

PNNL-33928

Development of Engineered Metal-Organic Framework (MOF) materials for perfluorooctane sulfonate (PFOS) Remediation

February 2023

PNNL Authors:

Radha Kishan Motkuri
Sayandev Chatterjee
Dushyant Barpaga
Xueyun Zheng
Yehia Ibrahim
CW Enderlin
BE Wells

Michael Reed, AVANTech LLC

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, **makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical
Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: <http://www.ntis.gov>

Development of Engineered Metal-Organic Framework (MOF) materials for perfluorooctane sulfonate (PFOS) Remediation

February 2023

PNNL Authors:

Radha Kishan Motkuri
Sayandev Chatterjee
Dushyant Barpaga
Xueyun Zheng
Yehia Ibrahim
CW Enderlin
BE Wells

Michael Reed, AVANTech LLC

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99354

Abstract

In this project, an engineered form of a Metal-Organic Framework (MOF) based material is developed for the removal of perfluorooctane sulfonate (PFOS) for real-world applications. The powdered MOF material has been demonstrated at the Pacific Northwest National Laboratory (PNNL) to selectively capture PFOS from distilled (DI) water with a large performance advantage over granulated activated carbon (GAC). In this project, the powdered material was transformed into an engineered form (using a polymer) to demonstrate PFOS adsorption capacity in tap water. PNNL developed and processed the MOF material in the engineering form (granules). After thorough characterization and stability testing, these engineered MOF granules were provided to an industrial collaborator, AVANTech, LLC, for testing and demonstration of continuous, long-term PFOS removal from tap water. The preliminary results showed PFOS sorption capacities at parts per billion (ppb) concentrations in tap water under a flow system. Also provided insight into sorbent-based material utilization in a continuous flow system. Further studies are required to optimize and understand sorption in such industrial-scale applications.

Acknowledgments

The research described in this report was conducted under the Laboratory Directed Research and Development (LDRD) Program as a strategic investment at the Pacific Northwest National Laboratory (PNNL), a multi-program national laboratory operated by Battelle for the U.S. Department of Energy. PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

Acronyms and Abbreviations

Environmental Protection Agency (EPA)
Granular activated carbon (GAC)
Metal-organic framework (MOF)
Pacific Northwest National Laboratory (PNNL)
Per- and polyfluoroalkyl substances (PFAS)
Perfluorooctanesulfonate (PFOS)
Distilled water (DI)
Groundwater (GW)
X-ray diffraction (XRD)
Nuclear Magnetic Resonance (NMR)

1.0 Introduction

Perfluorooctane sulfonate (PFOS) is one of the most dominant environmental contributors to the class or family of anthropogenic chemicals known as per- and polyfluoroalkyl substances (PFAS). [1] Over the last few decades, their extensive use in civilian, military, commercial and industrial sectors has meaningfully increased their environmental abundance.[2] Because of their high environmental stability and physiological persistence, thus make PFAS a cumulative threat linked to health issues, including cancer, obesity, elevated cholesterol, immune suppression and endocrine disruption.[3,4]. The United States Environmental Protection Agency (US EPA) has set a health advisory level in drinking water to as low as 70 ng/L. [5] Pacific Northwest National Laboratory (PNNL) has developed various sorbent materials, including metal-organic frameworks (MOFs), with exceptional selectivity, sensitivity, and sorption capacity of various guest molecules, including fluorocarbons.[6, 7] These materials have shown the highest fluorocarbon sorption capacity reported to date and have been further tailored for selective PFOS capture from DI water.[8] In previous tests, PNNL-designed MOFs have significantly outperformed the traditionally used activated carbon sorbent, which showed little to no sorption of PFOS under comparable concentrations [9]. Based on this result, we developed this project on bulk PFOS sorption capability in tapwater using a continuous flow system at an industrial facility.

This project aims to (i) design a water-stable, MOF-based material, synthesis and characterization (ii) transform the powder MOF into the engineered format, test the stability, and then (iii) transfer it to the industrial facility to test its PFOS sorption capacity in tap water in a continuous flow system. PNNL identified and developed a MOF material, Cr-MIL-101, which was successful in PFOS sorption in DI water compared to GAC material [9]. In order to advance the readiness level of the MOFs (in engineered form) as a PFOS-remediation capability and expand commercialization opportunities, provided to AVANTech for demonstration of continuous, long-term PFOS removal from tap water.

The following sections are organized as follows:

Section 2.0: PNNL material synthesis, characterization, and testing

Section 3.0: PFOS sorption testing using engineered MOF at AVANTech LLC.,

2.0 PNNL Material Synthesis, Characterization, and Testing

2.1 MOF Development

This work used a water stable, chromium-based MOF material (represented as Cr-MIL-101) for PFOS capture application. The MOF, Cr-MIL-101, was synthesized under hydrothermal conditions as previously reported in the literature [8-9]. Briefly, in a Parr reactor liner, chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 3.36g) and terephthalic acid (BDC, 1.39g) were added to distilled water (40 mL) and stirred vigorously for 30 min. The liner was sealed in the vessel and placed in an oven at 200°C for 24h. After cooling to room temperature, the as-synthesized product was centrifuged and washed with water (3x30mL). To isolate the MOF, the filtered product was repeatedly washed with N,N-dimethylformamide (3x30mL) over 24h. Finally, the solvent was exchanged with methanol (3x30mL) for another 24h. The product was dried in a vacuum oven at 70°C overnight and activated at 150°C for 24h prior to characterization. The synthesis procedure was repeated four times for the preparation of ~8 g of Cr-MIL-101 powder material.

2.2 MOF-polymer Engineered form (Granule) preparation

A test batch of the engineered form (granules) of Cr-MIL-101 was prepared to test the sorption properties. Eight grams of activated Cr-MIL-101 powder materials were submersed in the solvent dichloromethane (CH_2Cl_2)-Solution-A. In a separate container, 0.8 g of polymer binder (polyacrylic acid) was dissolved in the same solvent, CH_2Cl_2 , Solution-B. The MOF slurry solution (Solution-A) was combined with the polymer solution (Solution-B) while stirring vigorously and allowed to dry for a few hours in the air. The dried MOF-polymer mixture (10:1 ratio) was sieved to granules of particle sizes between 600-850 μm . The

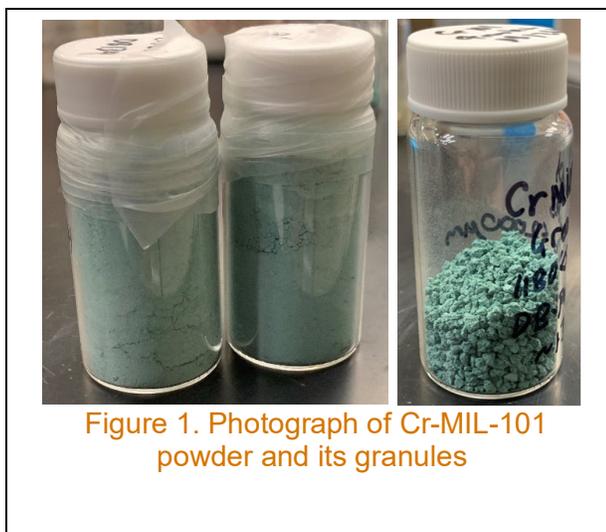


Figure 1. Photograph of Cr-MIL-101 powder and its granules

The granules were subsequently activated at 150°C under a vacuum for 12h to remove the solvent from the pores. Activated granules were re-sieved and re-heated for robustness. Approximately 4.5 g of MOF-polymer composite granules were obtained.

2.3 MOF powder and MOF-polymer Engineered form (Granule) Characterization and testing

Both the MOF powder and the MOF-polymer composite granules were subjected to thorough characterization. A sample of powder and granules was characterized using powder X-ray diffraction (XRD) for crystallinity and BET surface area measurements using N_2 sorption at 77K for surface area and pore-size distribution measurements. This is to confirm minimal surface area loss (due to binder addition) and retention of crystallinity, respectively. As shown in Figure 2, the PXRD clearly shows the crystallinity after granules preparation. The N_2 adsorption measurements showed a slight decrease in surface area and pore volume from powder form to granules. This can be expected and in line with the previously reported literature. Another sample of granules was tested in a packed column with continuous distilled (DI) water flow to confirm the robustness and stability of the particles. This testing was done using a column 6.5 mm in diameter and 55 mm in height filled with the granular material; water flowed at 2 mL/min for 6 hours (Figure 3).

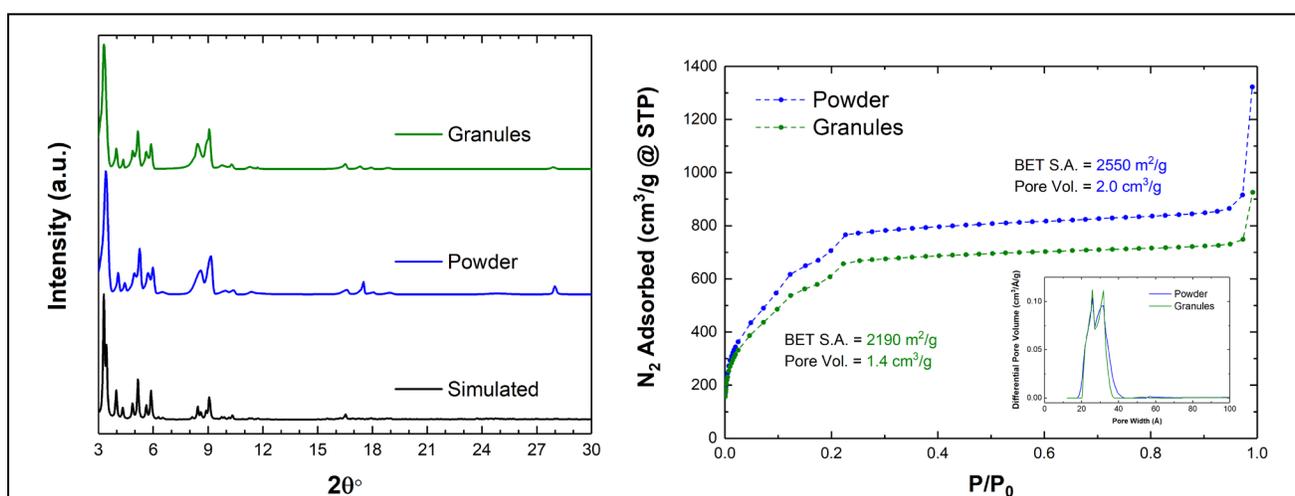


Figure 2. (left) Powder XRD and (right) BET surface area measurements (N_2 adsorption isotherms) for Cr-MIL-101-powder and granules.



Figure 2. Photograph of MOF-polymer granules (engineered form) packed column for stability test

2.4 PFOS capture (Large scale testing-AVANTech LLC)

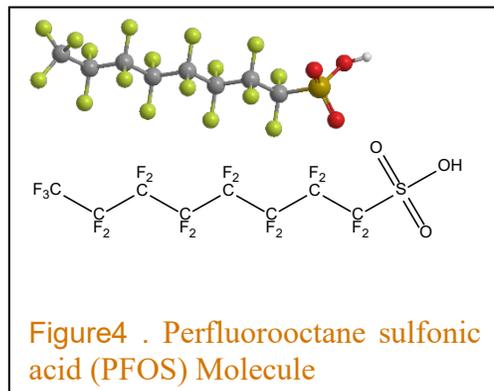
The engineered Cr-MIL-101 granules were packed, sealed, and shipped to the industry partner, AVANTech LLC, for testing the PFOS capture in tap water in a continuous flow experiment. The details are below:

Column Construction: HDPE tube with approximately 5 mm diameter and 8 in length was constructed with inert packing on top and bottom of the column. This column was connected with peristaltic pumps, tubing, and 30-gallon HDPE drums for PFOS water. The tubing was arranged to allow a upflow through the column to remove any air bubbles forming during the water flow. Pressure gauges are attached on both the upstream & downstream of the columns to measure pressure drop.

PFOS in Tapwater: Columbia, SC tap water was considered for preparing 10 ppb (20nM) PFOS solution for the testing. The tap water was allowed to sit overnight for the dissipation of chlorine. A 10 ppb PFOS solution was prepared using PFOS (from Sigma Aldrich) in dechlorinated tap water. The Inlet (initial) samples were taken to determine if any background PFOS was present. The effect of contact time in a flow reactor is very important, and based on the batch tests at PNNL, considered 5.3 mL/min flow rate for the entire sorption study.

Sorption testing: For column testing, 30-liter PFOS solution (10 ppb, 20nM) was prepared using city tap water and allowed overnight for chlorine to dissipate. Then the PFOS solution passed through the column in the first several days. After 24 hours of running the solution through the column, a sample of 1mL was collected, and two more 1mL samples were collected for comparison. The flow was continued and then collecting the outlet samples every 24h (1 mL samples, at least 2 or 3) for three more days. All the collected samples (1 mL) were sealed in an HDPE jar. After 4 days of running, another 30-liter PFOS solution (10 ppb, 20nM) was passed through the column while collecting after 24h, respectively. A total of 60-liter POS containing tap water was passed though the 2g Cr-MIL-101 over a period of 8 days. All eight days of samples (both inlet and outlet samples) sealed properly and were sent to PNNL for analysis. All the samples were subjected to LC-MS/MS analysis and the results are shown in Figure 5.

Interestingly, none of the inlet samples showed the prepared 10 ppb (20nM) concentration. This reduction might be due to the PFOS sorption by the HDPE containers. Literature suggests that HDPE adsorbs up to 30% over a period of 10 days [10]. In this case, the sorption testing to analysis was more than 60 days and there is a chance that the containers sorbed some of the PFOS from tap water. When comparing the Inlet and outlet concentrations, it was observed that at least 65% of PFOS sorbed in tap water in the first 24h under these flow conditions. The sorption capacities are varied from 65.23% to 38.9% over 8 days period. The results show that the sorbent was not saturated even after ~60-liter PFOS water flowed on the sorbent for over 8 days. This suggests more optimization is required to understand the sorption efficiently, which includes (i) increasing the contact time between the host sorbent and guest PFOS by slowing down the flow rate; (ii) increasing the PFOS concentration; (iii) adding internal standards for each day sorption for more accurate analysis; (iv) amount of sorbent versus the PFOS solution (2 g for 60-liter might be very less sorbent?), (iv) a similar comparison with commercially available Granular Activated Carbon (GAC) Material and (v) finally, repetition of the experiment. Some preliminary studies using GAC material were performed, but because of some technical issues, unable to complete the sorption/analysis of the samples, and work is in progress.



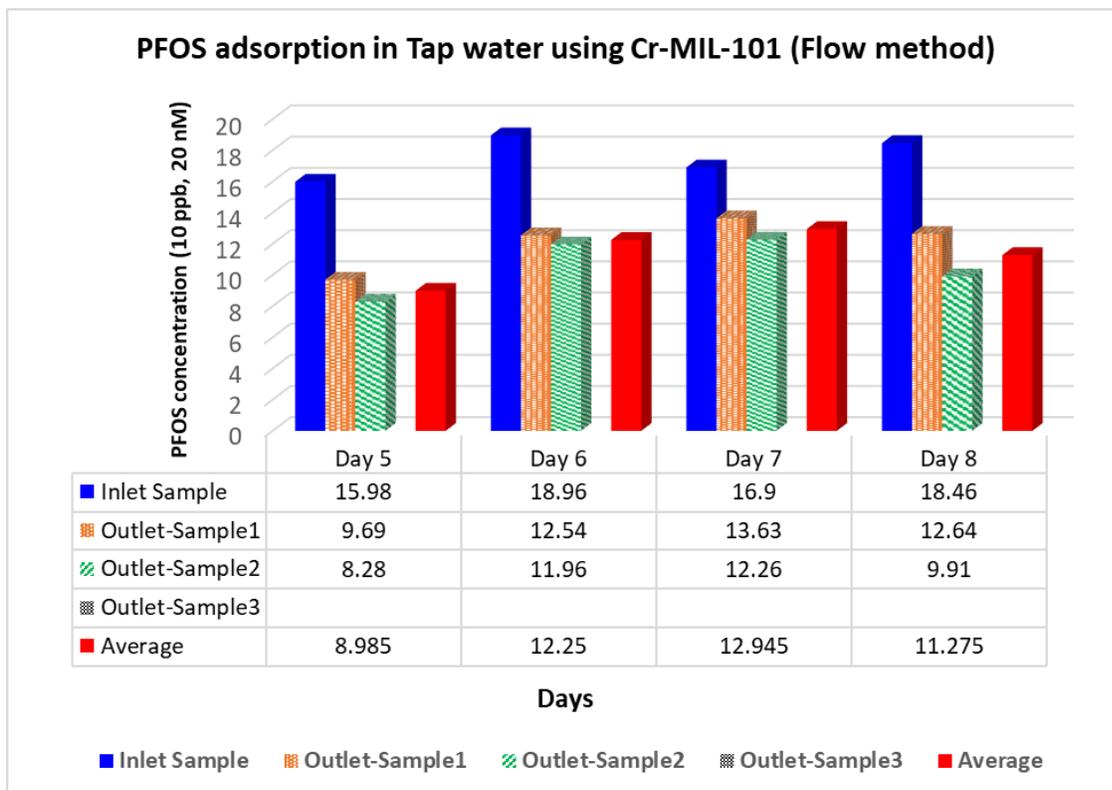
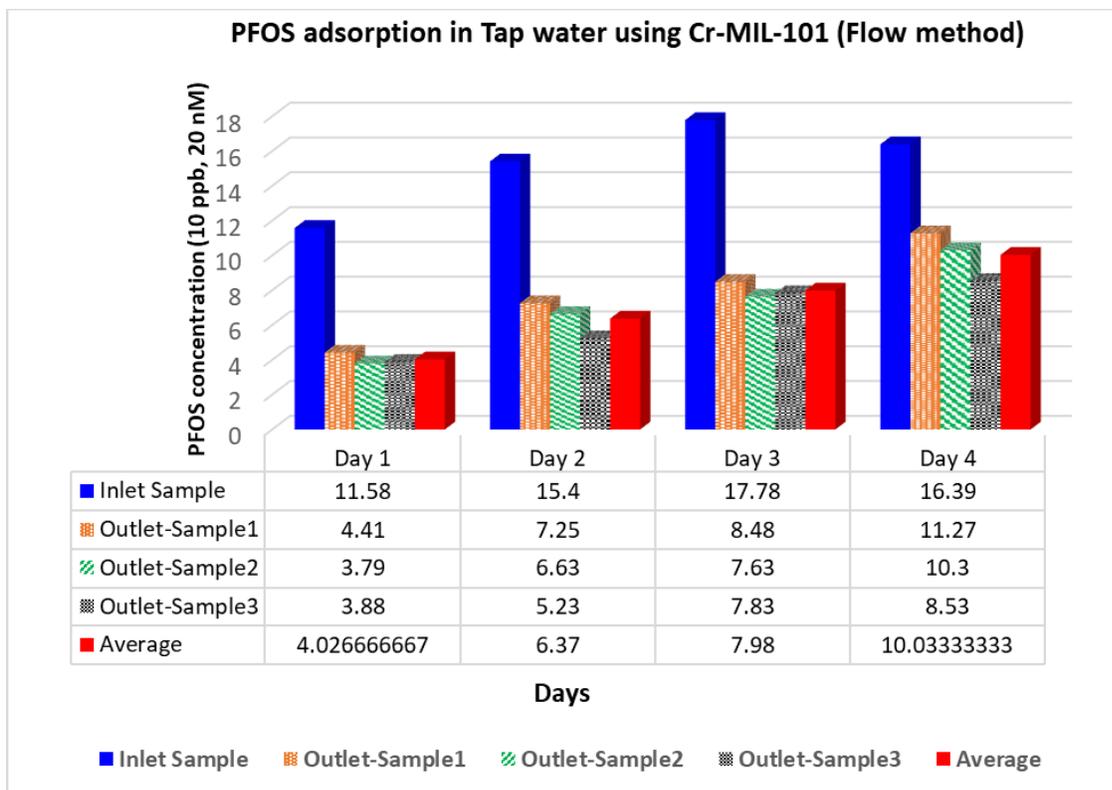


Figure 3. PFOS (10 ppb) sorption results in Tapwater under a flow system using Cr-MIL-101 over 8 days (60-liter).

Conclusions

PNNL has successfully developed an engineered MOF, (Cr-MIL-01) using a polymer as a binder and tested for PFOS sorption in tap water. The engineered form (MOF-polymer granules) were successfully tested for their stability in water before testing PFOS sorption. PFOS sorption tests were performed by flowing a known concentration of PFOS solution through a tube packed with MOF granules. Triplicate samples were collected from the outlet for the first four days and duplicate on rest four days, and concentration was tested using LC-MS/MS at PNNL. The preliminary testing of PFOS at low concentrations (10 ppb, 20 nM) in tap water showed a decent performance in PFAS removal of up to 65% from the water within 24h. The MOF granules could not completely remove PFOS from the solution, but interestingly, the saturation was not reached even after 8 days after flowing 60-liter solution, indicating more optimization is required.

3.0 References

- [1] X. Chen, X. Xia, X. Wang, J. Qiao, H. Chen, *Chemosphere*, 83 (2011) 1313-1319.
- [2] in: H.a.E.C.D.-O.o. Water (Ed.), United States Environmental Protection Agency, 2016, pp. 88.
- [3] P. Grandjean, E.W. Andersen, E. Budtz-Jorgensen, F. Nielsen, K. Molbak, P. Weihe, C. Heilmann, *Jama-J. Am. Med. Assoc* 2012, 307 (4), 391– 397
- [4] V. Barry, A. Winqvist, K. Steenland, *Environ. Health Perspect.* 2013, 121 (11–12), 1313–1318
- [3] K.A. Barzen-Hanson, S.C. Roberts, S. Choyke, K. Oetjen, A. McAlees, N. Riddell, R. McCrindle, P.L. Ferguson, C.P. Higgins, J.A. Field, *Environ Sci Technol*, 51 (2017) 2047-2057.
- [4] D. Barpaga, V.T. Nguyen, B.K. Medasani, S. Chatterjee, B.P. McGrail, R.K. Motkuri, L.X. Dang, *Sci Rep-Uk*, 9 (2019) 10289.
- [5] J. Zheng, D. Barpaga, O.Y. Gutiérrez, N.D. Browning, B.L. Mehdi, O.K. Farha, J.A. Lercher, B.P. McGrail, R.K. Motkuri, *ACS Applied Energy Materials*, 1 (2018) 5853-5858.
- [6] Y.H. Cheng, D. Barpaga, J.A. Soltis, V. Shutthanandan, R. Kargupta, K.S. Han, B.P. McGrail, R.K. Motkuri, S. Basuray, S. Chatterjee, *Acs Appl Mater Inter*, 12 (2020) 10503-10514.
- [7] D. Barpaga, J. Zheng, K.S. Han, J.A. Soltis, V. Shutthanandan, S. Basuray, B.P. McGrail, S. Chatterjee, R.K. Motkuri, *Inorg Chem*, 58 (2019) 8339-834
- [8] Zheng, J.; Barpaga, D.; Gutiérrez, O. Y.; Browning, N. D.; Mehdi, B. L.; Farha, O. K.; Lercher, J. A.; McGrail, B. P.; Motkuri, R. K., *ACS Applied Energy Materials* 2018, 1 (11), 5853-5858. 2.
- [9] D. Barpaga, J. Zheng, K.S. Han, J.A. Soltis, V. Shutthanandan, S. Basuray, B.B. McGrail, S. Chatterjee, R.K. Motkuri, *Inorg Chem* 2019, 58 (13), 8339-8346
- [10] E. Jenny E. Zenobio, Omobayo A. Salawu, Ziwei Han, Adeyemi S. Adeleye, *Journal of Hazardous Materials Advances*, 2022, Volume 7,100130

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354

1-888-375-PNNL (7665)

www.pnnl.gov