NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2021 Project Summary

1. Student name & home university:

Nicholas Lowe - Vanderbilt University

2. ND faculty name & department:

Dr. Nosang V. Myung - Department of Chemical and Biomolecular Engineering

3. Summer project title:

Water Remediation *via* Electrospun MIL-101@ZIF-8-Embedded Nanofibers as Copper Filters

4. Briefly describe new skills you acquired during your summer research:

Before the summer, I had no prior research experience. Thus, I first learned a lot about how research labs are structured and how research ideas are realized. I gained insightful background on electrospun nanofibers, a branch of the lab's overarching theme of nanoengineered materials for various applications, as well as water remediation by copper adsorption similar to work by Xue et. al. [1] and Zhang et. al. [2]. The experience had two main aspects- time in the lab and at a desk- both of which I grew to love. In the lab, I learned and developed standard operating procedures (SOP's) for a variety of high-end instruments and practiced in electrospinning. I also learned, over time, independent problem solving by fluidly, adapting experiments and protocols. Time spent in the office area was used to design efficient experiments, discuss research progress with my mentors, and disseminate research findings to my peers and community, and prepare effective research communication. This included using PowerPoint, Excel, Origin, Vesta (molecule visualization software), and ImageJ. I have also grown an appreciation for the ratio of time spent at a desk to that in the lab. As a whole, I learned that I truly enjoy research and wish to continue it in the future.

5. Briefly share a practical application/end use of your research:

Electrospun nanofibers are a promising material for a wide variety of fields, and the Myung Lab takes advantage of the nanomaterial for various applications, such as gas sensing material, reusable battery components, piezoelectrics nanogenerators, and environmental remediation. This project specifically focuses on their use in water filtration of a variety of contaminants, with a main focus on heavy metals. Similar to lead, copper pipes can corrode and pollute drinking water. Copious uptake of this contaminant can lead to adverse health effects in humans including organ failure, severe illnesses, or death [3]. Typical carbon filters used in homes are inefficient in removing heavy metals; therefore, this project aims to produce electrospun nanofiber membranes embedded with metal organic frameworks (MOFs) capable of copper adsorption for point-of-use filters in households. Electrospinning is a favored production method due to its ease of accommodating wide variety of materials, cost-effectiveness, and industrial scalability, making an optimized product readily deployable to the wide market. The use of composite MOFs, i.e. MIL@ZIF, is novel in electrospinning, and provides the potential to make filters reusable and capable of copper detection.

6. 50- to 75-word abstract of your project:

Point-of-use water filters via electrospun nanofibers can enable safe drinking water practices. In this work, MIL-101@ZIF-8, a highly efficient copper adsorbent with a core-shell MOF@MOF design [4], was optimally electrospun into functional nanofibers. MIL-101@ZIF-8 was critical in retaining zinc and thus the structure of ZIF-8, which would keep water pure and create potential for filter reuse. The as-

spun nanofibers were tested for copper removal efficiency with the goal of meeting standards set by the EPA.

7. References for papers, posters, or presentations of your research:

[1] Xue, J.; Wu, T.; Dai, Y.; Xia, Y. Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00593 (accessed Jul 23, 2021).

[2] Zhang, Y.; Xie, Z.; Wang, Z.; Feng, X.; Wang, Y.; Wu, A. Unveiling the adsorption mechanism of zeolitic imidazolate framework-8 with high efficiency for removal of copper ions from aqueous solutions. https://pubs.rsc.org/en/content/articlelanding/2016/dt/c6dt01827k#!divAbstract (accessed Jul 13, 2021).

[3] Engwa, G. A.; Ferdinand, P. U.; Nwalo, F. N.; Unachukwu, M. N. Mechanism and Health Effects of Heavy Metal Toxicity in Humans. https://www.intechopen.com/books/poisoning-in-the-modern-world-new-tricks-for-an-old-dog-/mechanism-and-health-effects-of-heavy-metal-toxicity-in-humans (accessed Jul 13, 2021).

[4] Zhang, L.; Wang, J.; Ren, X.; Zhang, W.; Zhang, T.; Liu, X.; Du, T.; Li, T.; Wang, J. Internally extended growth of core–shell NH2-MIL-101(Al)@ZIF-8 nanoflowers for the simultaneous detection and removal of Cu(II). https://pubs.rsc.org/az/content/articlelanding/2018/ta/c8ta07349j/unauth#!divAbstract (accessed Jul 13, 2021).

[5] Technical Data Sheet - ACS Material Zeolitic Imidazolate Framework-8 (ZIF-8). https://www.acsmaterial.com/zeolitic-imidazolate-framework-8-zif-8.html (accessed Jul 10, 2021).

[6] Lowe, N. Water Remediation *via* Electrospun MIL-101@ZIF-8-Embedded Nanofibers as Copper Filters. Poster Presented at: Notre Dame Summer Undergraduate Research Symposium. Notre Dame, IN.

One-page minimum project summary that describes problem, project goal and your activities / results:

Heavy metals are toxic contaminants found in drinking water that present adverse health effects in humans including, but are not limited to, severe illness, organ failure, or death [3]. Historically, lead has been a prevalent contaminant due to lead piping for houses contaminating the water. These have often been replaced by copper, which has been shown to corrode into drinking water recently and thus has become a more prevalent contaminant. Development of efficient, high-capacity point-of-use heavy metal filters is critical, as carbon filters, typically used by popular water filter brands like Brita, cannot remove heavy metals. My research addressed this challenge using electrospun nanofiber filters as a support scaffold for a composite of metal organic frameworks (MOFs), MIL@ZIF, which has a high surface area capable of collecting contaminants and has not been spun before. MOF-embedded electrospun nanofibers have emerged as a superior filter design for their high porosity, flexibility, MOF immobilization, scalability, and ease of use.

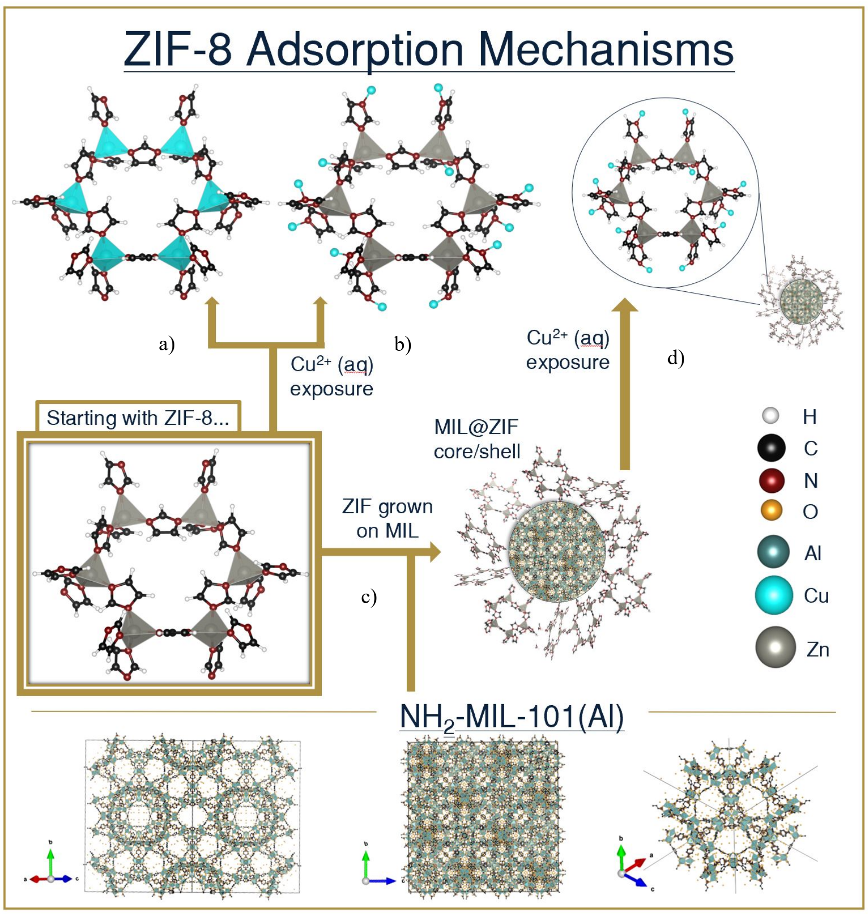

Figure 1. *Schematic of ZIF-8 adsorption mechanisms as synthesized and grown on* NH_2*-MIL-101(Al).*
(a) Zinc in ZIF-8 is replaced by copper cations. (b) Copper cations bond to the nitrogen in ZIF-8's imidazolate framework. (c) ZIF-8 grown on MIL-101 in a core-shell fashion. (d) Core-shell MIL-101@ZIF-8 forces copper cations to bond only to the nitrogen in ZIF-8's imidazolate framework.

Developing filters first requires an adsorbent to electrospin; the MOF ZIF-8 in particular is efficient in removing copper [2]. There are two potential mechanisms of copper adsorption onto ZIF-8. In one mechanism, the metal in ZIF-8 (zinc) is replaced by copper ions and then leached into the water (*Figure 1a*). The other mechanism is a coordination reaction in which copper ions form a covalent bond with nitrogen in the ligand of ZIF-8 (imidazole), leaving zinc untouched in the structure (*Figure 1b*). While zinc is a nutrient, its presence in drinking water is EPA regulated, making the second mechanism more desirable. Additionally, zinc retainment in the second mechanism creates the potential for filter reuse, as the structure and morphology of the MOF is preserved.

In order to constrain copper adsorption to the second mechanism, this research presented a core-shell MOF@MOF design, in which ZIF-8 (shell) was synthesized on NH_2-MIL-101(Al or Fe) (core) (*Figure 1c, d*) [4]. Collection of ultraviolet-visible spectroscopy (UV-Vis) data also revealed that compared to freestanding ZIF-8, the MOF@MOF composite better decreased the concentration of copper in polluted water (*Figure 2*). This will be further quantified using inductively coupled plasma-optical emission spectrometry (ICP-OES). Scanning electron microscope (SEM) images on my synthesized hybrid nanomaterials should indicate that using a MOF-based core forced ZIF-8 to grow in nanosheets rather than its typical rhombic dodecahedral and cubic morphology (*Figure 3*), though the nanosheets are still unclear and need to be further refined. However, characterization of the MIL@ZIF via powder X-ray diffraction (pXRD) reveals the presence ZIF-8 surrounding MIL-101 with high purity, indicating synthesis success (*Figure 4*). This nanosheet morphology makes zinc sites inaccessible to copper cations, forcing the preferred mechanism of copper uptake; the current, unexpected morphology will also be analyzed for zinc retainment.

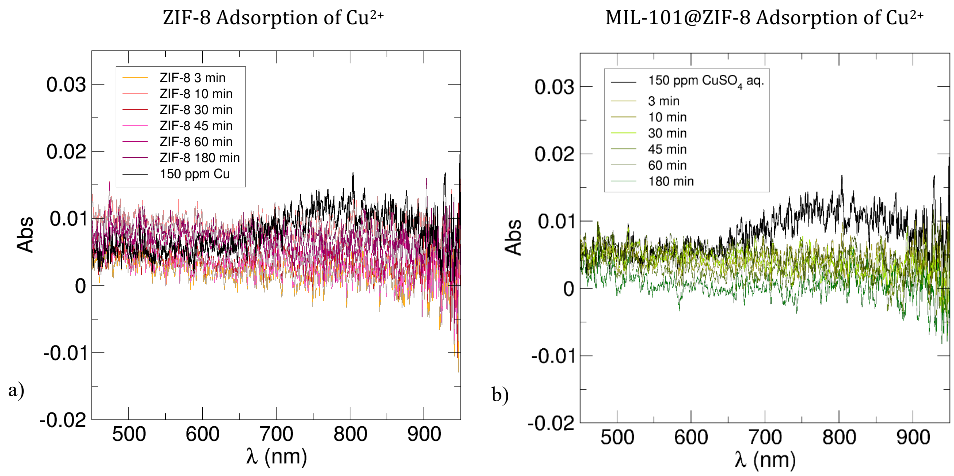

Figure 2. *UV-Vis Spectra of $CuSO_4$ solution over time after exposure to (a) commercial ZIF-8 and (b) as-synthesized MIL-101@ZIF-8.*

a) b)

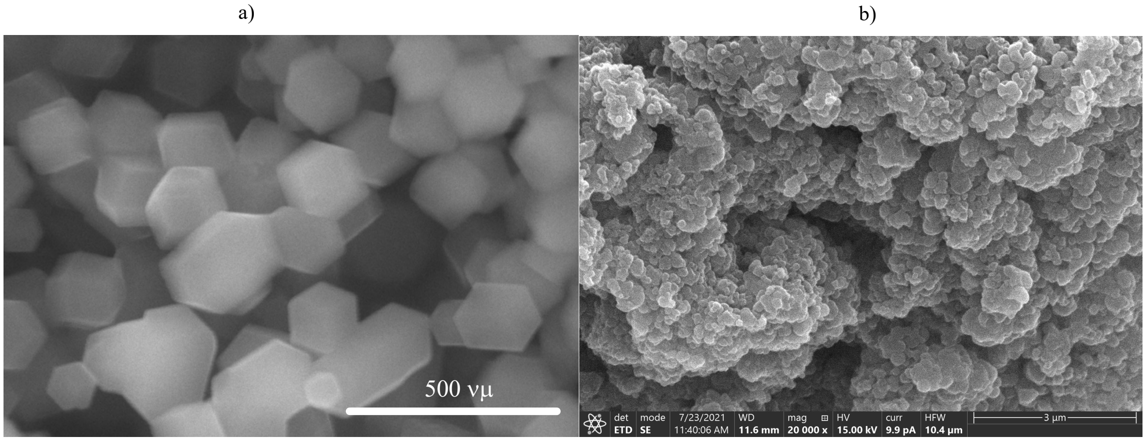

Figure 3. *SEM Images of (a) commercial ZIF-8 [5] and (b) as-synthesized MIL-101@ZIF-8.*

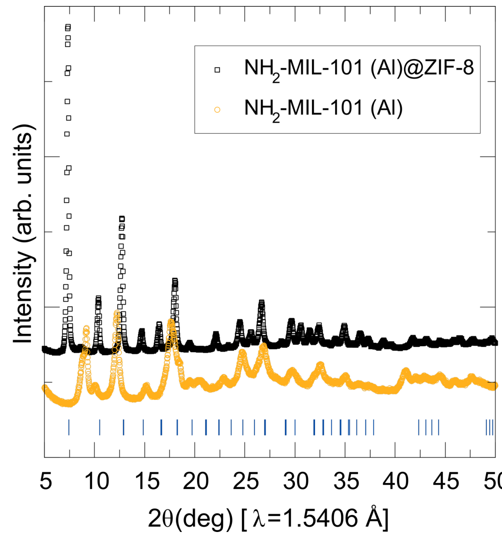

Figure 4. *pXRD data for MIL-101 and MIL-101@ZIF-8.*

The novelty of this work is utilizing MIL@ZIF by electrospinning it within a polymer scaffold for household water filters that remove heavy metals and limit zinc leaching. SEM imaging enables the study of morphological changes within the nanofibers before and after adsorption of copper.

Nanofibers that contained evenly dispersed ZIF-8 in PAN (*Figure 5 a, b*) were treated with a copper sulfate solution. Upon copper adsorption, the morphology of ZIF-8 changes drastically in the fibers, thus destroying the structure (*Figure 5c*) and indicating that the copper adsorption mechanism in *Figure 1a* primarily occurred, as expected. To prevent this, I designed the MIL-101@ZIF-8 embedded nanofibers as shown in *Figure 6 a, b, and c*; upon copper adsorption shown in *Figure 6d*, ZIF-8 morphology retains some dodecahedral form, indicating that the copper adsorption mechanism in *Figure 1c and 1d* occurred. While the MIL-101@ZIF-8 fibers are preliminary designs that need further adjustments to form optimized morphology and filters, this is a promising indication for the design's success. After optimizing solution and electrospinning conditions, these filters will be tested for copper removal efficiency using a peristaltic pump set-up (*Figure 7*).

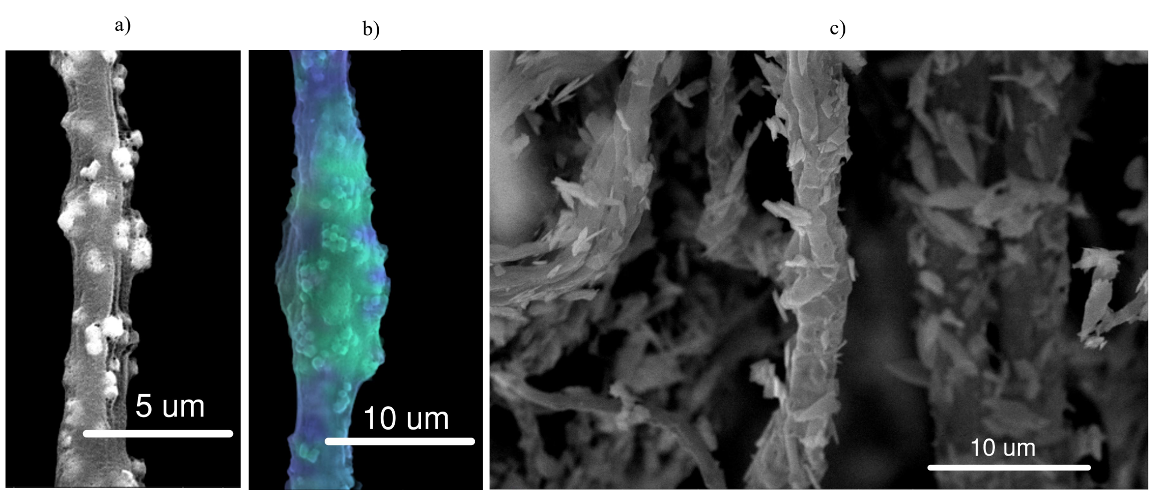

Figure 5. *Electrospun ZIF-8 Emdedded Nanofibers.*
(a) Backscattered electrons, dispersed ZIF-8 appearing white in grey PAN. (b) Color SEM, with green as zinc and blue as carbon. (c) The nanofibers after treamtment with a copper solution.

a) b) c) d)

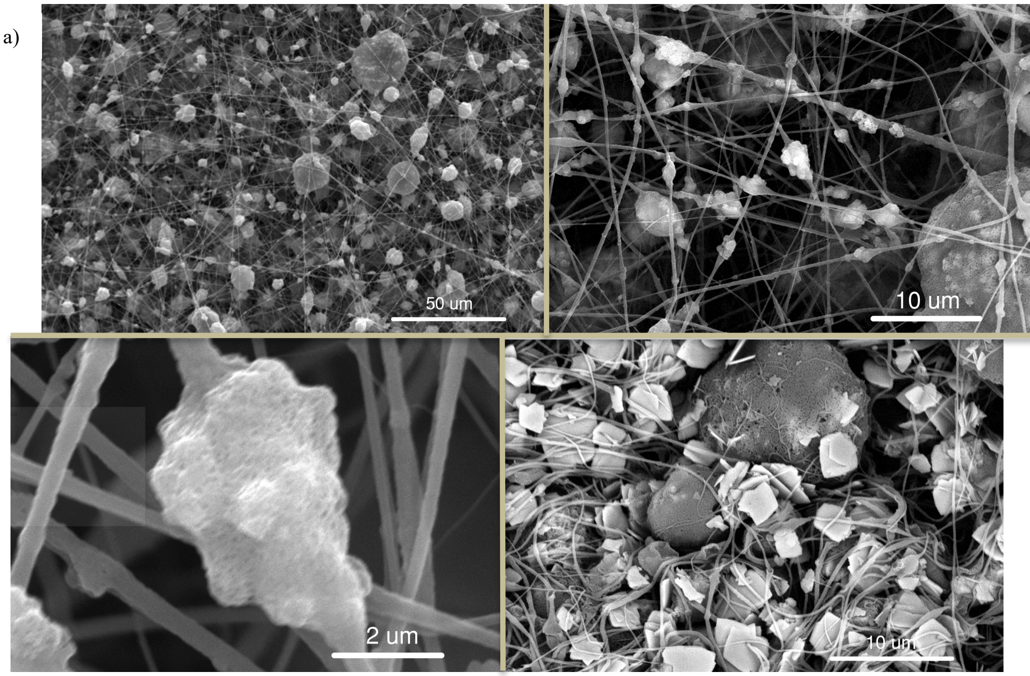

Figure 6. *Eectrospun MIL-101@ZIF-8 Embedded Nanofibers.*
(a) (b) and (c): images of preliminary electrospun MIL-101@ZIF-8 nanofibers on varying scales. (d) The nanofibers after treatment with a copper solution.

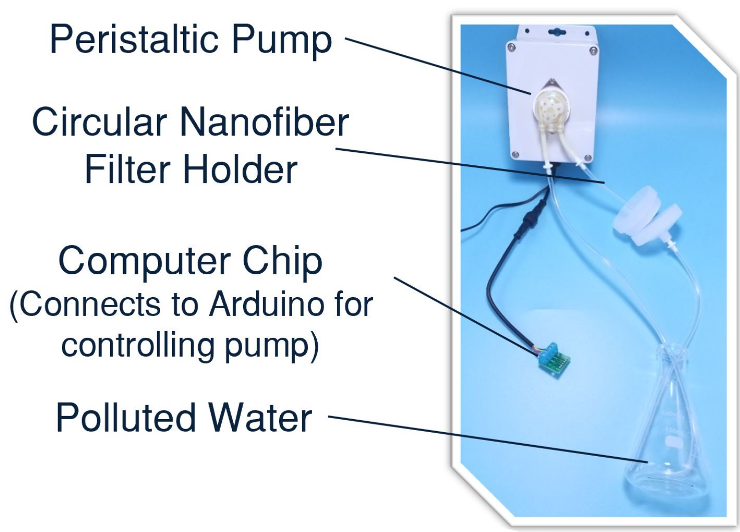

Figure 7. *Peristaltic Pump Set-Up for testing Filter Efficiency.*

This filter design sets the stage for future work in making these filters reusable, as zinc and thus the ZIF-8 structure can be retained, as well as enabling real-time detection of aqueous copper via the reported fluorescence properties of MIL@ZIF [4]. While the project needs to be further developed before publication, my electrospun MOF@MOF filter design provides promise for effective point-of-use water remediation.