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D5.1 Preliminary evaluation of tested hybrid processes

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Introduction

PFAS are a class of synthetic organic pollutants significantly occupying the attention of the public in the recent years due to their recalcitrance and ubiquity (Richardson & Kimura, 2020). The carbon-fluorine bond is the strongest bond in organic chemistry, from which PFAS draw their thermal stability, resistance towards acids, bases and most oxidizing agents (i.e., $F + e^- \rightarrow F^-$, $E_0 = 3.6V$). For the aforementioned reasons, a single process is more than likely not feasible for PFAS removal. *In-situ* PFAS degradation would require complex solutions, expensive equipment, and high specific operation costs due to trace amounts. The overarching goal of this research project is the design of a hybrid process for the removal and/or mineralization of per- and polyfluoroalkyl substances (PFAS) from water sources.

Therefore, two main factors have driven our decision to pursue the two concepts discussed in this report; one being simplicity of operation and efficacy for a wide concentration range, while the other was capability to remove very low concentrations of PFAS in the ng/L range with low operational costs.

Modularity, adaptability and economic feasibility are factors of great significance for this project and will be taken into consideration when performing Life Cycle Assessments (LCA) and calculating energy balances and operating costs. Outcomes of these assessments will greatly impact the final performance review of the discussed hybrid processes.

Pursued hybrid concepts

Through extensive literature review, we have identified two fundamentally different directions in which to conduct our research.

Ultrasonic degradation as a treatment method for membrane filtration concentrate – enrichment before treatment

Ultrasonic cavitation shows promise in literature for various applications, from improved synthesis (Gharat & Rathod, 2020) to in-situ degradation of pollutants in water (Cao et al., 2020). Regardless, real world applications are lacking. This is true mainly due to the fact that ultrasonic degradation requires a high energy input in order to operate. PFAS degradation occurs efficiently only at high specific energy input ($>300\text{W/L}$ of water)(Vecitis et al., 2008), as this energy directly affects the energy of bubble collapse and therefore the generated thermal energy at the bubble collapse sites. Due to high thermal stability of PFAS, the challenge is to find a golden middle between high energy input and efficient degradation of pollutants, both time- and energy-wise.

This is where the idea of a filtration-sonication hybrid system comes to focus. Filtration is a sure way of removing most moieties from water via size exclusion. However, the main argument against using these processes is that the remaining concentrate still carries the undesired compounds, and leaves us with a disposal issue. As the input energy of ultrasonic degradation depends on water volume rather than the PFAS concentration in the water, it is an ideal opportunity to employ the strengths of both processes while reducing the effect of the mentioned drawbacks.

Since filtration is already a well-studied and understood process, the accent of this project is to research and explore how different sound frequencies and energy densities affect PFAS degradation, before attempting to optimize this process through reactor design and operational parameters (e.g., hydrostatic pressure which is hypothesized to increase the energy of bubble collapse and could thus reduce the required specific energy input for efficient degradation). Ideally, we wish to achieve high enough collapse energy in order to accomplish complete destruction of the pollutant, which highly depends on the bubble collapse energy. The collapse energy in turn directly depends on sound frequency and energy density of the system.

As the regulations being put in place both in Europe and USA discuss sum amounts of PFAS present in a water sample, it is of paramount importance to optimize this process in order to achieve complete mineralization of the pollutants, rather than generate a variety of intermediate products, which has been shown to happen in preliminary studies at less-than-ideal operational conditions.

Adsorption using target-specific tailored adsorbents as a post treatment step for biological processes

Adsorption is known to be a low input energy process with high efficacy at very low concentrations when the adsorbent is selected carefully. However, as PFAS are a group of >5,000 different compounds, all with different properties and structures, traditional adsorbents show varying success when it comes to PFAS removal (Zhang et al., 2019), in most cases underwhelming. Currently employed solution in treatment facilities are filter beds using granular activated carbon (GAC)(Kim et al., 2020). GAC shows satisfactory success at removing longer chain PFAS due to their large hydrophobic tail. However, the shorter the PFAS carbon chain, the more polar these compounds get, and shorter chain PFAS cannot be ignored. They too are a health hazard with unknown consequences on human health at high exposure, and are to be equally regulated with the upcoming water safety directives.

From the aforementioned, the need for novel materials engineered to the specific needs of PFAS adsorption is clear.

Through the expertise of the ESR and the project collaboration partner, we aim to identify trends in behavior through a fundamental study of materials from the family of metal-organic frameworks (MOFs). By studying structural effects (by testing isostructural MOFs shoulder to shoulder) and post-synthesis modifications, be it modification of starting materials or by creating hierarchical composites, we are hoping to establish patterns in behavior and pioneer the field of tailored, highly-stable adsorbents for PFAS removal at trace concentrations.

In order to achieve this goal, priority in design needs to be given to achieving high selectivity towards PFAS, high capacity for adsorption and thus large treated volumes of contaminated water and above all, extraordinary stability of the adsorbent structure both towards water and towards potential regeneration solvents.

We aim to eliminate competitive adsorption as a factor through careful modification and alteration of the nanomaterial surface chemistry and structure, by using the porosity of the material in our favor, employing it as a molecular sieve and thus not allowing penetration of larger molecules in water to the adsorption sites. The surface chemistry on the other hand would work in our favor by accenting the interactions between PFAS molecules and grafted functional groups on the pore surface. With such a designed material, a welcome side-effect of high selectivity towards PFAS would result in the ability to treat large volumes of water before the need to replace the material arises.

The biggest obstacle in such a hypothetical material being used as a standard adsorbent for PFAS removal is high production cost. Even though operational costs of an adsorption system are nominal, procurement of fresh adsorbent and disposal of saturated adsorbent are significant. This is why we set regenerability of the adsorbent as our second major goal in this project.

Putting these materials to use as a post-treatment step for a biological process which has low to no capability to degrade PFAS will ensure very large treatment volumes between regeneration steps and additionally reduce matrix impact on the material performance by focusing on the removal of only recalcitrant PFAS present in the biological treatment step effluent.

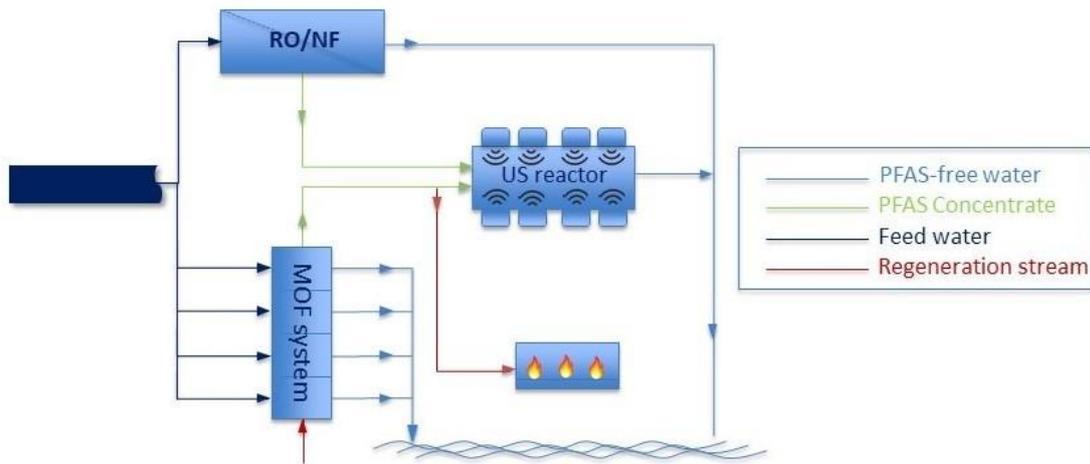


Figure 1 – Schematic representation of the hybrid concepts explored within this project effort

Current progress and outlook

Report on ultrasonic degradation treatment

Due to a lack of consistency in the reporting found in available literature, it is of paramount importance to establish trends on how basic operational parameters affect PFAS degradation. The initial conclusion based on literature was that reactor geometry played a significant role in soundwave propagation (Johansson et al., 2017) and consequently PFAS degradation. Additionally, higher frequencies have proven to be more efficient at degrading PFAS (Cao et al., 2020).

For this reason, the initial effort was to source a reactor that had direct contact between the transducer and the treated solution in order to minimize energy losses and provide consistent data on frequency effect. Finding such a reactor fabricated with a high frequency transducer proved to be a challenge with only a few companies around the globe being able to procure such a setup. As this phase of the project is supposed to provide us with preliminary information on which to build further and design a larger scale system, we reached out and established a collaboration with the Center for Energy and Environmental Chemistry at the University of Jena, which was already in possession of such a system.

The transducer unit represented in gray color on Figure 2 can resonate at different frequencies (375, 580, 858 and 1138kHz), covering the range of frequencies which includes all optimal degradation frequencies reported in literature.

With this reactor setup we are able to perform an array of tests focusing on operational parameters in order to establish the optimal conditions for PFAS degradation. As we are looking into three different PFAS (i.e., PFOA, PFOS, GenX), we need to perform a separate experimental set for each of the PFAS individually using synthetic water samples in order to eliminate possible matrix effect interference.

Until now, only degradation of PFOA has been assessed. Each of the four frequencies is operated for the duration of 120 minutes at three different power densities (200, 300 and 400 W/L) in order to have a clear image of how degradation is affected by frequency.

Our sampling times during these experiments are 0, 10, 20, 30, 45, 60, 75, 90 and 120 minutes. At these intervals we sample a small volume of the solution in order to later quantify the amount of PFAS present via LC/MS-MS. As we have recently obtained an ion selective electrode, we aim to in future experiments also quantify amount of fluoride ions present in the solution at every sample time as the amount of present fluoride is a direct indicator of mineralization of PFAS. For the experimental results presented here however, fluoride content was only measured after the experiment was completed (i.e. after 120 minutes) since fluoride

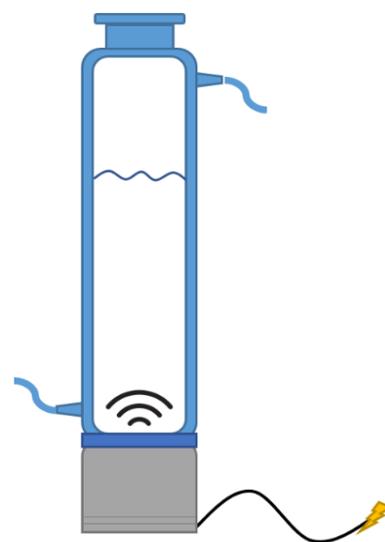


Figure 2 – lab scale ultrasound reactor layout

quantification using ion chromatography requires sample volumes that we were not able to procure for every data.

Two observations can be made from the data obtained so far. Firstly, degradation efficiency increases with increase in power density with each frequency. Secondly, there is a significant difference in performance between different frequencies that needs to be studied further.

The calculated degradation constant is taken from the linearized form of the first order kinetics equation:

$$\ln ([PFOA]_t / [PFOA]_0) = -kt \quad 1$$

Figures 3 and 4 represent an overview of results from the PFOA experimental series, where in Figure 3 we can see the linearization of degradation kinetics at 400 W.

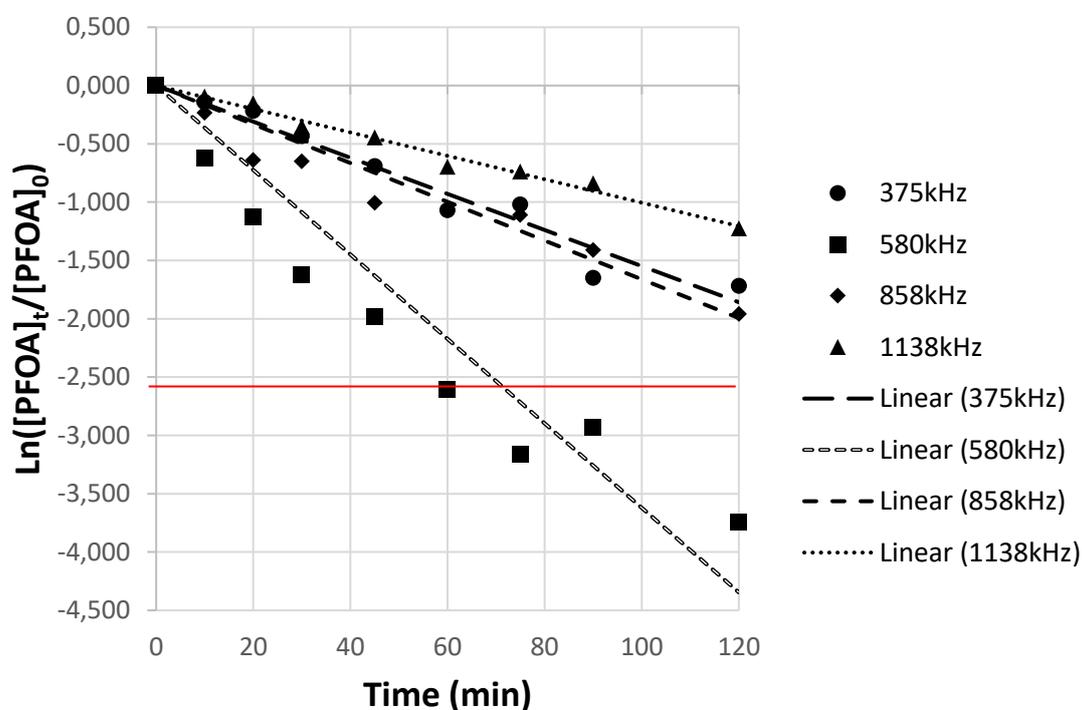


Figure 3 – Degradation kinetics at different frequencies of ultrasound at 400W/L. The red line represents 90% degradation

Data plots for 200 W and 300 W are not shown in this report but the rate constants are summarized in Table 1.

Table 1 – Overview of degradation constants at different frequencies and power densities, based on first order kinetics

Degradation constant, <i>k</i>	375kHz	580kHz	858kHz	1138kHz
200 W/L	0.0026	0.0140	0.0062	0.0067
300 W/L	0.0045	0.0204	0.0099	0.0082
400 W/L	0.0155	0.0362	0.0166	0.0100

In Figure 4, we can see a performance comparison between all power densities and frequencies. The percent of degradation was determined as a difference between concentration values at 0 and 120 minutes, and the mineralization is calculated as a percent amount of fluoride ions present in the solution compared to the theoretical maximum of fluoride ions if the initial concentration of PFOA was to be completely mineralized. From the provided graph we can see how important it is to conduct a study of frequency and power effect. At the best performing frequency of 580 kHz, we achieve higher degradation and mineralization of PFOA already at a power density input of 300 W/L than we do at highest power with other tested frequencies.

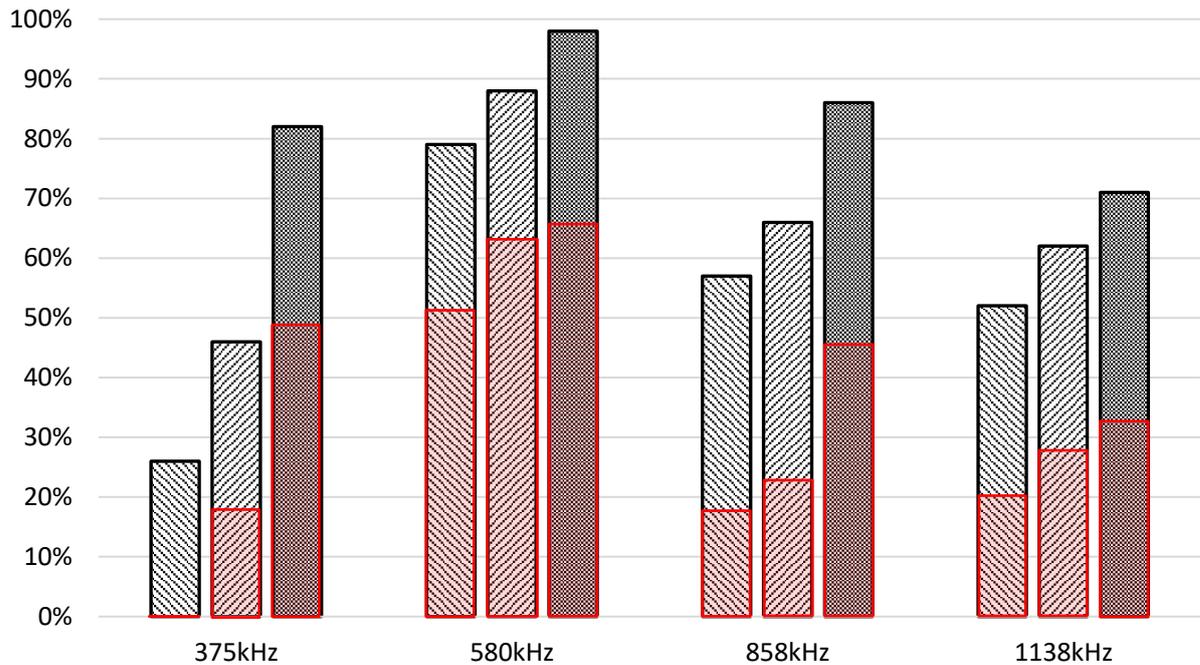


Figure 4 – degradation of PFOA after 120 minutes at the initial concentration of 1 mg/L. The degradation percentage is determined based on concentration difference between initial and final concentration of sample. The mineralization is determined by concentration of free fluoride ions in the final solution and weighing this against theoretically released fluoride calculated from initial concentration.

The study needs to be conducted for the remaining two PFAS before we can proceed with more detailed studies. Degradation efficiency at different frequencies has not yet been reported for the new generation PFAS known as GenX to the best of our knowledge.

After an optimal frequency is established for all three studied PFAS, all further experiments will be conducted only at the optimal frequency and power density. After these core parameters are established, we aim to start treating real filtration concentrate in batch phase in order to obtain information on matrix effects in nanofiltration concentrates, as we increase the concentration of most accompanying contaminants along with PFAS. Only then we can proceed towards designing a hybrid process combining nanofiltration and ultrasound as a solution for primarily industrial wastewater decontamination.

Report on fabrication of MOFs as target specific adsorbents for PFAS

As the currently used solution in water treatment plants is GAC, the first step in this study is to evaluate these benchmark materials for PFAS adsorption. Therefore, during the literature research period and discussions with our collaboration partner on the topic of hypotheses and research plan, we conducted initial experiments testing the adsorption kinetics and establishing isotherms of GAC.

This also proved to be the best approach to establish and test experimental protocols, as the experimental protocol had to be designed according to previous experience and limited literature information. Consequently, some values needed to be assumed and there were multiple iterations of experiments before we achieved satisfactory reproducibility. The effect of optimization can best be seen in Figure 5, where we demonstrate the difference before and after we reduced the solution volume, stirring speed, changed the sampling strategy to include immediate filtration of the sample and adjusted the sorbent loading to achieve 80% removal.

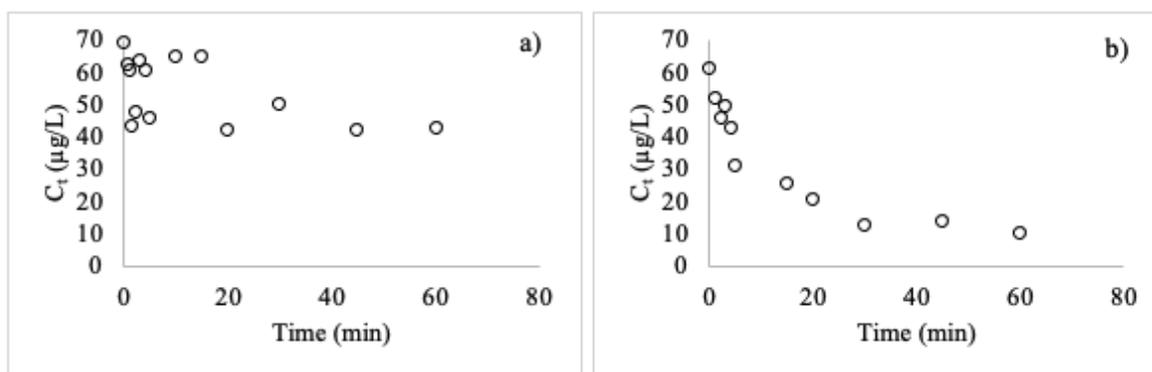


Figure 5 - PFOA ($[PFOA]_0 = 50 \mu\text{g/L}$) adsorption onto GAC over time, resulting from the a) original kinetics experimental design, and b) optimized kinetics experimental design

Additionally, isotherm experiments were conducted with high accuracy as can be seen in Figure 6. The values from the isotherms will be extracted and used as a baseline for comparison with the best performing MOF adsorbents.

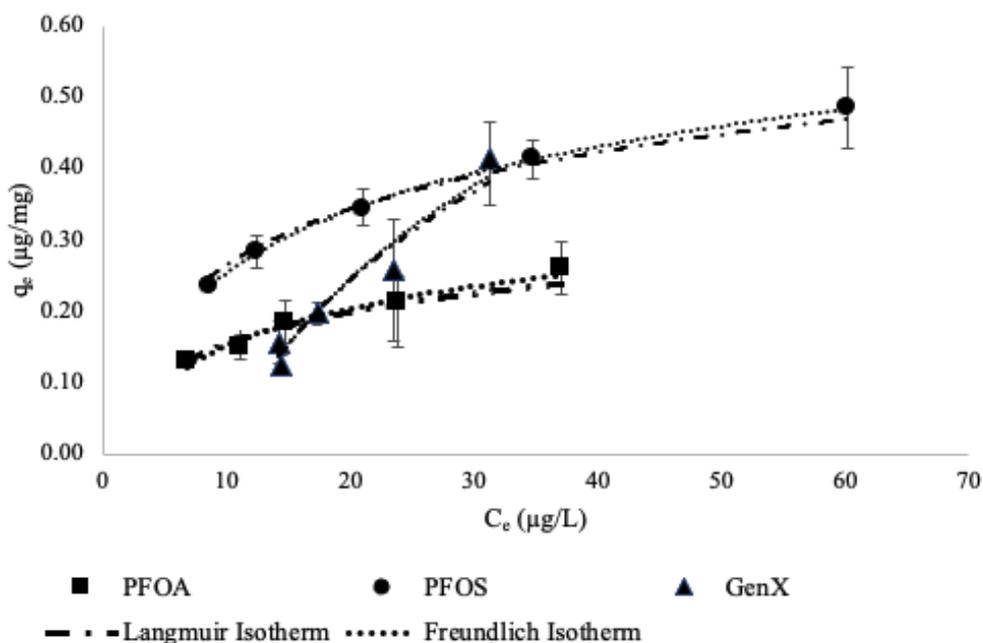


Figure 6 - Langmuir and Freundlich isotherms at 50 $\mu\text{g/L}$ with various GAC loading (2, 4, 6, 8, 10 mg) in 25 mL

In order to perform a detailed study of correlation between structure and performance when using MOFs as target-specific adsorbents, it was very important to carefully select the starting point on which we can build.

After careful consideration of literature, the family of UiO-66 MOFs was selected as a structure with high stability at a wide range of pH values as well as structural stability towards water. It is also a well-studied material with many synthesis approaches and therefore the capability of structural manipulation in order to reach our goal. To start the study, we decided to, alongside the regular UiO-66 MOF test three isostructural analogues, one already studied previously in literature for PFAS capture and two for which the performance is not reported in literature. While the regular UiO-66 MOF has hydrogen on the aromatic ring of the ligand and therefore on the outer surface and pore space, the three tested analogues have 1) an electron rich functional group (NO_2), 2) an electron deficient functional group (i.e. protonated NH_2), and 3) a hydrophobic surface where all hydrogen atoms were substituted for fluorine. The chemical structure of the ligands used can be seen side by side in Figure 7.

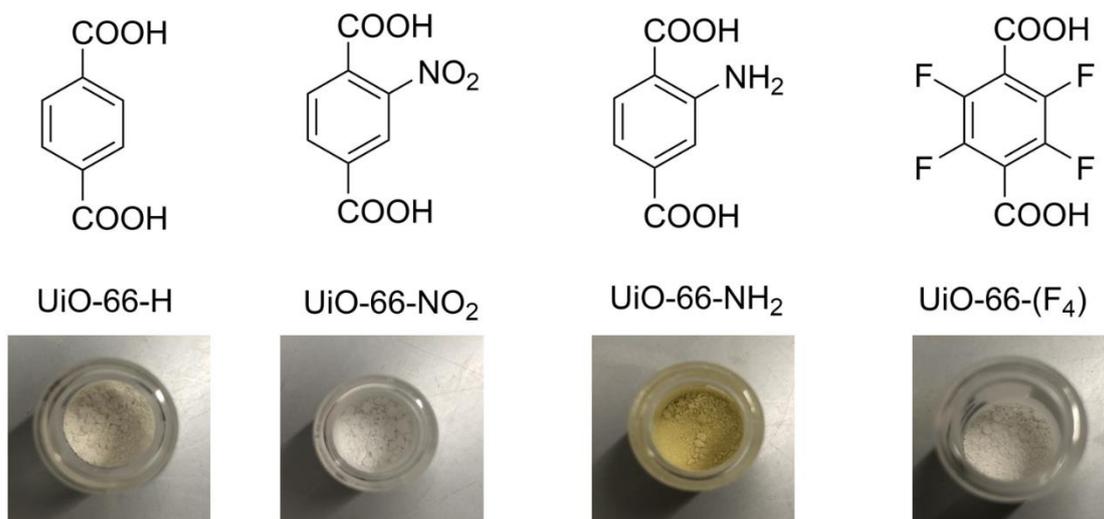


Figure 7 – Structure of used ligands for different UiO-66 materials and the corresponding MOF powder used for experiments

The initial experiments performed with UiO-66 MOFs produced data that were unreliable. Each of the batches within a single triplicate experiment would give data with significant variations. Both isotherms and kinetic tests were proving to be unreliable. Isotherm linearization was resulting in negative slope fits, an example of which can be seen in Figure 8 for UiO-66. Such an occurrence is impossible with isotherm data, indicating a significant error within the experimental setup. Kinetics experiments were showing inconsistency in removal values with significant fluctuation in concentration values and could therefore not be used for any planned modelling nor comparison of performance.

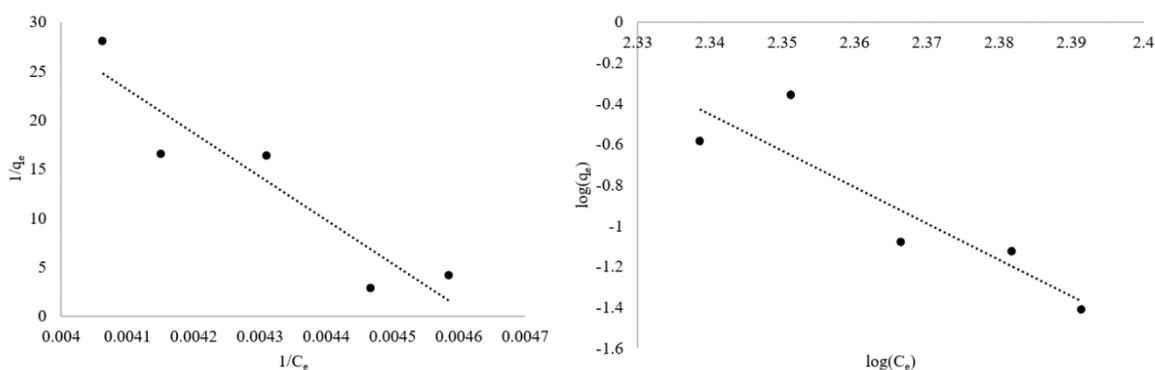


Figure 8 – Langmuir (left) and Freundlich (right) linearization of UiO-66 isotherm experimental data indicating issues in experimental design

Considering that these inconsistencies were occurring regardless of the experimental protocol optimization performed with GAC, we decided to look into the material preparation itself as the material was the only difference between the experiments. The conclusion was that the

activation under vacuum performed by our partners, followed by milling the materials in a mortar was not a satisfactory level of material preparation. We introduced an extra step of rehydration and assisted dispersion of materials by sonicating the ultrapure water containing the MOF for one full hour. After a visual confirmation that the suspension was without material clumps, we would spike our PFAS and mark this moment as our experiment initiation.

The new experimental design is showing very reliable reproducibility with values within a triplicate being close to identical. Further studies and experiments need to be performed in order to obtain a full picture of performance between the different MOFs, as the protocol confirmation was done with only one PFAS and with simplified removal experiments in order to reduce experimental cost and laboratory time. The new data is encouraging that all the issues have been removed from the experiments and that we can now proceed with a detailed study of material performance.

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