Adsorption of a PFAS Utilizing MOF-808: Development of An Undergraduate Laboratory Experiment in a Capstone Course

Tyler M. VanOursouw,‡ Trevor Rottiger,‡ Kiley A. Wadzinski,‡ Brian E. VanderWaal,‡ Madison J. Snyder,‡ Riley T. Bittner,‡ Omar K. Farha,† *Shannon C. Riha,‡ and *Joseph E. Mondloch‡

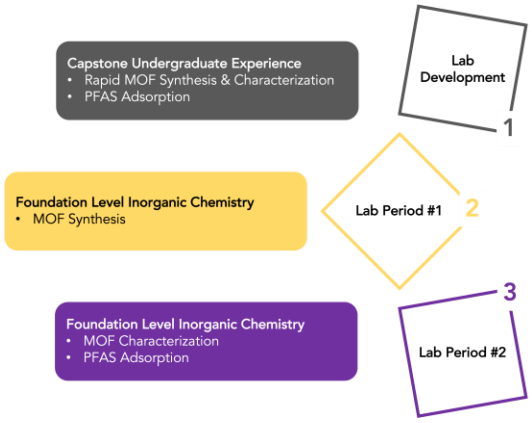
† International Institute for Nanotechnology, Institute for Sustainability and Energy at Northwestern, and Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States; Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

‡ University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States.

ABSTRACT

A two-component undergraduate laboratory experience has been developed by students in a senior level capstone course. The first component is a 3 h laboratory experience dedicated to the rapid synthesis of a metal–organic framework (MOF-808) in aqueous solution using readily available reagents and equipment. During the second component, MOF-808 was characterized via a suite of instruments: powder X-ray diffraction (PXRD), thermal gravimetric analysis (TGA), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In addition, quantitative $^{19}F\{^{1}H\}$ NMR spectroscopy was utilized to quantify the amount of perfluorobutane sulfonate (PFBS), one example of a poly- or perfluoroalkyl substance (aka PFAS), adsorbed from solution. The two 3 h laboratory experiences were subsequently deployed in a foundation level inorganic chemistry course. This two-component, multi-instrument lab experience provides students an opportunity to synthesize a modern porous solid and utilize it in an emerging application of MOF science.

GAPHICAL ABSTRACT



KEYWORDS

Second-Year Undergraduate, Upper Division Undergraduate, Inorganic Chemistry, Hands-On Learning/Self Instruction, Materials Science, Solid State Chemistry, Multi-Instrument Lab Experiment

INTRODUCTION

A common theme when developing new laboratories for the undergraduate curriculum is introducing students to exciting, cutting-edge research topics within a particular discipline.[1] As an example, in inorganic chemistry a rapidly expanding area of research has focused on a class of solid-state materials termed metal–organic frameworks (aka MOFs) and significant effort has been dedicated to introducing these materials into the undergraduate laboratory curriculum.[2-15] MOFs are built up from metal-based nodes and organic linkers.[16] Some intriguing features of these materials include the ability to readily modify their components (both the nodes and linkers), their propensity to be crystalline, and the presence of void spaces which has opened up a host of applications centered around the principles of adsorption including catalysis, separation, and filtration.[16]

One emerging application is the use of MOFs for the removal of poly- and perflouroalkane substances (aka PFAS) from aqueous solution.[17] "PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl (*i.e.*, $–CF_3$) or methylene carbon (*i.e.*, $–CF_2$) atom (without a H/Cl/Br/I atom attached to it), and some well-known examples are shown in Figure 1.[18] These man-made chemicals exhibit useful properties such as non-stick behavior as well as heat-, stain- and water-resistance.[19] These properties make PFAS extremely stable, but also persistent in the environment. Unfortunately, some PFAS have been linked to adverse human health effects,[20] and therefore there has been interest in removing them from point sources as well as the environment.

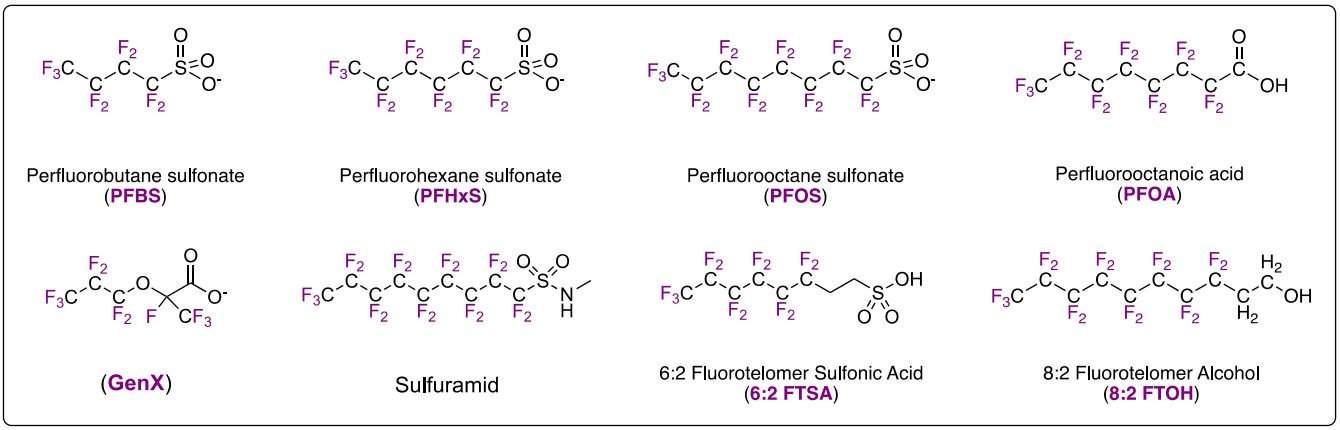


Figure 1. Some well-known PFAS and their chemical structures.

MOFs containing Zr-based nodes and carboxylate-based linkers are capable of removing PFAS from aqueous solution.[17, 21] Unfortunately, many of the synthetic procedures employed for the synthesis of MOFs containing Zr-based nodes and carboxylate containing linkers aren't compatible with a typical undergraduate laboratory time period (*e.g.*, 3 h). (It's worth mentioning that this isn't unique to MOF chemistry and it is often challenging to bring cutting-edge research into the undergraduate classroom.[1]) Here undergraduate students in a senior level capstone course (CHEM 446) developed a two-component, multi-instrument laboratory experience. During the first component a Zr-based MOF, MOF-808, was rapidly synthesized in acidic aqueous solution using readily available reagents and equipment during a single 3 h lab period. In a second 3 h lab period, students developed a strategy to characterize MOF-808 using PXRD, TGA, and DRIFTS, and further used MOF-808 to quantify the adsorbtion of a PFAS, perfluorobutanesulfonate (PFBS), from aqueous solution utilizing $^{19}F\{^{1}H\}$ NMR. To test the viability of this two-component, multi-instrument lab sequence, it was deployed in an intermediate inorganic chemistry course (CHEM 355).

EXPERIMENTAL OVERVIEW

This experiment was designed to be carried out during two 3 h laboratory periods. During the first lab period students synthesized the porous solid, MOF-808. The synthetic procedure for MOF-808 is summarized in Figure 2, and was modified from the procedure from Liu et al.[22] The reaction was

carried out utilizing a round bottom flask, reflux condenser, sand bath, and a stir/hot plate. MOF-808 was washed with water and acetone and isolated via centrifugation (*i.e.*, the purification process). Finally, the resultant white powder was dried in a gravity oven at 80 °C until the following laboratory period. Together, the reflux and purification take approximately 2 h 15 min leaving adequate time for set up and clean up during a 3 h lab period. During the second lab period students utilize multiple instruments to validate the successful synthesis of MOF-808. Specifically, students determined the mass of MOF-808, characterized their samples via powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Additionally, they also carried out a PFAS adsorption experiment utilizing the potassium salt of perfluorobutane sulfonate (PFBS). The amount of PFBS adsorbed was determined via $^{19}F\{^{1}H\}$ NMR spectroscopy using trifluoroethanol (TFE) /deuterium oxide (D_2O) as an internal standard. Some additional tips and tricks for the instructor are outlined in the Supporting Information (Notes for Instructors.docx and .pdf).

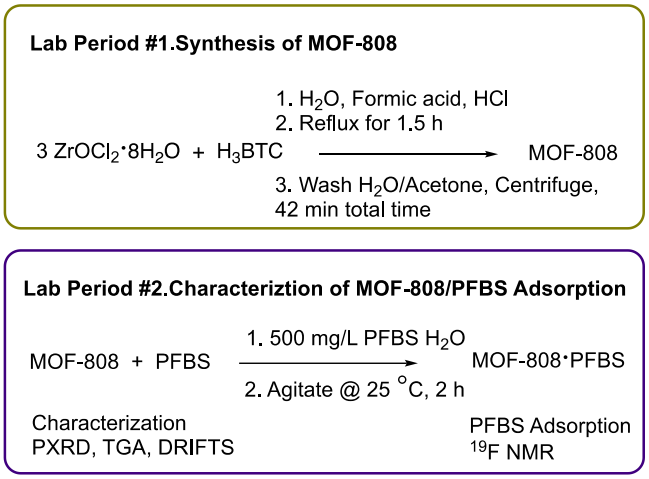


Figure 2. An overview of the two-component laboratory experience developed herein.

SAFETY HAZARDS

Appropriate personal protective equipment, especially gloves and googles, should be worn for the entirety of the experiment. The synthesis of MOF-808 should be carried out in a fume hood, including the addition of formic and hydrochloric acid to the Zr-containing solution. All chemicals should be treated as toxic and/or hazardous if ingested and key elements of their individual safety data sheets

(SDS) are shown in Table 1. Both instructors and students are encouraged to consult SDS for additional safety information as needed.

Table 1. Safety Precautions for the Compounds used in this Experiment.

Compound	Key Hazards
Zirconyl chloride octahydrate	Danger. Causes severe skin burns and eye damage.
1,3,5-tricarboxylic acid	Not a hazardous substance.
Formic acid	Danger. Flammable liquid and vapor. Causes sever skin burns and eye damaged. Toxic if inhaled (use in hood).
Hydrochloric acid	Danger. Causes sever skin burns and eye damaged. May cause respiratory irritation (use in hood).
Trifluoroethanol	Danger. Flammable liquid and vapor. Causes serios eye damage. May damage fertility or the unborn child.
Deuterium oxide	Not a hazardous substance.
Perfluorobutanesulfonate	Danger. Causes serious eye damage.
Potassium bromide	Warning. Causes serious eye irritation.
MOF-808	Not a hazardous substance. Avoid breathing dust.

RESULTS AND DISCUSSION

Development of MOF-808 Synthesis & PFBS Adsorption

Keeping in mind our desire to develop an undergraduate laboratory experience, we chose to modify Liu et al.'s[22] synthetic procedure for MOF-808 for several reasons: (i) all the reagents are commercially available; (ii) it makes use of water as the solvent, a less toxic and cost prohibitive alternative to solvents such as dimethylformamide (DMF) which are often used for the synthesis of MOFs; and (iii) the equipment required for synthesis—stir/hot plates, round bottom flasks, reflux condensers, and centrifuges—should be readily available at many institutions. The solid-state structure of MOF-808 is shown in Figure 3a. It is built up from $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]^{12+}$ nodes (Figure 3c) and 1,3,5-benzene tricarboxylate linkers (btc), Figure 3d. The remaining cationic charge on the node is compensated by a combination of non-structural formate (HCO^-) ligands and/or pairs of OH^- and H_2O ligands (Figure 3b).[23] The generalized empirical formula for MOF-808 is $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(btc)_2(formate)_{6-x}(OH)_x(H_2O)_x$. For sake of simplicity, the non-structural charge compensating ligands shown in Figure 3b are

represented as OH^-/H_2O pairs, *i.e.* x = 6 in the aforementioned formula, despite the likelihood of formate incorporation.[23] The presence of OH^-/H_2O pairs on the $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]^{12+}$ nodes has been shown to be important for driving PFAS adsorption and therefore we hypothesized that those same ligand pairs might enable PFAS adsorption by MOF-808.[21]

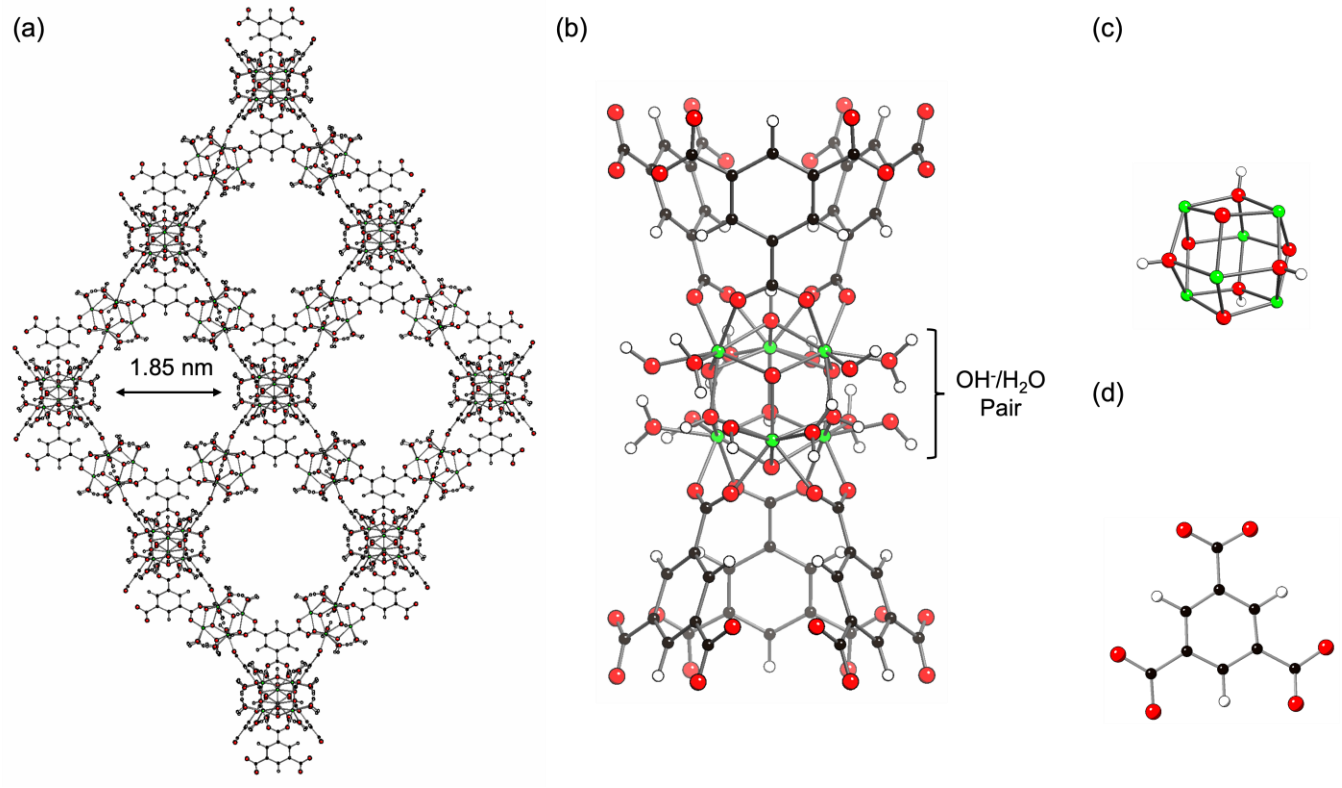


Figure 3. Key structural representations of MOF-808 including: (a) its extended structure; (b) its node highlighting the location of a OH^-/H_2O ligand pair; (c) the $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]^{12+}$ building brick; and (d) the btc linker.

Six undergraduate students in a capstone chemistry course (CHEM 446) developed the synthetic protocol for MOF-808, shown back in Figure 2, over the course of two semesters. Two key variables were modified from Liu et al's procedure to ensure MOF-808 could be synthesized within a single 3 h laboratory period.[22] The literature protocol requires a 24 h purification step (*i.e.*, a combination of washing and centrifugation to remove left-over solvent and reactants from the synthesis), however there is evidence that purification, at least for other MOFs, can be significantly shortened.[24] We were hopeful that the purification protocol could be shortened for MOF-808 and attempted the literature

synthesis (Table 2, entry 1) utilizing a significantly shorter time frame (Table 2, entry 2). Pore volume measurements (an example of which is shown in Figure 4a), which are proportional to the total amount of gaseous nitrogen taken up by a sample as measured by nitrogen adsorption analysis, indicated that the purification time could be significantly reduced. Powder X-ray diffraction (Figure 4b) also confirmed that MOF-808 could be synthesized using the shortened purification protocol.

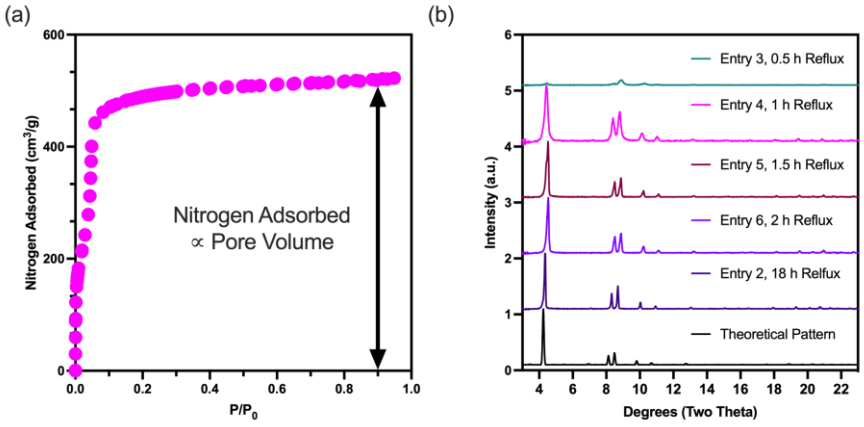


Figure 4. An example nitrogen adsorption isotherm (a) and key PXRD patterns from developing the rapid synthesis of MOF-808 (b).

Table 2. Effects of Key Synthetic Parameters on the Synthesis of MOF-808.

Entry	Purification Time (min)	Reflux Time (min)	Total Time (min)	Pore Volume (cm^3/g)
1	1440	1080	2520	0.86
2	42	1080	1122	0.83
3	42	30	72	0.24
4	42	60	62	0.35
5	42	90	132	0.62
6	42	120	162	0.86
7	30	120	150	0.28
8	24	120	144	0.32

While carrying out the synthesis of MOF-808, CHEM 446 students observed that a white precipitate formed approximately 30 min into the reflux. Analysis of the white precipitate after 0.5 h and 1 h (Table 2, entries 3 & 4) indicated the pore volume and crystallinity (Figure 4b) of the sample were not acceptable. However, after 2 h of reflux (Table 2, entry 6) the pore volume and crystallinity

were identical to that of the sample from the 18 h reflux. Unfortunately, the 2 h reflux coupled with the 42 min purification protocol leaves little time for setup and clean up in the laboratory. Attempts to reduce the purification protocol time (Table 2, entries 7 & 8) were unsuccessful leading to decreased pore volume and crystallinity (Figure 4b). Decreasing the reflux time to 1.5 h, while maintaining the purification protocol at 42 min (Table 1, entry 5) led to a reduced, albeit very reasonable, pore volume for MOF-808 as well as good crystallinity (Figure 4b).

A protocol for quantifying PFBS adsorption was also developed by students in CHEM 446. Approximately 10 mg of MOF-808 was weighed into a centrifuge tube and 1 mL, per mg of MOF, of a 500 ppm PFBS solution was added to the centrifuge tube. The solution was agitated at room temperature and 300 rpm for 2 h. Subsequently, the solution was centrifuged and 700 microliters was removed and added to an NMR tube along with 50 microliters of a trifluoroethanol (TFE) deuterium oxide (D_2O) internal standard. Quantitative $^{19}F\{^1H\}$ NMR utilizing a 20 s relaxation delay to ensure reliable integration (Figure S2, Notes to Instructors) coupled with equation 1 was used to determine the concentration of PFBS before and after adsorption.

$$[\text{PFBS}] = \frac{I_{\text{PFBS}}}{I_{\text{TFE}}} \cdot \frac{N_{\text{TFE}}}{N_{\text{PFBS}}} \cdot [\text{TFE}] \quad (1)$$

Here [PFBS] and [TFE] are the respective molar concentrations, I_{PFBS} and I_{TFE} are the integrals from the $^{19}F\{^1H\}$ NMR spectrum, and N_{TFE} and N_{PFBS} are the number of F atoms that give rise to each NMR signal. An example $^{19}F\{^1H\}$ NMR spectrum before (bottom) and after (top) adsorption is shown in Figure 5. The resonance at -76.00 ppm is due to the $-CF_3$ group of TFE, while the resonance at -80.15 ppm arises from the $-CF_3$ group of PFBS. The difference in PFBS concentration before and after adsorption is assumed to be adsorbed by MOF-808. The average of three trials from a CHEM 446 student yielded 1.2(1) x 10^{-4} M PFBS adsorbed utilizing this protocol.

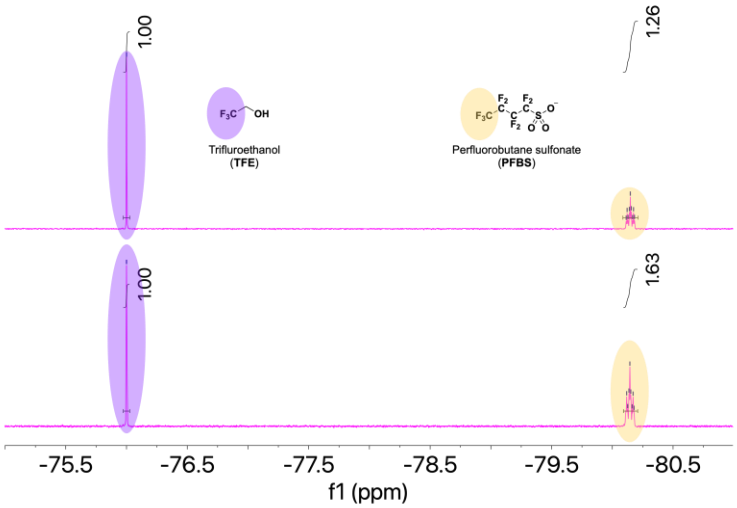


Figure 5. A representative $^{19}F^{1}H$ NMR spectrum before (bottom) and after (top) PFBS adsorption.

Deployment of MOF-808 Synthesis, Characterization & PFBS Adsorption

In the Spring of 2022, seven students in a foundation level inorganic chemistry course, CHEM 355, carried out the synthesis of MOF-808 utilizing the 1.5 h reflux and 42 min purification protocol (*i.e.*, Entry 5 in Table 2) developed by the CHEM 446 students. After drying their samples at 80 °C for 1 week, students isolated on average 0.332 +/- 0.134 g of MOF-808. Students characterized their MOF-808 samples via PXRD, TGA, and DRIFTS and examples of their results are shown in Figure 6. The PXRD pattern (Figure 6a) is consistent with the theoretical PXRD pattern of MOF-808 as well as a sample synthesized by CHEM 446 students. Prominent peaks are present at present at 4.2, 8.1, 8.5, 9.8, and 10.7 degrees two-theta. The TGA trace (Figure 6b) shows three distinct mass loss events: (i) loss of solvent molecules (25–150 °C, physisorbed and chemisorbed water can also be removed over this temperature range); (ii) loss of formate ligands (150–400 °C), and (iii) decomposition of the MOF-808 framework (400–600 °C).[23] A representative DRIFTS spectrum collected by a CHEM 355 student is shown in Figure 6c. The strong broad stretch centered at 3440 cm^{-1} is consistent with water physisorbed in the MOF, the band at 1624 cm^{-1} corresponds to C–C stretching of the aromatic ring in the btc linker, and the stretches at 1574, 1450, and 1385 cm^{-1} correspond to the symmetric and antisymmetric C–O stretches of the btc linker.[25]

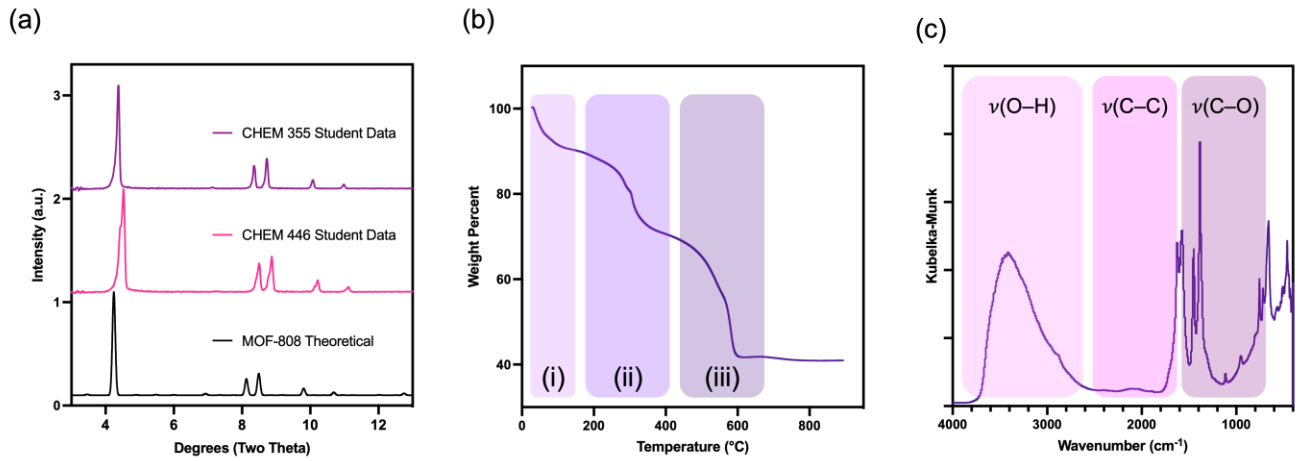


Figure 6. Representative MOF-808 characterization data: (a) PXRD data collected by a CHEM 446 and 355 student; (b) TGA data collected by a CHEM 355 student and (c) DRIFTS data collected by a CHEM 355 student.

Students in CHEM 355 also carried out PFBS adsorption experiments utilizing the procedure developed by CHEM 446 students. Concentrations for the TFE/D_2O solution and the initial PFBS solution were provided by the instructor (but could be prepared and collected by students as well). All students were able to obtain clean and easily integrated $^{19}F\{^1H\}$ NMR spectra that were similar to that shown in Figure 5. On average, student prepared MOF-808 samples adsorbed 2.8(8) x 10^{-4} M PFBS. This value does not take into account the dilution factor that results when combining the TFE/D_2O internal standard in the NMR tube. This results in an increase in the amount of PFBS adsorbed to 3.0(8) x 10^{-4} M. As a point of reference, the dilution corrected value, corresponds to 101(27) mg/g or 0.30(8) mmol/g PFBS adsorbed which are the more commonly reported units in the PFAS adsorption literature.

LEARNING OBJECTIVES & ASSESMENT OF STUDENT OUTCOMES

An important learning objective for students enrolled in CHEM 446 is to "*design and construct experiments that address scientific questions using appropriate methods, techniques, and modern chemical instrumentation*". Students were given the option to identify a project on their own or select from topics provided by the instructor which center around faculty expertise at our institution. As an example, the following statement was an instructor provided topic and served as the inspiration for the work detailed herein: "*Per- and poly-fluoroalkyl (PFAS) substances are emerging environmental*

contaminants. Current methods for remediation suffer from poor selectivity and/or slow adsorption kinetics. Porous solids, such as metal–organic frameworks (MOFs), exhibit several features that could help overcome these shortcomings. For this project you will synthesize a MOF and subsequently test its ability to extract PFAS from water". To help students find focus for their project, relevant background literature (*e.g.*, regarding PFAS and MOFs) was provided so students could start discussions with the instructor and faculty member. Initial discussions with students identified significant interest in a laboratory experience centered around MOFs and PFAS for CHEM 355—a course that many CHEM 446 students had taken in prior semesters. At the outset of this project, it was unclear what MOF would be best suited for incorporation into the classroom and that would also simultaneously work for PFAS adsorption. It was therefore suggested that students could investigate the MOF (*i.e.*, different combinations of metals and organic linkers), the solvents used for synthesis (*e.g.*, dimethyl formamide vs water), or the identity of the PFAS for adsorption. One very important early contribution from the CHEM 446 students was a focus on a green MOF synthetic route that utilized water instead of solvents such as DMF. This preference allowed students to focus in on MOF-808 rather quickly and start to identify how to optimize the synthesis for an undergraduate laboratory experience.

CHEM 446 students were required to submit a first-draft and final version of a research proposal containing background information (Introduction), a project design (Experimental and Timeline), and a budget. The project design was a key component used to address the learning outcome above, where students identified synthetic protocols as well as characterization and analysis methods in concert with the CHEM 446 instructor and/or faculty member. First-drafts of student research proposals were assessed via a blind peer review by their classmates in CHEM 446 as well as the instructor. Prior to submitting a final draft, students were expected to incorporate peer and instructor feedback into their proposal and address concerns associated with the project design. The final version of the proposal was only assessed by the instructor. Table 3 summarizes the number of students that did not meet, met, or exceeded expectations for the project design component (averaged point values from the criteria under the Experimental and Timeline sections of the Research Proposal rubric found in the SI) in the first and final drafts of their proposals. At a minimum all students met expectations based on their first draft of the proposal which suggests that students in the CHEM 446 course were able to

design experiments and identify key characterization methods for the synthesis of a MOF and its subsequent characterization, based on literature precedence. Fine tuning of their experimental design in the final draft of the proposal increased the number of students that exceeded expectations highlighting that students were able to learn from constructive feedback to strengthen their experimental design.

Table 3. Assessment of project design from student research proposals.

	Did Not Meet Expectations	Met Expectations			Exceeded Expectations
Grade (out of 4 points)	<2.5	2.5	3	3.5	4
1st Draft: Number of students	0	0	1	4	1
Final Draft: Number of students	0	0	0	2	4

Upon successful acceptance of their research proposal, students in CHEM 446 were further assessed on the practical component of the learning outcome, "*construct experiments that address scientific questions*" in the research laboratory. Informal assessment of the student's ability to "*construct experiments*" in the research laboratory was premised on whether the student was able to carry out a synthetic procedure or characterization method and then subsequently modify their experimental procedure based on observations and data interpretation if necessary. For example, in the development of the synthesis protocol, a student noticed a white precipitate after 30 minutes of reflux. Based on this observation, the student proposed a time-dependent study to optimize the pore volume yet keep the synthesis manageable for a 3-hour lab period. This suggests the student successfully demonstrated the practical side of the learning outcome. Many small, yet significant observations, such as this contributed to the success of this laboratory experience.

A second learning outcome for CHEM 446 is to "*evaluate, document, and communicate experimental data according to accepted scientific standards.*" Assessment of the student's ability to "*communicate experimental data according to accepted scientific standards*" was assessed through a written research paper and an oral presentation in the form of a poster at the end of the semester. Because the overall goal of the CHEM 446 project described was to develop an undergraduate laboratory experiment, the

research paper took the form of a student experiment handout. The student experiment handout was expected to include relevant background information, an experimental procedure, data treatment instructions, and post-lab questions. Additionally, a results section was required to serve as an instructor's guide. Evaluation was largely based on whether the student effectively communicated the importance of the experiment along with the experimental details at a level that could be understood by undergraduate students. The research paper was assessed by the CHEM 446 instructor and the results of that assessment are summarized in Table 4 (Note: grade reflects an average of points received for all criteria in Final Paper Rubric found in the SI, Notes to Instructor).

The poster presentation was used to assess the students' ability to analyze and interpret the results of their experimental work and make connections to the overall research questions and goals. Students presented their results to a broad audience, which included faculty and students within chemistry and biology, along with administrative personnel, parents, and industry representatives. Presenting their results at these venues challenges students to not only communicate their results according to scientific standards but also to distill their results down to a level the general public and/or someone outside the field can understand. As such, student poster presentations were evaluated by other faculty and staff rather than by the CHEM 446 instructor using the rubric found in the SI. Comments such as, "*very knowledgeable about the research project and its goals*", "*withstood my tough questions*", and "*excellent job explaining results*", were common among the six students that were involved in developing this laboratory experiment. Of the six, two students exceeded expectations and four student met expectations for this assessment, Table 4 (Note: grade reflects the scaled average point value received for all criteria in the Poster Rubric found in the SI, Notes to Instructor).

Table 4. Assessment of written and oral communication.

	Did Not Meet Expectations	**Met Expectations**			**Exceeded Expectations**
Grade (out of 4 points)	<2.5	2.5	3	3.5	4
Experimental handout: Number of students	0	0	0	4	2
Poster presentation: Number of students	0	0	1	3	2

Over the course of the semester, an overreaching learning objective for students in CHEM 355 is to "*build the skills necessary to synthesize and characterize inorganic compounds*". During this two-week laboratory experience students had the chance to build these skills by synthesizing a modern solid-state material, MOF-808, and subsequently characterizing MOF-808 via PXRD, TGA, and DRIFTS. Assessment of this learning objective was accomplished by examining student lab reports for the following items: (i) a synthetic yield; (ii) a PXRD pattern consistent with MOF-808; (iii) a TGA trace consistent with MOF-808; and (iv) a DRIFTS spectrum consistent with MOF-808. Each student reported a synthetic yield as well as a PXRD pattern, TGA trace, and a DRIFTS spectrum (examples of student data are shown back in Figure 6) consistent with MOF-808, ensuring that all students in CHEM 355 met this learning objective. It is noteworthy that this is an instructor assessment of the reported data to determine whether MOF-808 was successfully synthesized and does not rely on student interpretation of data. Furthermore, in principle a student could meet this learning objective even if they didn't successfully synthesize MOF-808 but still characterized their inorganic compound.

To assess whether students were able to identify if they synthesized MOF-808 we asked them to "*properly prepare, report, and interpret data in a professional format*". This learning objective was again assessed by examining student lab reports. As mentioned above, all students in CHEM 355 were able to provide PXRD patterns, TGA traces, and DRIFTS spectra (such as those shown in Figure 6) suggesting that they were all able to properly prepare data in a professional format. For this laboratory experience, properly reported data included yields reported to 0.xxx g, IR stretches to 1 cm^{-1} (with intensities); NMR resonances to 0.xx ppm (along with splitting pattern), PXRD peaks to 0.xx degrees, and decomposition temperatures from the TGA trace to the nearest 1 °C. The key for this assessment is shown below.

> Yield: 0.xxx g. DRIFTS (cm^{-1}): 3325 (m), 1624 (s), 1574 (s), 1450 (s), 1385 (s). ^{19}F NMR (400 MHz, D_2O): -76.65 (s), -80.93 (s). PXRD (degrees, two-theta): 4.2, 8.1, 8.5, 9.8, and 10.7. TGA (°C): 580 (decomposition).

The number of students that properly prepared data in each category are tabulated in Table 5. The yield, DRIFTS, and TGA data were reported correctly most often, while the ^{19}F NMR and PXRD data were reported correctly less often. In some instances, the number of students properly reporting data

tracks with the number of times the data had been reported in other lab reports over the course of the semester. For example, yields and DRIFTS data were reported by students several times prior to writing this lab report and nearly all students properly reported both. However, in other instances no correlation seems to be present. For example, NMR and PXRD data were properly reported by ~50% of students despite reporting that type of data in previous lab reports throughout the semester.

Table 5. Number of Students Properly Preparing Data in Each Category.

	Yield	DRIFTS	^{19}F NMR	PXRD	TGA
Number of Students Properly Reporting Data	6	7	3	4	7

Assessing students' ability to properly interpret data was probed by asking them to use their experimental data to demonstrate they made MOF-808. This is something that was emphasized for all lab reports submitted in CHEM 355 and students were asked to assign peaks, bands, etc.... not only for their compounds, but for impurities as well. For this lab report students most commonly used a combination of PXRD and DRIFTS data to support the fact that they synthesized MOF-808. The following student statements—"the PXRD pattern of 1 (MOF-808) shows peaks identical to the standard at 4.56, 8.46, 8.89, 10.23, and 11.17 two-theta" and "the MOF that was produced does appear to be MOF-808 since the predominant signals show up that are expected"—are representative examples of the range of depth provided by students to support their argument.

The DRIFTS data was harder to interpret. While all students were able to assign the broad peak around 3325 cm^{-1} to an O–H stretch for water, students assigned one or some combination of the bands at 1624, 1574, 1450, and 1385 cm^{-1} to the C–C and/or C–O stretching of the btc linker. (Recall the band at 1624 cm^{-1} corresponds to C–C stretching of the aromatic ring in the btc linker, and the stretches at 1574, 1450, and 1385 cm^{-1} correspond to the symmetric and antisymmetric C–O stretches of the btc linker.[25]). It may be fruitful to have students read the very recent study from Platero-Prats and co-workers to help further their knowledge of this subject.[25] While we identified some sticky points for students, on average students exceeded our expectations for this laboratory experience earning on average 93.5% of the points.

CONCLUSIONS

A modern two-component lab experience, encompassing the synthesis and characterization of MOF-808 and its use for the adsorption of PFBS, has been developed by students in a senior level capstone chemistry course. Both components were subsequently deployed in a foundation level inorganic chemistry lab that allowed students to rapidly synthesize MOF-808 in good yield and characterize it via PXRD, TGA, and DRIFTS. In addition, students utilized MOF-808 for the removal of a PFAS from water. We hope that this set of laboratory experiments generates excitement for students and allows them to see how modern inorganic materials, such as MOFs, can be utilized for practical applications (*e.g.*, PFAS adsorption). In the future we plan to assess couple this laboratory experience with a course-based undergraduate research experience that allows students to build on their knowledge of MOFs while enhancing their understanding of the research process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX.

Notes for Instructors (DOCX)

Notes for Instructors (PDF)

Students Handout (DOCX)

Student Handout (PDF)

AUTHOR INFORMATION

Corresponding Authors

Joseph E. Mondloch - University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States. *E-mail: jmondloc@uwsp.edu

Shannon C. Riha - University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States. *E-mail: sriha@uwsp.edu

Authors

Omar K. Farha – International Institute for Nanotechnology, Institute for Sustainability and Energy at Northwestern, and Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States; Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States; email o-farha@northwestern.edu

Tyler M. VanOursouw – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States.

Trevor Rottiger – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States. *E-mail: trott070@uwsp.edu

Kiley A. Wadzinski – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States. *E-mail: kwadz761@uwsp.edu

Brian E. VanderWaal – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States.

Madison J. Snyder – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States.

Riley T. Bittner – University of Wisconsin-Stevens Point, Stevens Point, WI, 54481, United States.

ACKNOWLEDGMENTS

J.E.M. and S.C.R. acknowledge support for this research provided by UWSP University Personnel Development Committee-Research and Creativities grant and the UWSP Pathways Internship Program. O.K.F. thanks the financial support of the National Science Foundation (NSF) DMREF/GOALI (2119433).

REFERENCES

1. Cooke, J., Syntheses of Four-Coordinate Nickel(II)-Phosphine Compounds and a Rapid Suzuki–Miyaura Cross-Coupling Reaction for Short Laboratory Sessions. *Journal of Chemical Education* **2019,** *96* (9), 2009-2014.

2. Todd, C.; Ceballos, C. M.; So, M. C., Synthesis, Characterization, and Evaluation of Metal–Organic Frameworks for Water Decontamination: An Integrated Experiment. *Journal of Chemical Education* **2022,** *99* (6), 2392-2398.
3. Lisensky, G. C.; Yaghi, O. M., Visualizing Pore Packing and Topology in MOFs. *Journal of Chemical Education* **2022,** *99* (5), 1998-2004.
4. Gao, Z.; Lai, Y.; Zhang, L.; Lin, Y.; Xiao, L.; Luo, Y.; Luo, F., Synthesis, Characterization, and Electrocatalytic Activity Exploration of MOF-74: A Research-Style Laboratory Experiment. *Journal of Chemical Education* **2021,** *98* (10), 3341-3347.
5. Sakamaki, Y.; Tsuji, M.; Heidrick, Z.; Watson, O.; Durchman, J.; Salmon, C.; Burgin, S. R.; Beyzavi, H., Preparation and Applications of Metal–Organic Frameworks (MOFs): A Laboratory Activity and Demonstration for High School and/or Undergraduate Students. *Journal of Chemical Education* **2020,** *97* (4), 1109-1116.
6. Panda, D.; Patra, S.; Awasthi, M. K.; Singh, S. K., Lab Cooked MOF for CO2 Capture: A Sustainable Solution to Waste Management. *Journal of Chemical Education* **2020,** *97* (4), 1101-1108.
7. Cheng, Y.; Shi, D.; Di Yuan, Y.; Zhao, D., Facile Synthesis of a Metal–Organic Framework for Removal of Methyl Blue from Water: First-Year Undergraduate Teaching Lab. *Journal of Chemical Education* **2020,** *97* (11), 4145-4151.
8. Liu, Y.; Myers, E. J.; Rydahl, S. A.; Wang, X., Ultrasonic-Assisted Synthesis, Characterization, and Application of a Metal–Organic Framework: A Green General Chemistry Laboratory Project. *Journal of Chemical Education* **2019,** *96* (10), 2286-2291.
9. Lyle, S. J.; Flaig, R. W.; Cordova, K. E.; Yaghi, O. M., Facilitating Laboratory Research Experience Using Reticular Chemistry. *Journal of Chemical Education* **2018,** *95* (9), 1512-1519.
10. Jones, D. R.; DiScenza, D. J.; Mako, T. L.; Levine, M., Environmental Application of Cyclodextrin Metal–Organic Frameworks in an Undergraduate Teaching Laboratory. *Journal of Chemical Education* **2018,** *95* (9), 1636-1641.
11. Wriedt, M.; Sculley, J. P.; Aulakh, D.; Zhou, H.-C., Using Modern Solid-State Analytical Tools for Investigations of an Advanced Carbon Capture Material: Experiments for the Inorganic Chemistry Laboratory. *Journal of Chemical Education* **2016,** *93* (12), 2068-2073.
12. Smith, M. K.; Angle, S. R.; Northrop, B. H., Preparation and Analysis of Cyclodextrin-Based Metal–Organic Frameworks: Laboratory Experiments Adaptable for High School through Advanced Undergraduate Students. *Journal of Chemical Education* **2015,** *92* (2), 368-372.
13. Crane, J. L.; Anderson, K. E.; Conway, S. G., Hydrothermal Synthesis and Characterization of a Metal–Organic Framework by Thermogravimetric Analysis, Powder X-ray Diffraction, and Infrared Spectroscopy: An Integrative Inorganic Chemistry Experiment. *Journal of Chemical Education* **2015,** *92* (2), 373-377.
14. Rood, J. A.; Henderson, K. W., Synthesis and Small Molecule Exchange Studies of a Magnesium Bisformate Metal–Organic Framework: An Experiment in Host–Guest Chemistry for the Undergraduate Laboratory. *Journal of Chemical Education* **2013,** *90* (3), 379-382.
15. Sumida, K.; Arnold, J., Preparation, Characterization, and Postsynthetic Modification of Metal−Organic Frameworks: Synthetic Experiments for an Undergraduate Laboratory Course in Inorganic Chemistry. *Journal of Chemical Education* **2011,** *88* (1), 92-94.
16. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M., The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013,** *341* (6149), 1230444.
17. Li, R.; Alomari, S.; Islamoglu, T.; Farha, O. K.; Fernando, S.; Thagard, S. M.; Holsen, T. M.; Wriedt, M., Systematic Study on the Removal of Per- and Polyfluoroalkyl Substances from Contaminated Groundwater Using Metal–Organic Frameworks. *Environmental Science & Technology* **2021,** *55* (22), 15162-15171.
18. Reconciling Terminology of the Universe of Per- and Polyfluoroalkyl Substances: Recommendations and Practical Guidance. (accessed August 18th 2022).
19. Buck, R. C.; Franklin, J.; Berger, U.; Conder, J. M.; Cousins, I. T.; de Voogt, P.; Jensen, A. A.; Kannan, K.; Mabury, S. A.; van Leeuwen, S. P. J., Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management* **2011,** *7* (4), 513-541.

20. Ding, N.; Harlow, S. D.; Randolph Jr, J. F.; Loch-Caruso, R.; Park, S. K., Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) and their Effects on the Ovary. *Human Reproduction Update* **2020,** *26* (5), 724-752.
21. Li, R.; Alomari, S.; Stanton, R.; Wasson, M. C.; Islamoglu, T.; Farha, O. K.; Holsen, T. M.; Thagard, S. M.; Trivedi, D. J.; Wriedt, M., Efficient Removal of Per- and Polyfluoroalkyl Substances from Water with Zirconium-Based Metal–Organic Frameworks. *Chemistry of Materials* **2021,** *33* (9), 3276-3285.
22. Liu, X.; Kirlikovali, K. O.; Chen, Z.; Ma, K.; Idrees, K. B.; Cao, R.; Zhang, X.; Islamoglu, T.; Liu, Y.; Farha, O. K., Small Molecules, Big Effects: Tuning Adsorption and Catalytic Properties of Metal–Organic Frameworks. *Chemistry of Materials* **2021,** *33* (4), 1444-1454.
23. Aunan, E.; Affolter, C. W.; Olsbye, U.; Lillerud, K. P., Modulation of the Thermochemical Stability and Adsorptive Properties of MOF-808 by the Selection of Non-structural Ligands. *Chemistry of Materials* **2021,** *33* (4), 1471-1476.
24. Ma, J.; Kalenak, A. P.; Wong-Foy, A. G.; Matzger, A. J., Rapid Guest Exchange and Ultra-Low Surface Tension Solvents Optimize Metal–Organic Framework Activation. *Angewandte Chemie International Edition* **2017,** *56* (46), 14618-14621.
25. Romero-Muñiz, I.; Romero-Muñiz, C.; del Castillo-Velilla, I.; Marini, C.; Calero, S.; Zamora, F.; Platero-Prats, A. E., Revisiting Vibrational Spectroscopy to Tackle the Chemistry of Zr6O8 Metal-Organic Framework Nodes. *ACS Applied Materials & Interfaces* **2022,** *14* (23), 27040-27047.