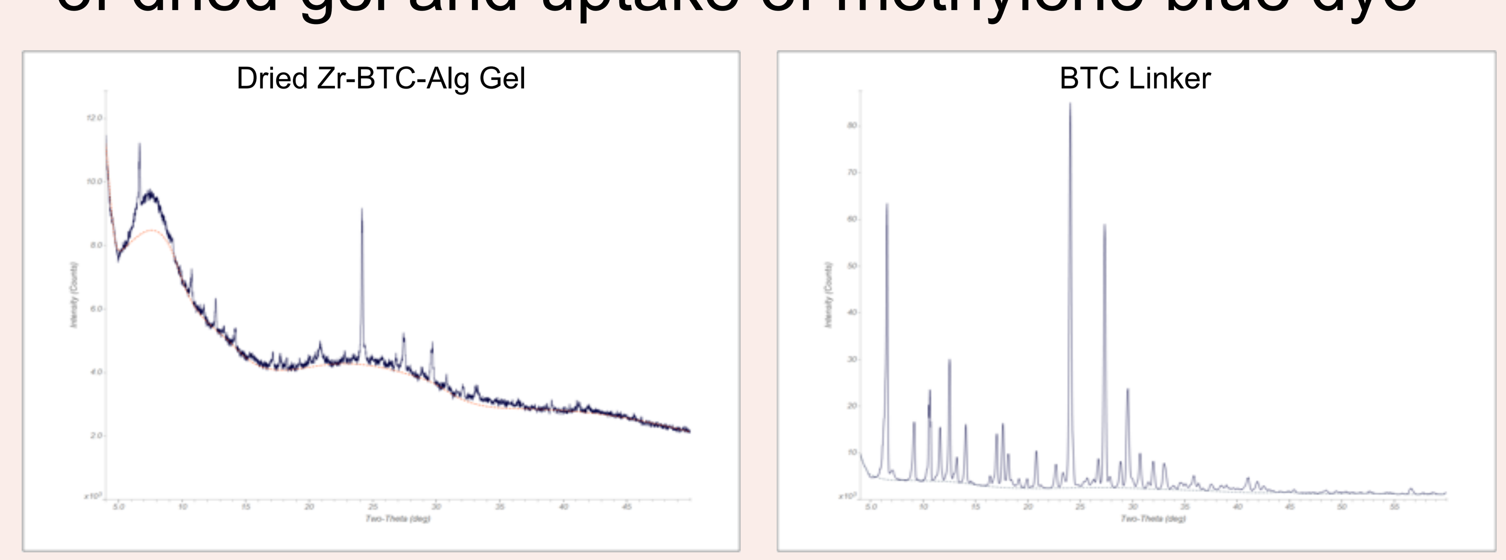

Figure 5. PXRD of dried Zr-BTC-Alg gel and BTC linker

Results

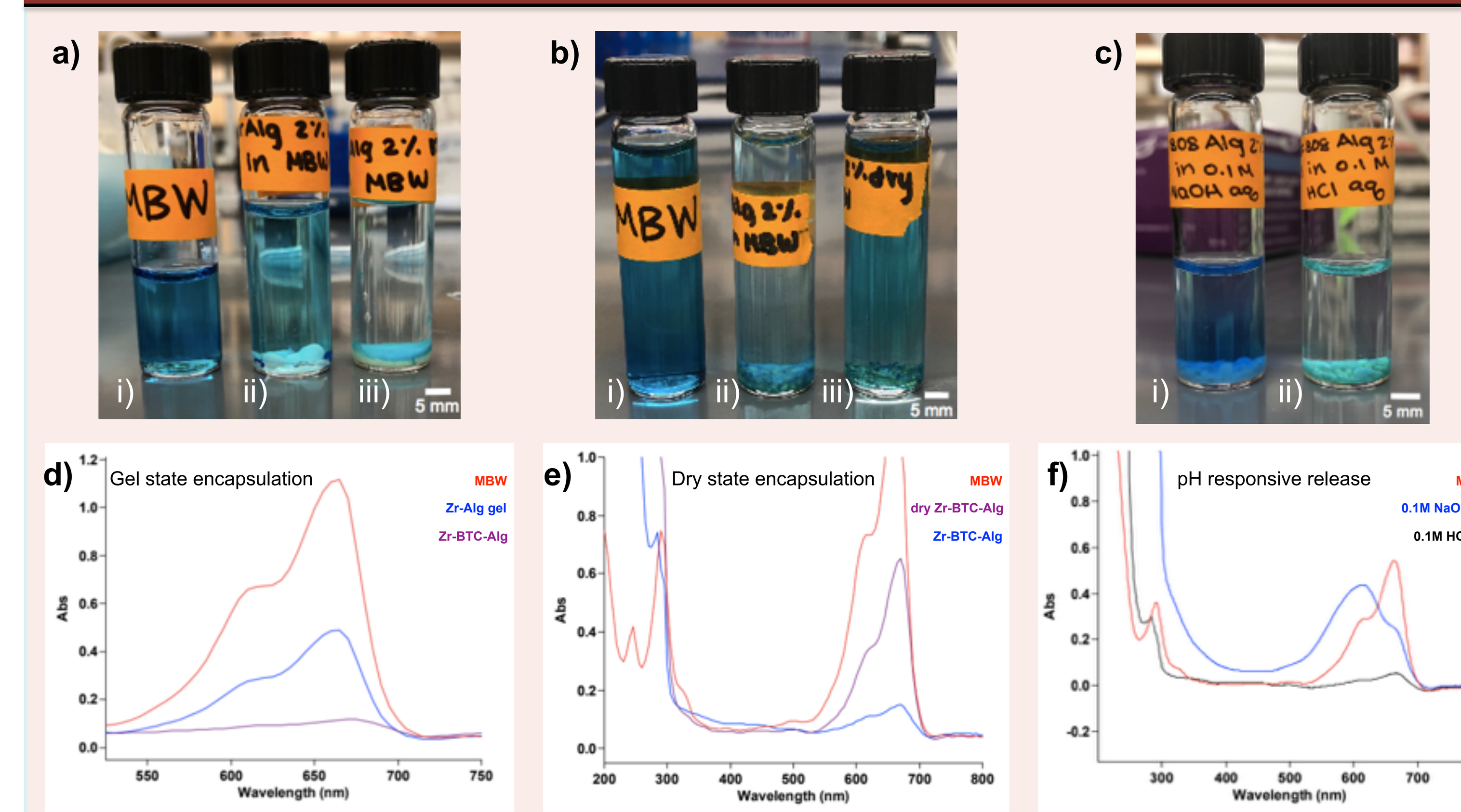

Figure 6. (a,b) Aqueous methylene blue (MBW) solutions (i,i) and resultant encapsulation solutions for zirconium ion cross linked alginate (ii,-), Zr-BTC-Alg gel (iii,ii), and dried Zr-BTC-Alg gel (-,iii). (c) Resultant solutions from methylene blue release in 0.1M NaOH aq (i) and 0.1M HCl aq (ii). UV-vis spectra of gel (d) and dry (e) state methylene blue encapsulation and pH responsive release (f).

Conclusion

- Red shifting in Zr-O and alginate carbonyl IR peaks confirmed presence of MOF precursors in the gel
- PXRD shows presence of only linker crystallinity in dried Zr-BTC-Alg gels
- Zr-BTC-alginate gels show increased loading capacity compared to zirconium ion cross linked and dried gel counterparts
- Gel's responsive properties reflected in MOF selective release
- Further characterization of gel state product needed to determine if complete MOF particles were formed within the alginate gel or if an interpenetrating network is present

References

[1] Lorenzo, F. D., et. al. (2018) The Carbonation of Wollastonite: A Model Reaction to Test Natural and Biomimetic Catalysts for Enhanced CO2 Sequestration. Minerals 8, 209.
[2] Zhu, H., Zhang, Q., and Zhu, S. (2016) Alginate Hydrogel: A Shapeable and Versatile Platform for in Situ Preparation of Metal–Organic Framework–Polymer Composites. ACS Applied Materials & Interfaces 8, 17395–17401.

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