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**Dispersion Study of Metal-Organic Frameworks and Synthesis of MOF-
High-Density Polyethylene Fibers**

By

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DEDICATION

To my parents, Mr. Suresh Kumar Gondi and Mrs. Rajani Gondi, and my sister Ms. Srilikhita Gondi for their love and support throughout my life. I hope I make you proud.

To my friends who turned into my extended family, I will be grateful for the love and encouragement given by you.

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ABSTRACT

Dispersion Study of Metal-Organic Frameworks and Synthesis of MOF- High-Density Polyethylene Fibers

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Metal-Organic Frameworks (MOFs) are a highly versatile class of materials with a wide range of potential applications in gas storage, separation, catalysis, drug delivery, and sensing. The ability to tailor the properties and functionalities of MOFs by varying the organic linkers and inorganic nodes makes them highly attractive for a wide range of applications. The unique properties of MOFs also make them promising materials for fundamental studies in materials science and chemistry. The current investigation focuses on the dispersion study of MOFs and the synthesis of MOF-Polymer composites. The dispersions of MOFs in various organic solvents like ethanol, isopropanol, tetrahydrofuran, N-methyl-2-pyrrolidine, triethylene glycol, and acetone are studied and characterized using UV-Vis Spectroscopy to study the absorbance of the MOFs in the solvents and to determine the extent of dispersion in the solvents. Both the visual and spectroscopic studies showed similar results. Later the MOF-polymer composites are synthesized taking High-Density Polyethylene and are tested for the capture of CO₂.

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Chapter 1. Introduction

1.1 Metal-Organic Frameworks:

Metal-organic frameworks (MOFs) are a class of crystalline materials that consist of inorganic nodes, typically metal ions, or clusters, connected by organic linkers to form comprehensive frameworks with high surface area and tunable pore sizes. These materials have gained considerable attention recently due to their potential applications in gas storage, separation, catalysis, drug delivery, and sensing [1,2]. MOFs are highly porous materials, and the high porosity of MOFs is due to the presence of well-defined pores and channels within the framework that can be altered for specific applications.

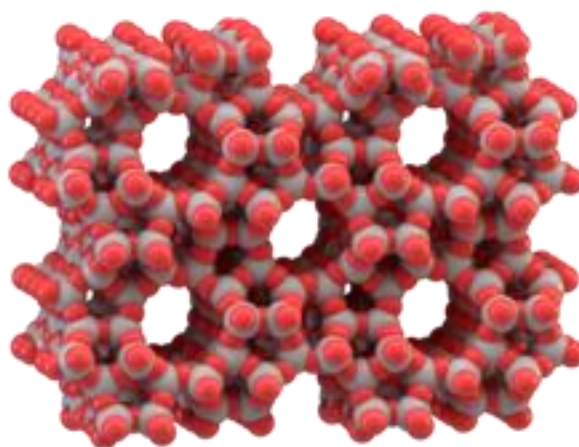


Figure-1.1 General Structure of MOFs

The organic linkers used in MOFs can be chosen from various functional groups, such as amine, carboxyl, or hydroxyl groups, which depends on the requirements of their chemical or physical properties, and the inorganic nodes can be chosen from a wide range of metals, including transition metals, lanthanides, and main-group metals. [3] This flexibility allows for the design of MOFs with a wide range of properties and functionalities.

One of MOFs most important applications is gas storage and separation. [4] MOFs have high selectivity and adsorption capacity for specific gases like hydrogen, methane, carbon dioxide, or nitrogen. This makes them attractive materials for gas storage and separation technologies, such as carbon capture and hydrogen storage. MOFs are also promising materials for drug delivery applications and Catalysis. [5]

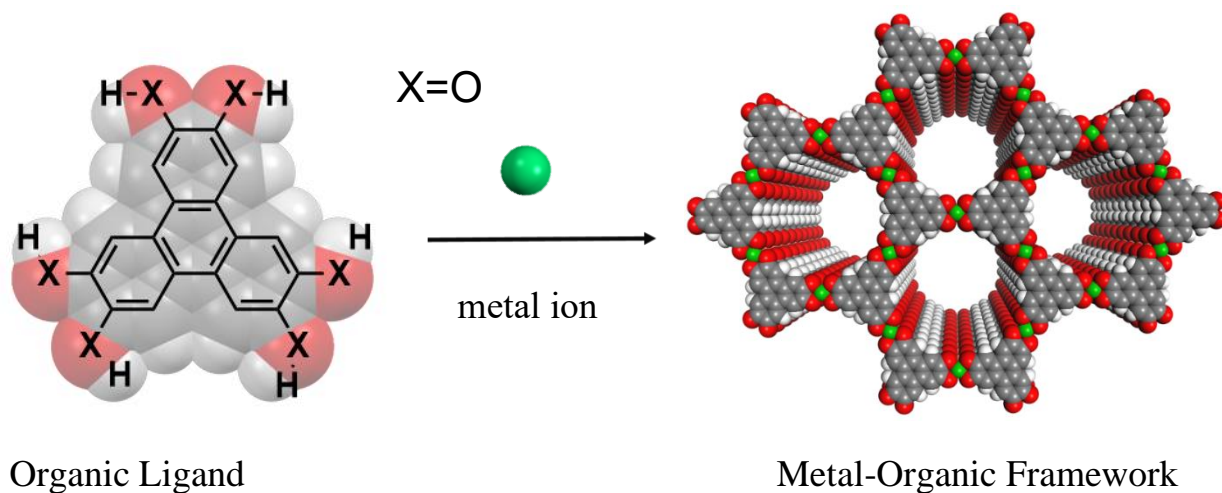


Figure-1.2 Typical method of formation of MOFs

The MOF that we currently use in our study is $M_3(\text{HHTP})_2$. Where **M** stands for metals that are Copper (Cu) and Nickel (Ni), and **HHTP** stands for the organic linker 2,3,6,7,10,11 hexahydroxy triphenylene. Below are the structures of the MOFs that we used.

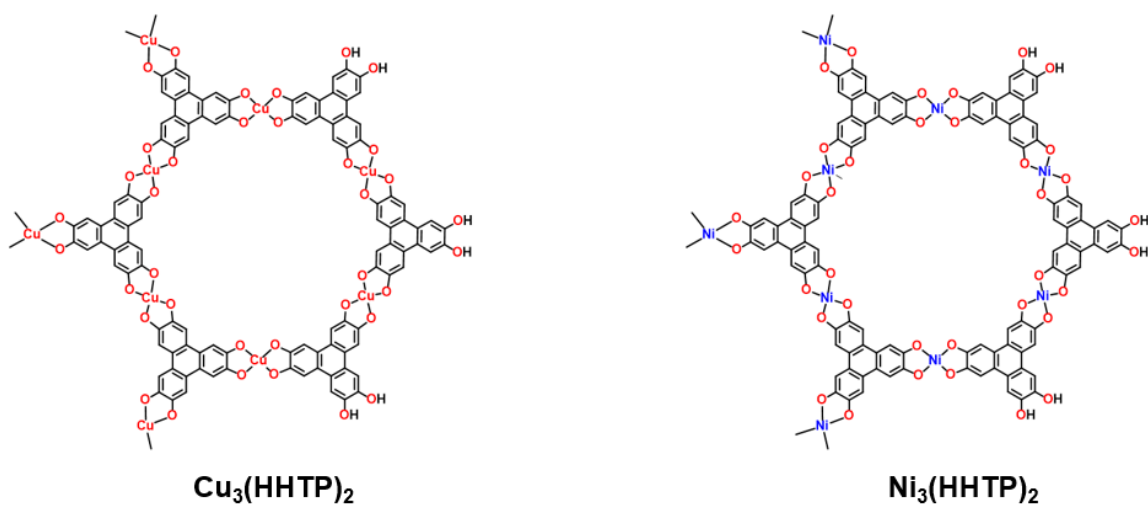


Figure-3.3 Structure of MOFs used for the research

1.2 High-Density Polyethylene (HDPE):

High-Density Polyethylene (HDPE) is a type of polyethylene, a common plastic material. It is a thermoplastic polymer widely used in food packaging, bottles, and other commercial containers because of its low cost and availability. HDPE is also known for its durability, strength, and chemical resistance. HDPE is also easy to reuse and recycle compared to many other polymers available for daily use. [6]



Figure-1.5 HDPE Pellets

HDPE is one of the forms of polymer Polyethylene that is used extensively. Some other types of Polyethylene that coexist are Low-Density Polyethylene (LDPE) and Ultra-High-Molecular weight polyethylene (UHMW-PE). The differences in their molecular structure, chemical, and physical properties make HDPE a more accessible polymer than the other forms of Polyethylene.

HDPE composites are also easy to synthesize because of their simple structure. The composites are widely used where we require high mechanical strength and electrical conductivity. HDPE composites are also making their way into bio-medical applications as they can increase the bio response of inorganic particles.

1.3 MOF-Polymer composites:

The MOFs are porous and primarily available in crystalline powder form, making them easily tunable. This tunability of MOFs paves the way for their applications [7], such as molecular separation, energy storage, catalysis, gas adsorption, luminescent sensing, drug delivery, etc. However, some practical applications could be improved by the nature of MOFs, as it is very easy to be crumbled. To overcome this disadvantage, MOFs are induced into the polymers so that the mechanical properties of the polymers are enhanced to the MOFs, and the resulting composites can be used for a wide range of applications.[8] MOFs in crystalline powder states have high pore density and high surface areas. Most of the pores being micropores results in less surface accessibility. The strategy for improving the accessibility to good surface area and flexible processing is adding polymers. Such modifications enhance existing properties or introduce new, non-native functionalities to the MOFs.

Chapter 2. Literature Review

2.1 Methods of Formation of MOF-Polymer Composites:

There are several methods to synthesize MOF-polymer composites, and the choice of technique often depends on the specific properties and applications of the resulting material. To date, many methods are used to synthesize MOF-Polymer composites. The most common ways include in situ polymerization, solution mixing, melt processing, and layer-by-layer assembly.

2.1.1 In situ polymerization: The first option is the polymerization in situ of monomers directly in MOF pores. Monomers may enter the pores via the gas or liquid phase [14,15]. After entering the pore, polymerization may be stimulated by thermal, light, or chemical catalysts or directly mediated reactions between the MOF structure and the monomer. The polymer formed can be stabilized within the MOF pores with a "ship in a bottle" method, in which the polymer chains could increase in size over the MOF pores and become stuck inside. Other times, polymers may be stabilized inside MOF pores via strong intermolecular interactions between the MOF walls and the guest species not native to MOF. This method allows linear polymers that have repeating units to be commonly made. Such in-situ polymerization processes have a variety of advantages and drawbacks. One of the benefits is that the MOF is pre-formed for the advantages, which means that the reactions can be applied to nearly every framework.



Figure -4.1 In-situ polymerization [16]

Additionally, the chosen reactions can be moderate, which is crucial when it comes to thermally or chemically unstable MOFs. Although in-situ polymerization reactions tend to be simple, there are negatives to be aware of. In the case of instance, the process may be difficult to regulate. Determining whether the monomers have dissolved homogeneously across the entire MOF template is impossible. Therefore, in-situ polymerization may result in inhomogeneities of the final composite. In some instances, polymerization reactions may occur primarily at the MOF surface, thereby blocking the pores. Additionally, it is essential to consider whether the selected MOF is compatible with the initiator or other chemical species used for in-situ polymerization. If the two components are incompatible, MOF decomposition could occur due to the reacting nature of the initiator.

2.1.2 Solution Mixing: The process of solution mixing is dissolving both the MOF and polymer MOF particles using the same solvent. This is a crucial step as the choice of the suitable solvent will significantly affect the dispersion and distribution of MOFs in the matrix of the polymer. After creating this mix the mixture is either made into a mold [17] or extruded for the desired product.

After that, the solvent is then evaporated. This process, usually accomplished by heating or vacuum, forms the mixture, creating the MOF-polymer mixture. The main benefit of this process is its simplicity, and it is a good choice for various polymers, comprising thermosetting as well as thermoplastic polymers.

Even with these advantages, there are many issues that come with this technique. The most significant challenge is to ensure that MOF particles are distributed evenly particles in the polymer matrix. This is essential to ensure homogeneous properties in this composite. If MOF particles and the polymer have different affinities for the solvent [18] or for each other, the MOF particle could aggregate, resulting in an uneven distribution within the finished composite. Additionally, the choice of solvent may also affect the structure and function of the MOF.

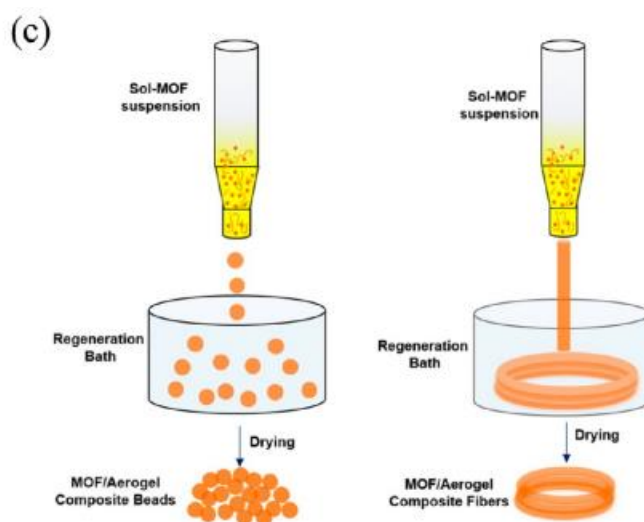


Figure -2.2 Solution Mixing

It is, therefore, crucial to consider the selection of MOF and solvent while using the technique of mixing solution to create MOF-polymer composites. Making these choices the best ones will allow you to solve the problems that this technique presents and facilitate the creation of composites with the desired properties.

2.1.3 Melt processing: The melt processing process is used for making MOF-polymer composites. This method combines MOF particles and a polymer that is in its melting state. Methods for accomplishing this include melting, blending, or extrusion. When the pieces are equally distributed throughout the mix, then it cools and forms into a composite.

The technique is highly flexible and adaptable, which makes it an ideal choice for large-scale industrial applications. This technique is particularly effective when using thermoplastic polymers which can stand up to the extremely high temperatures necessary to melt without experiencing chemical modifications.[20]

One of the significant drawbacks of this method is the limited selection of MOFs. There are a few MOFs that will withstand the intense temperatures that melt processing requires. [21] MOFs need to have high thermal stability, as well as not degrade or lose structure when processing temperatures rise. The careful choice of MOF as well as the polymer, is vital for this process to guarantee the durability and quality of the final MOF-polymer blend.

These challenges extend to creating a uniform distribution of MOF particles in the polymer matrix as MOFs are prone to aggregate when processing melts. It is essential to take care to ensure an even distribution of MOFs, to maintain that the intended properties are maintained in the composite. Despite the challenges melting processing is an attractive method to create MOF-polymer composites. This is particularly true to use the properties inherent in thermoplastic polymers.

2.1.4 Layer-by-layer assembly: This technique involves the alternating deposition of MOF particles and a polymer on a substrate, forming a multilayered composite. The deposit can be achieved through various methods, [22] such as spin, dip, or spray. The layer-by-layer assembly allows precise control over the composite structure and the MOF-polymer interactions. This method can be applied to thermoplastic and thermosetting polymers and MOFs with different particle sizes and shapes. However, scaling up this method for large-scale applications may take time and effort.

Chapter 3. Experimental Methods

3.1 Dispersion study of MOFs:

The study of MOF dispersion in organic solvents is crucial for several reasons, as it provides valuable information regarding the stability, processability, and potential applications of MOFs. Some of the critical reasons for investigating MOF dispersion in organic solvents are:

3.1.1. Stability assessment: Studying the dispersion of MOFs in organic solvents can reveal information about their chemical stability in various solvent environments. MOFs can be sensitive to specific solvents, which might cause structural degradation, reduced porosity, or loss of functionality. Understanding the dispersion behavior of MOFs in organic solvents can help identify suitable solvents for specific MOFs, ensuring their stability during synthesis, processing, and applications.[9]

3.1.2. Processability: The dispersion of MOFs in organic solvents is essential for their processability. A good distribution of MOF particles in a solvent is necessary to prepare MOF-based materials, such as films, coatings, or mixed-matrix membranes. [9] Homogeneous dispersion ensures uniform distribution of MOF particles in the final material, leading to consistent and optimal performance. In addition, the choice of solvent can significantly influence the processing method and the resulting material properties, such as viscosity, adhesion, or film formation.

3.1.3. Composite material synthesis: The investigation of MOF dispersion in organic solvents is particularly important when preparing MOF-polymer composites. [10] As discussed earlier, combining MOFs and polymers can lead to materials with enhanced properties and a more

comprehensive range of applications. Understanding the dispersion of MOFs in a solvent is vital to ensure compatibility between the MOF and the polymer matrix, resulting in a homogeneous composite material with strong interfacial interactions and improved overall performance.

3.1.4. Solvent selection for applications: The dispersion of MOFs in organic solvents is also relevant for specific applications, such as catalysis, gas adsorption, or drug delivery. In some cases, the choice of solvent can influence the adsorption capacity, catalytic activity, or drug-release behavior of MOFs. Studying the dispersion behavior of MOFs in various solvents can help identify optimal solvent systems for specific applications, ensuring the best performance and stability of the MOFs.[11]

3.1.5. Fundamental understanding: Investigating the dispersion of MOFs in organic solvents contributes to a better understanding of their interactions with different solvents and the underlying factors that govern their dispersion behavior. This knowledge can provide insights into MOF design and synthesis, paving the way for developing novel MOFs with tailored properties and improved application performance.

The dispersions of MOFs in various organic solvents are studied. Firstly, to prepare the samples for dispersion, we took 5mg of MOF and added 10 ml of the solvent. This mixture is then sonicated in the bath sonicator for about 20 minutes and then kept aside to allow the dispersions to settle. We ensured they were not disturbed for about four weeks to observe the stability of MOF in various solvents. [19]

The solvents chosen for this study are distilled water, ethanol, isopropanol, triethylene glycol, acetone, N-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF). The MOFs that are used for the study are $\text{Cu}_3(\text{HHTP})_2$ and $\text{Ni}_3(\text{HHTP})_2$. These dispersions are visually observed and then tested using UV-Vis Spectroscopy.

3.2 Formation of MOF gel:

To prepare the MOF-polymer composites the initial approach was to use techniques like the solution mixing and melt processing. However, to overcome the disadvantages of both techniques in this research, we prepared the gel with Metal-organic frameworks first. Then we tried to extrude the composite fibers using the twin screw extruder.

In this research, we tried to minimize the use of chemicals so that the structure and functionality of MOF don't change. In the first trial, we tried using ethanol and adding distilled water to make the gel. It didn't go as expected. Later, we tried many ways, like using Aloe vera to form the gel. We tried using aloe vera because it has that viscous nature and because it is biodegradable, and when heated to high temperatures, it can quickly be evaporated and also it doesn't have any chemical reactivity. Even this didn't go as expected.

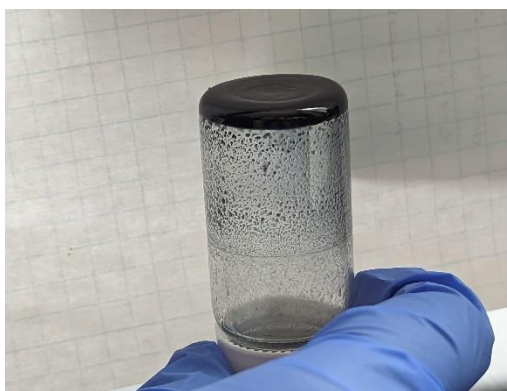


Figure-3.1 Formation of MOF gel

After so many trials, we finally managed to form the gel by adding very little amount of the gelatin. We dissolved about 0.5 mg of gelatin in about 5 ml of hot water and allowed it to dissolve at 60°C and then added it to the MOF dispersed in the isopropanol. This mixture is properly mixed allowed to cool for about 2 minutes and is used immediately after preparation.

3.3 Extrusion of MOF-HDPE fibers:

3.3.1 Methodology: The $\text{Cu}_3(\text{HHTP})_2$ -HDPE microfibers are synthesized using an MC5 Xplore twin-screw extruder and a Fiber Line Winder Setup. The HDPE pellets are fed into the extruder with optimal processing parameters once the fibers are extruded and pulled using the winder at a constant speed.

3.3.2 Twin screw extruder:

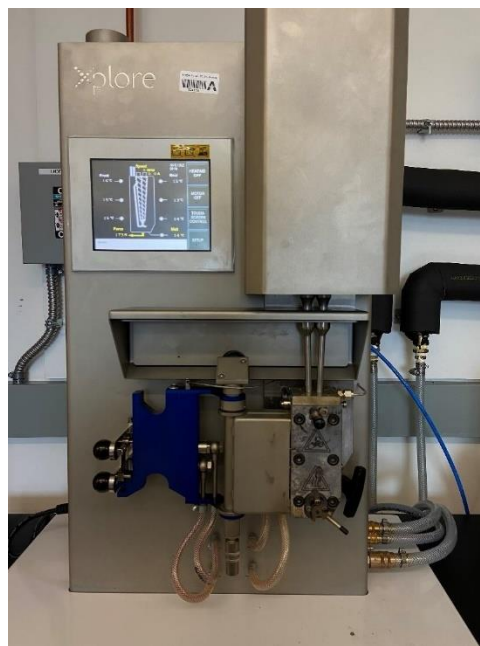


Figure-3.2 Twin Screw Extruder

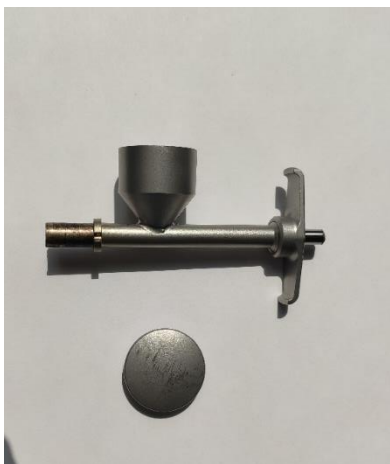


Figure-3.3 Feed Hopper

It is a vertical twin-screw compounder manufactured with Xplore instruments. The maximum capacity of the extruder is 5 cm³. Materials are fed into the extruder in pellets made of the polymer through the inlet. The extruder regulates the temperature and motor speeds needed to make the best extrusion. There are three heating zones situated on the barrel of the extruder. They provide perfect control of the temperature at which processing occurs. [26] Twin screws give greater torque, allowing uniform mixing inside the extruder. Good mixing speeds up processing duration. The extruder comes with two dies with 0.5-millimeter and 2-millimeter diameters. The melt of the polymer is released as filaments. Polymers that have a melting temperature that is up to 400 degrees can be extruded. Extruders have an air-cooling system and a water-cooling bracket that provides an adequate cooling system once extrusion is completed. The image shows the MC 5 extruder used to perform extrusions in a research lab.

3.3.3 Fiber Winding Unit: The winding unit was designed to gather small amounts of filament-like materials in conjunction with an extrusion device. The winding unit serves to extend and stretch the filament-like material created. Fiber lines allow you to get long, continuous fibers with less than 5-10 grams of material supplied to the extruder. The Winding unit is comprised of a godet as well as an uptake roll. The group consists of a godet that is [27] controlled by speed and an uptake roller. It is then employed to determine the size of the filament. The unit is cooled by air. the unit to make it function properly. The image below illustrates the fiber winding device that is present within the laboratory.

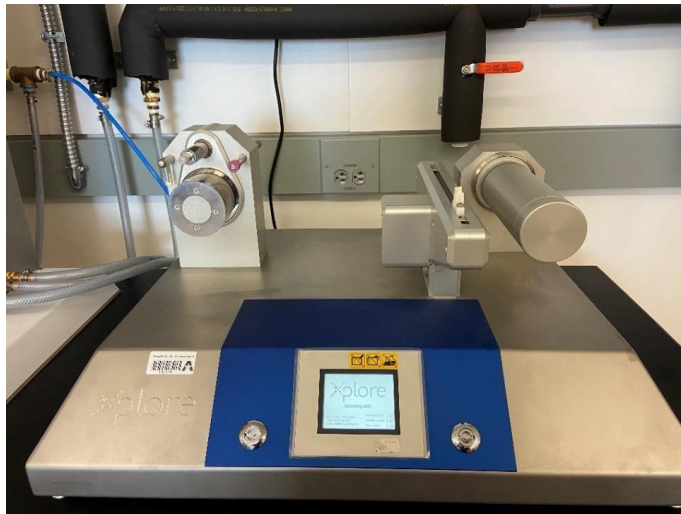


Figure-3.4 Fiber Winding Unit

Chapter 4. Results and Discussions

4.1. Analysis of MOF dispersions:

4.1.1. Visual observations:

MOF Dispersions can settle for about four weeks, and the vials are observed for stability.

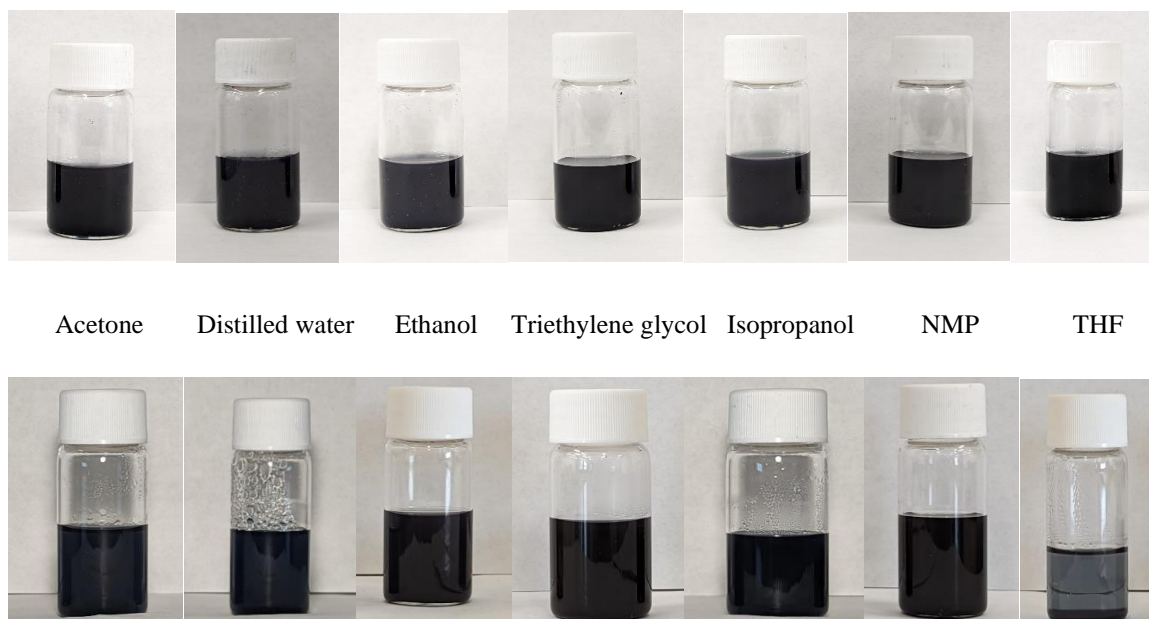


Figure-4.1 Cu_3HHTP_2 MOF in acetone, distilled water, ethanol, triethylene glycol, isopropanol, *N*-methyl-2-pyrrolidone(NMP), and tetrahydrofuran (THF) immediately after sonification(on top) and after four weeks of sonification (on bottom)

The dispersions of metal-organic frameworks in the solvents are kept aside for about 4 weeks and the images were taken frequently as we tried to notice if there are any changes in the stability. The Cu-MOF didn't show any differences in the solvents except for the (THF) Tetrahydrofuran. In all the other taken solvents, the MOF is very stable from the time it is sonicated. The long-term stability of MOFs in these solvents was studied and it can be concluded that the metal-organic framework that we have taken for this study showed long-term stability in acetone, distilled water, ethanol, isopropanol, tri ethylene

glycol are more stable than NMP. It is well dispersed but there are very few particles that are settled at the bottom of the vial. While the Ni-MOF exhibited long-term stability in acetone, distilled water, triethylene glycol, and isopropanol. The Ni-MOF got settled in the first 5 days in the case of ethanol. In NMP and THF, the Ni-MOF didn't show any suitable dispersions from the start. The MOF suspensions were cloudy after day 1 and are settled by day 2. Hence there's no stability in these solvents for the taken MOF.

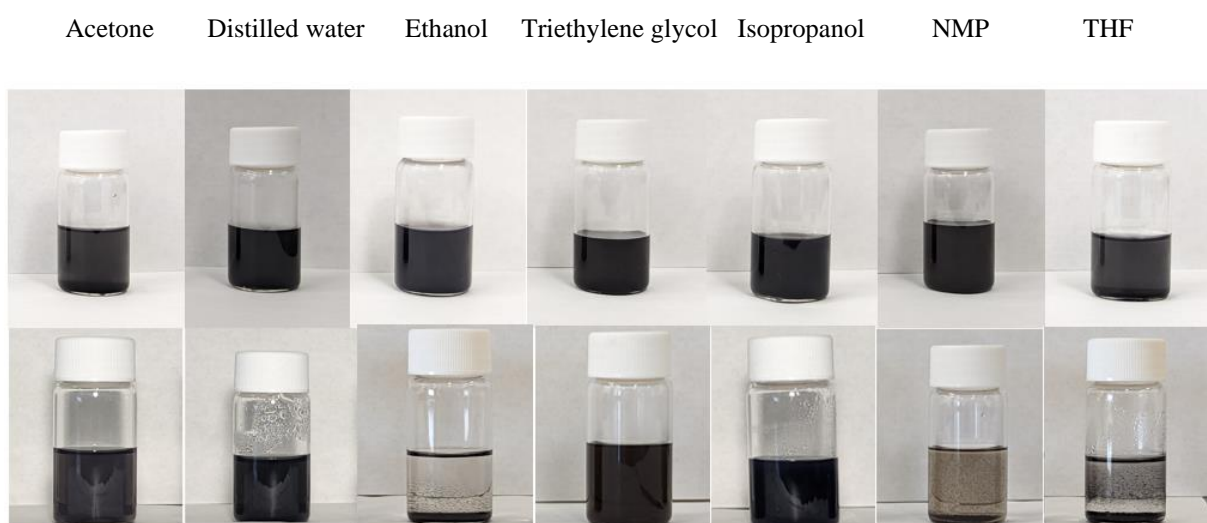


Figure-4.2 Ni₃HHTP₂ MOF in acetone, distilled water, ethanol, triethylene glycol, isopropanol, N-methyl-2-pyrrolidone(NMP), and tetrahydrofuran (THF) immediately after sonification(on top) and after four weeks of sonification (on bottom)

4.1.2. UV-Vis Spectroscopy:

Ultraviolet-visible (UV-Vis) spectroscopy is a type of spectroscopy that utilizes light in the visible and ultraviolet regions of the electromagnetic spectrum. This technique is often used to measure the absorption of light by a sample and to determine the absorptivity of the sample. Here for this research, we used LAMDA 35 UV-Vis spectroscopy.



Figure-4.3 LAMDA 35 UV-Vis Spectroscopy



Figure-4.4 Sample slot

The dispersions were analyzed using the UV-Vis to determine the absorptivity, and the results were noted, plotted, and shown below. The spectra were plotted based on the solvents and the MOF along with the baseline.

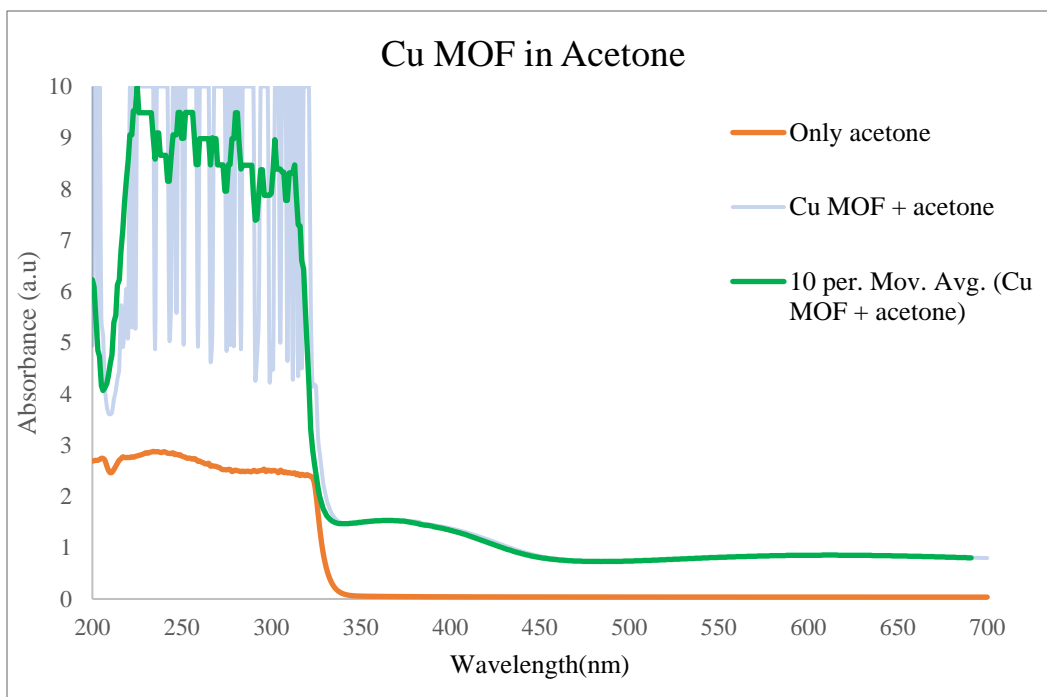


Figure-4.5 UV-Vis Spectra of Cu-MOF in Acetone

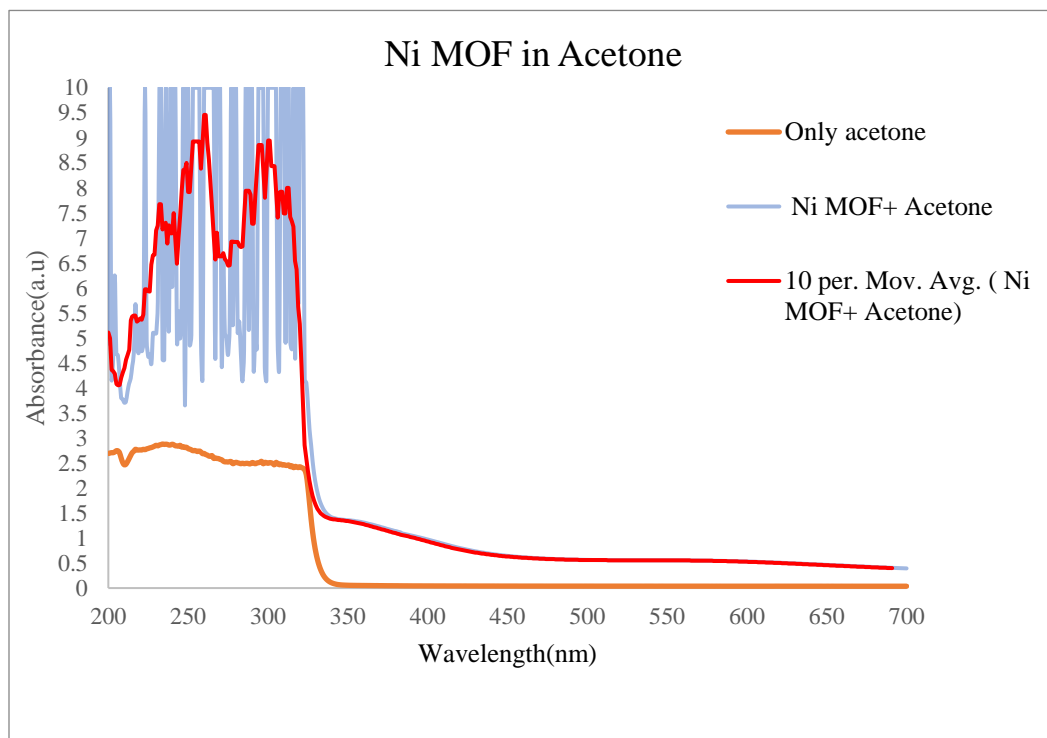


Figure-4.6 UV-Vis Spectra of Ni-MOF in Acetone

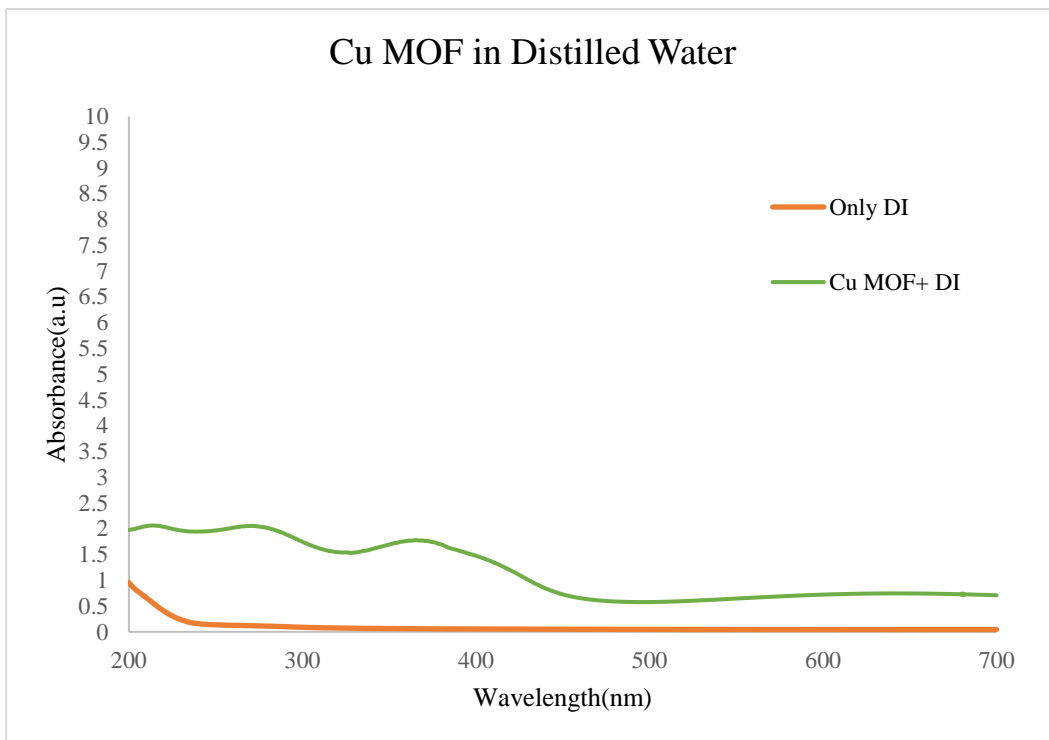


Figure-4.7 UV-Vis Spectra of Cu-MOF in Distilled water

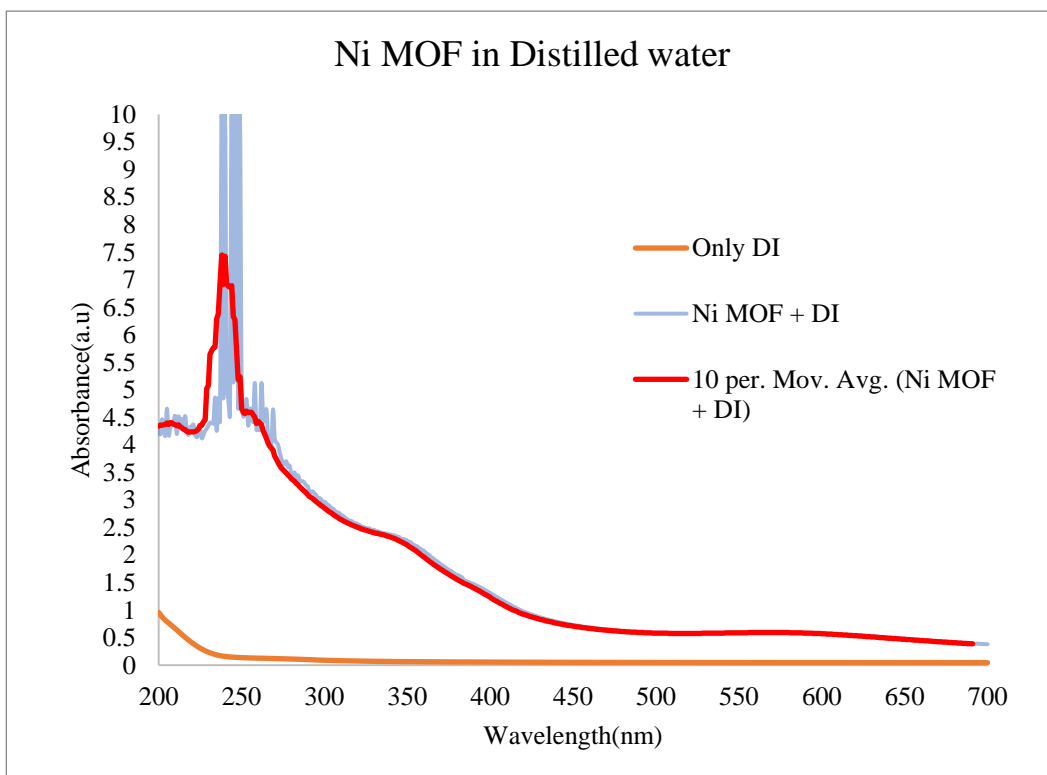


Figure-4.8 UV-Vis Spectra of Ni-MOF in Distilled water

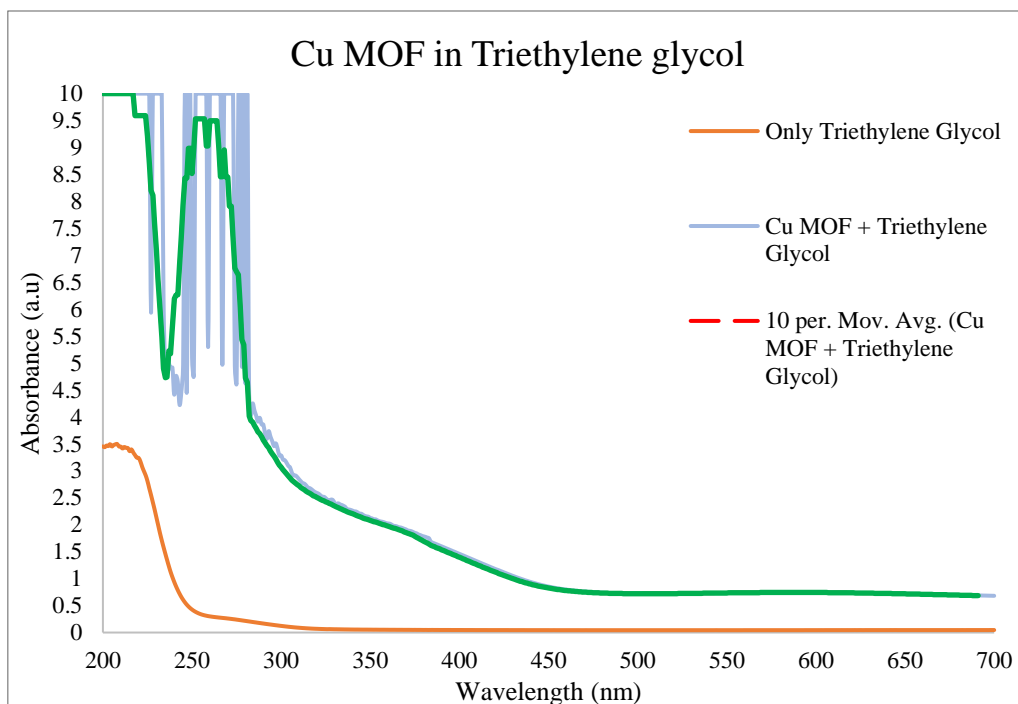


Figure-4.9 UV-Vis Spectra of Cu-MOF in Triethylene glycol

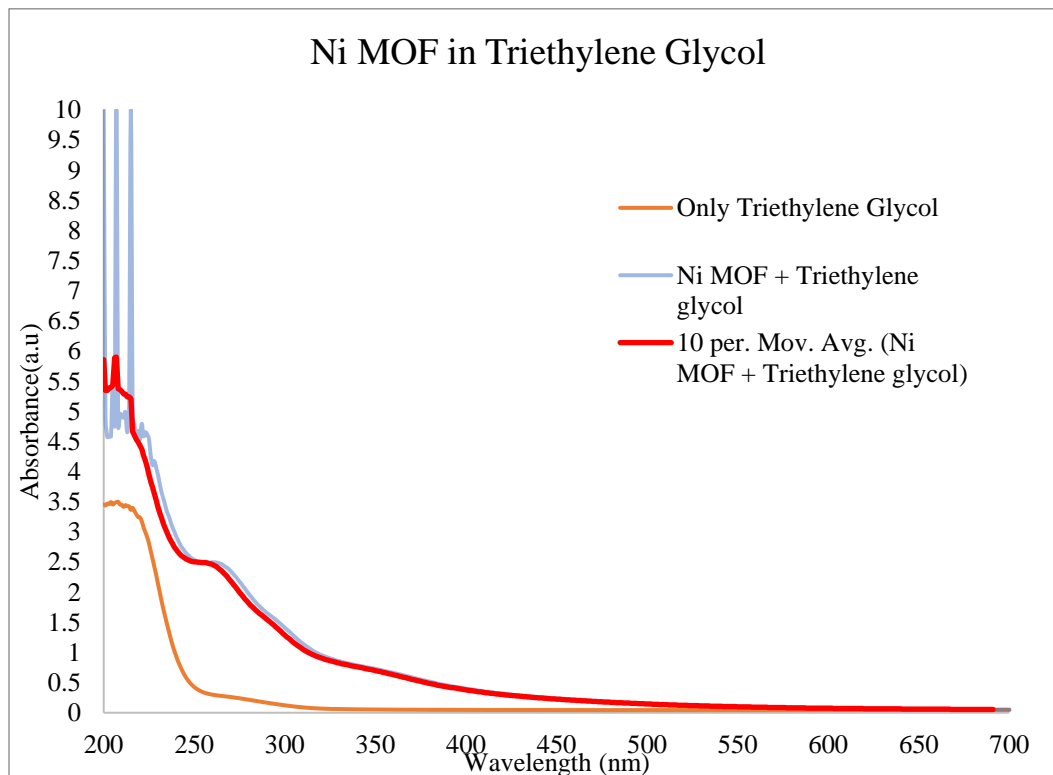


Figure-4.10 UV-Vis Spectra of Ni-MOF in Triethylene glycol

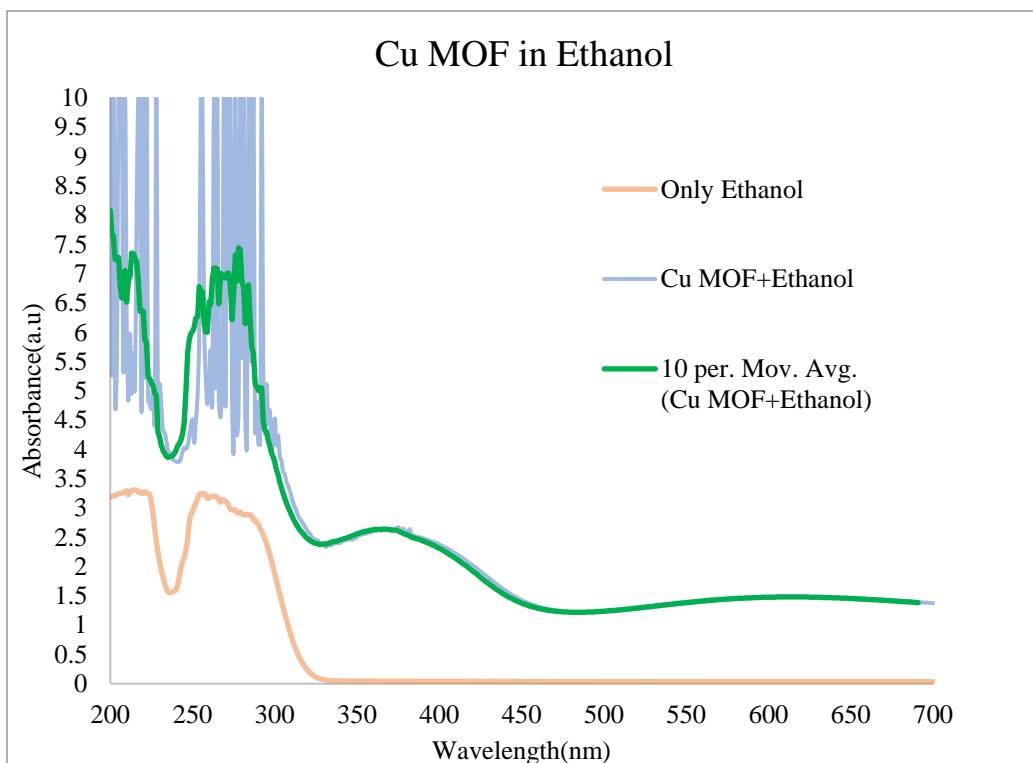


Figure-4.11 UV-Vis Spectra of Cu-MOF in Ethanol

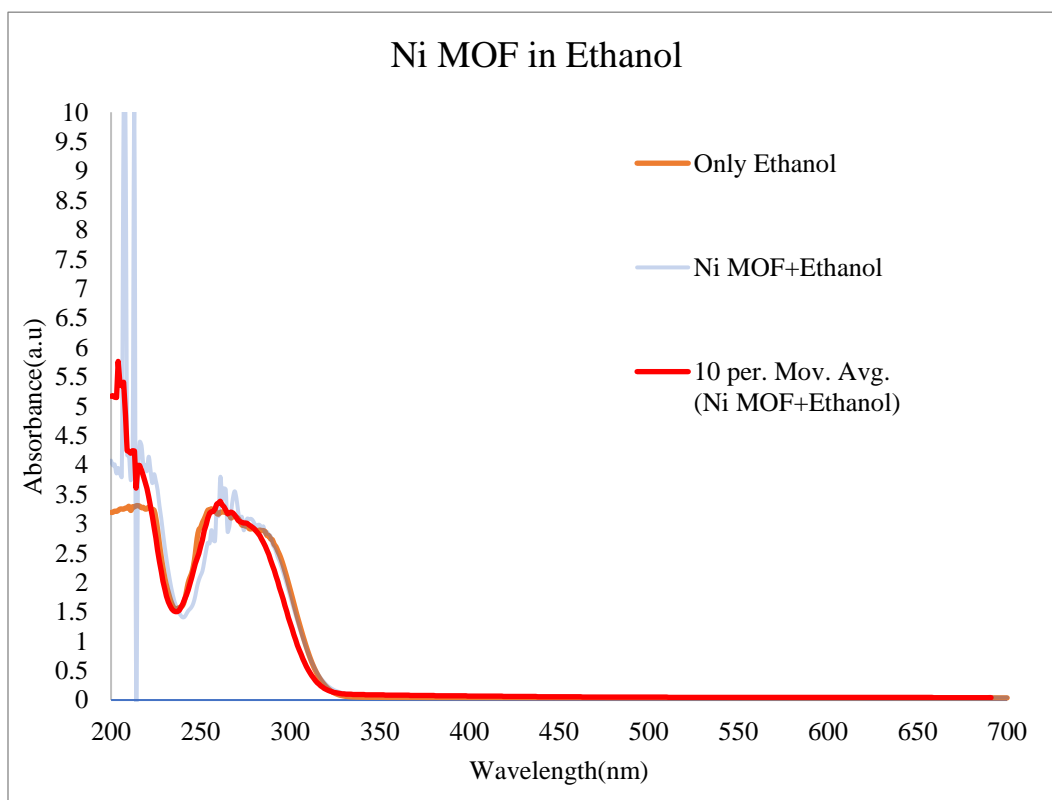


Figure-4.12 UV-Vis Spectra of Ni-MOF in Ethanol

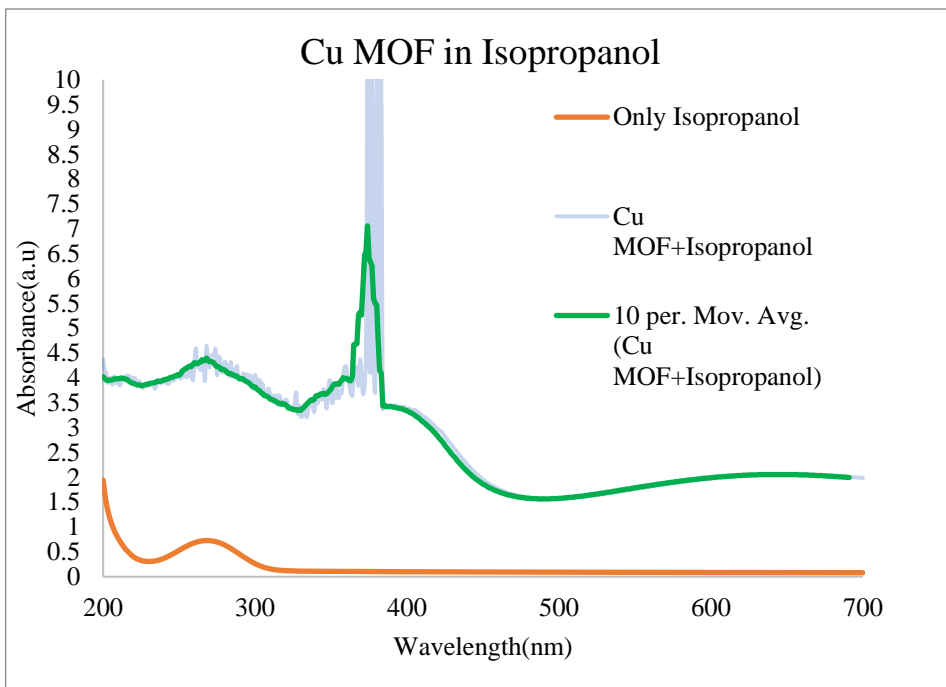


Figure-4.13 UV-Vis Spectra of Cu-MOF in Isopropanol

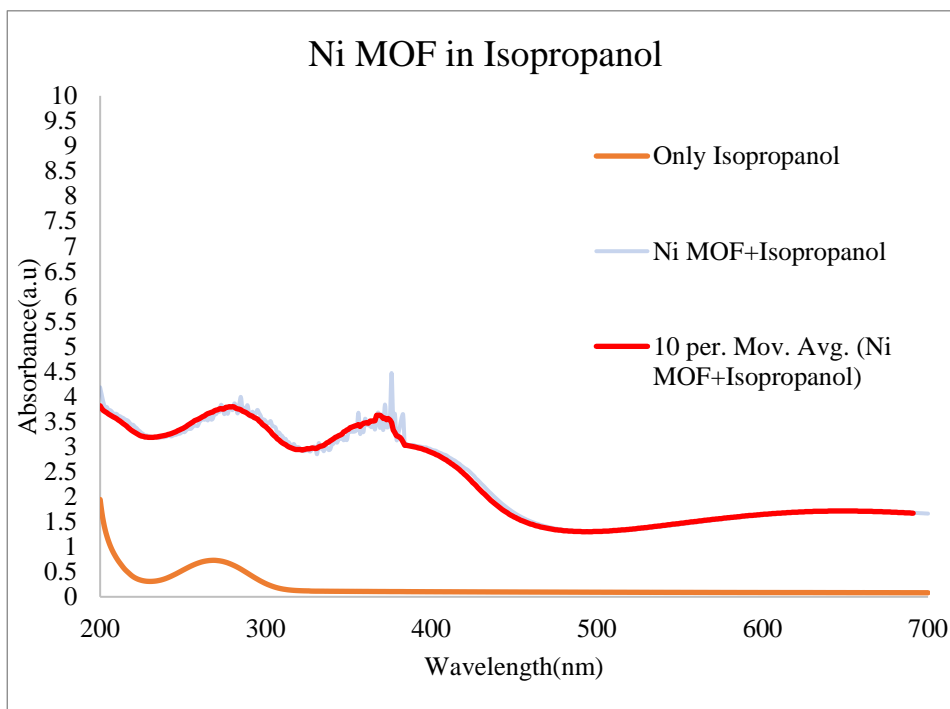


Figure-4.14 UV-Vis Spectra of Ni-MOF in Isopropanol

If we observe the spectra that are plotted, we can find the absorbance of the solvent and also the presence of metal-organic frameworks in it. The spectra are plotted in such a way that we take the moving average for every ten readings. In each of the spectra, we compared the behavior with respect to the solvent and analyzed the spectra. For instance, if we take the spectra with acetone, both Cu and Ni MOFs are well dispersed and the absorbance of energy from the light clearly depicts the same. In the case of Tetrahydrofuran, if we look at the spectra it is clear that there is no absorbance at all and the spectra with the presence of MOFs is similar to that of the solvent. Mostly all the solvents followed a similar trend in the absorption spectra. In the case of ethanol, we can clearly see that Cu-MOF is well dispersed and Ni-MOF doesn't show much dispersion in the spectra, and this is what even the visible tests demonstrated. Hence, we can clearly say that the results obtained from the UV-Vis spectroscopy analysis supported the conclusions that were drawn by visible observations.

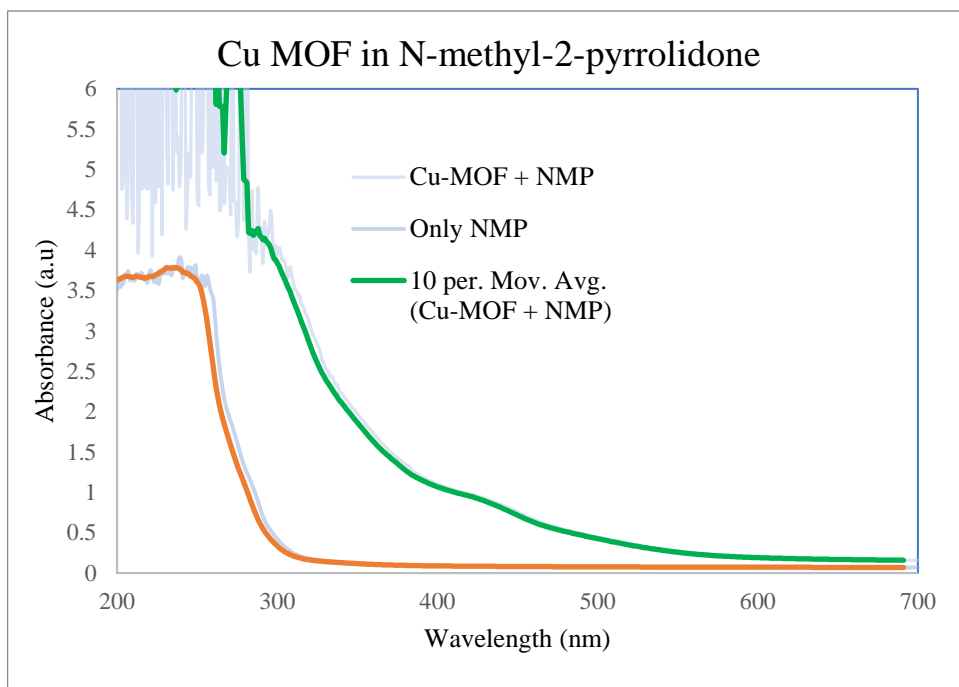


Figure-4.15 UV-Vis Spectra of Cu-MOF in N-methyl-2-pyrrolidone

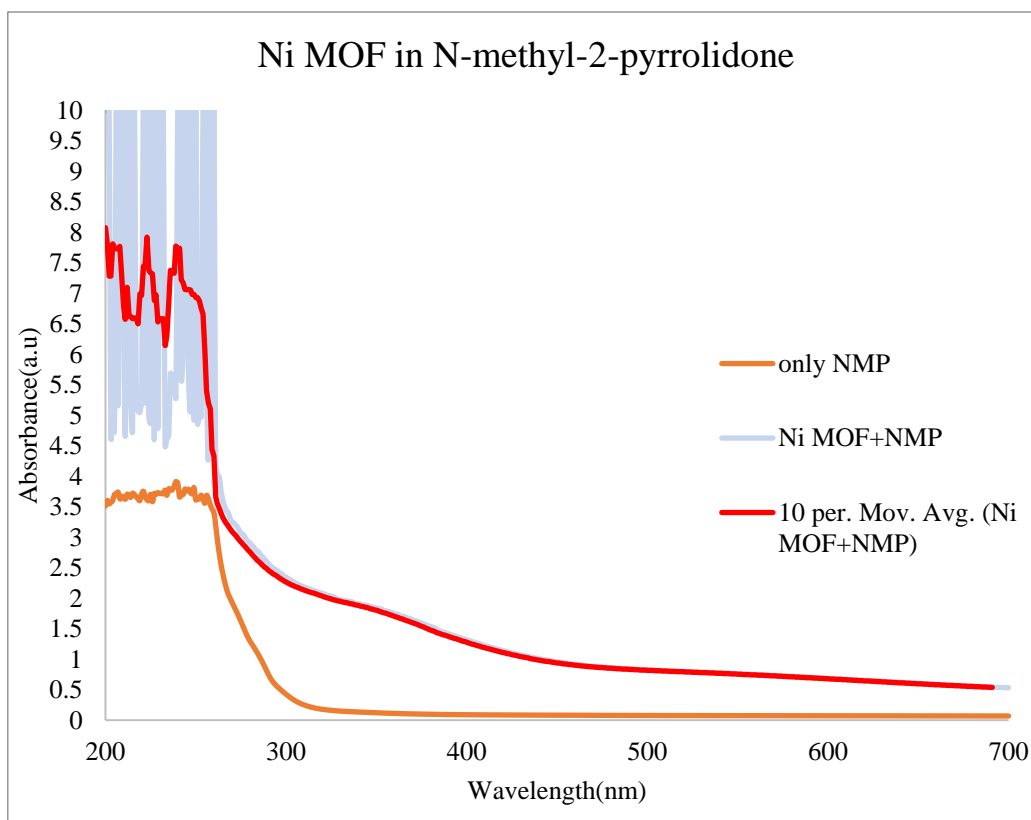


Figure-4.16 UV-Vis Spectra of Ni-MOF in N-methyl-2-pyrrolidone

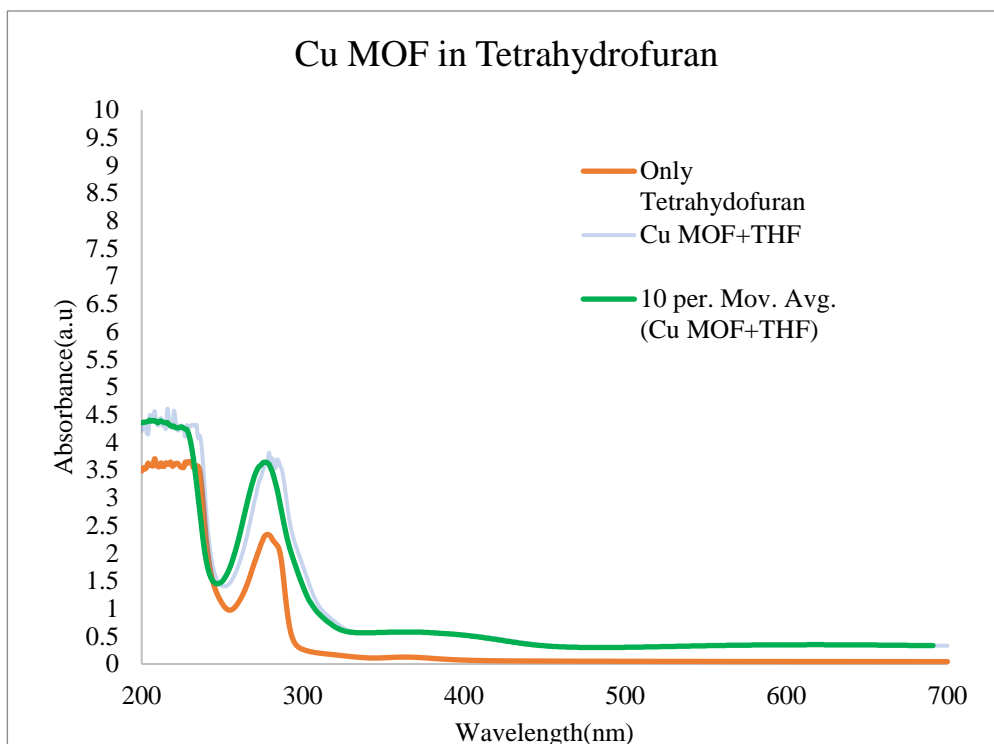


Figure-4.17 UV-Vis Spectra of Cu-MOF in Tetrahydrofuran

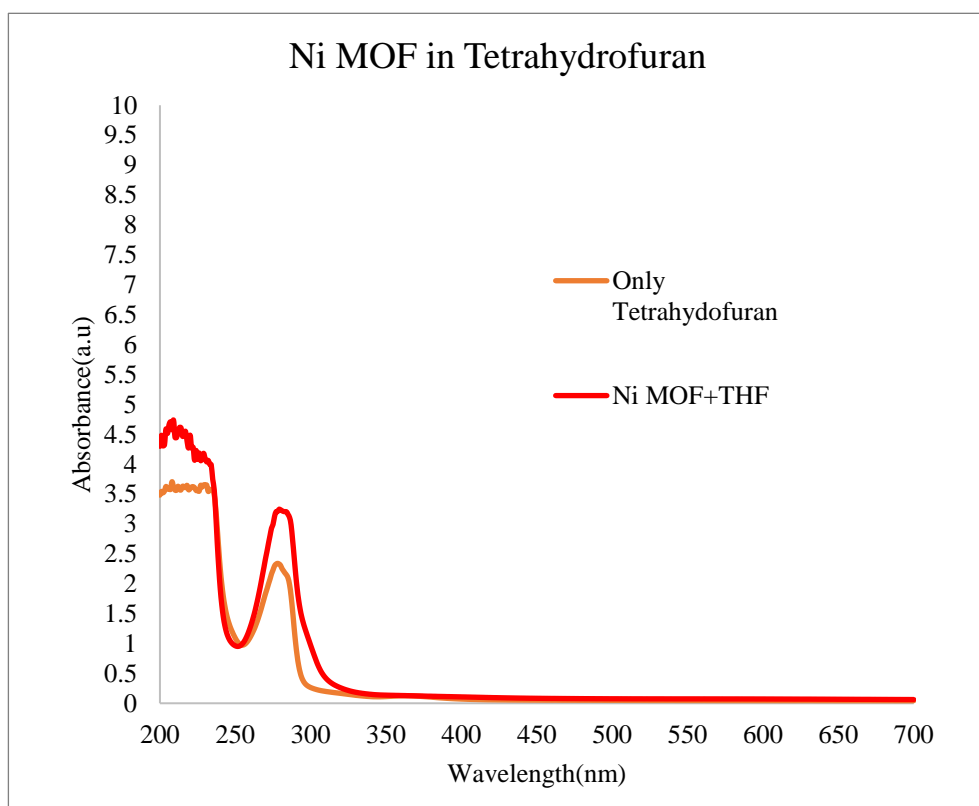


Figure-4.18 UV-Vis Spectra of Ni-MOF in Tetrahydrofuran

4.2 CO₂ Capture test:

The MOF-HDPE fibers extruded are used to test for the capture of CO₂. Our fellow lab mates designed this test as a part of their Ph.D., and we used their setup for the test. In an insulated CO₂-jacketed chamber, the sensor designed by them is placed and used to determine the concentration of CO₂ present in the chamber. We first allowed the gas to stabilize, and the initial concentration was noted. Then the fibers were placed inside the chamber on a petri dish, and the chamber was closed. Then we took the concentration readings every 15 minutes for about 8h. The time vs. Concentration results were plotted below and are compared.

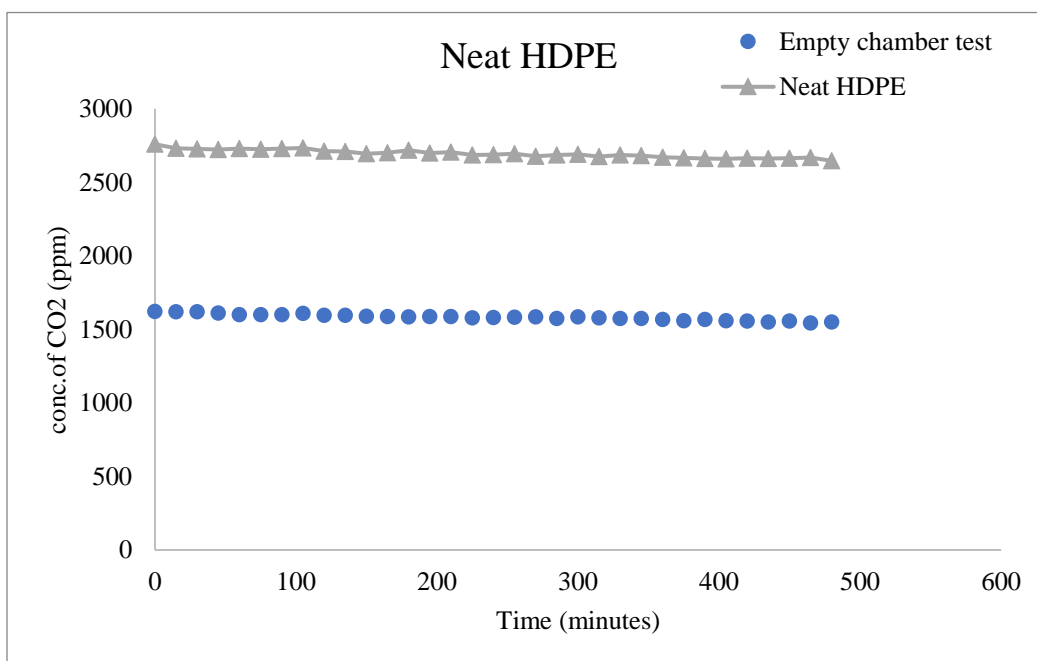


Figure-4.19 Time VS Concentration of CO₂ for Neat HDPE fibers

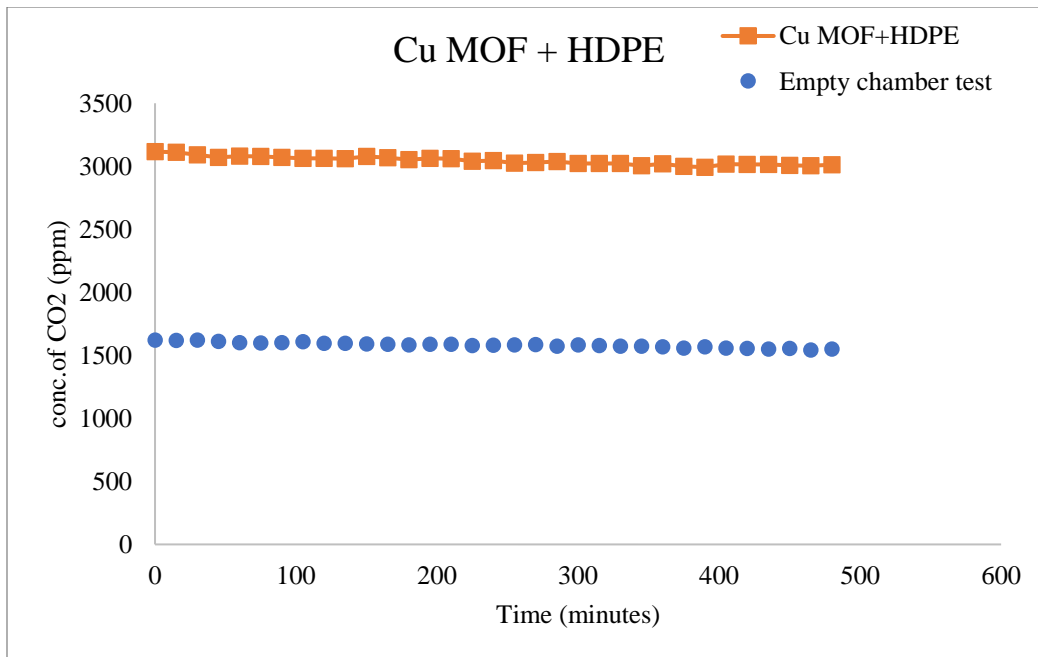


Figure-4.20 Time VS Concentration of CO₂ for Cu MOF- HDPE fibers

Initially, we have taken 2.8g of neat HDPE fibers and tested them for CO₂ absorption. In this case, the amount of CO₂ captured by the neat HDPE fibers is 36.428ppm/g. Later when testing for the MOF-HDPE fibers, we have taken 2.5g of fibers and the result was 42 ppm/g. Here the concentration of Cu-MOF in MOF-HDPE fibers is 0.01wt%.

Conclusions and Future Work

We have studied the dispersions of MOFs in various organic solvents. The MOFs we have used in this research are of the structure $M_3(\text{HHTP})_2$. The metals we had for our study were Cu and Ni. The Cu-MOF dispersions are very much stable in isopropanol, ethanol, and distilled water compared to those in triethylene glycol, NMP, and THF. Whereas Ni-MOF is stable in isopropanol and ethanol. It initially showed good stability in distilled water and acetone but then started to form cloudy suspensions; in the case of NMP and THF, it didn't show any strength from the initial days.

We performed UV-Vis Spectroscopy for the samples, and the results obtained from the UV-Vis are like the visible observations. In the case of forming the gel with the MOFs, keeping note of the previous works, we tried to overcome the disadvantages and attempted to make an effective gel with fewer chemicals and additives. Though we managed to make the gel, this gel we synthesized couldn't be better for the extrusion of fibers. We couldn't get neat, smooth textured yarns when extruding the threads using the gel. The distribution of the MOF gel into the fibers is not uniform. We should work on this to make uniform distribution of MOFs.

The CO_2 tests were performed with the extruded fibers and compared with neat fibers. The results can be improved by increasing the concentration of MOF in the fibers and can be further studied. In the future, we would like to test the MOF gel prepared directly to capture CO_2 as it's a hydrogel. And will also try to test the fibers for their mechanical and chemical properties and also for their thermal, electrical, and optical properties and compare them against the neat fibers.

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