

Application of MOF-based membrane in oil-water separation

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Abstract. In addition to being a serious threat to human health and the natural environment, the rising volume of oily wastewater and oil spills also causes resource depletion. Thus, there is a lot of interest in effective oil-water (O/W) separation. Scientists have looked at and suggested a variety of creative separation techniques in an attempt to address this issue. Unfortunately, the majority of these techniques have technical issues with low separation efficiency and significant energy usage. It is crucial to develop an effective oil-water separation membrane in order to address this issue. Because of their large surface area, low density, high porosity, controllable wettability, and variable pore size, have a lot of potential in this sector. This paper first categorizes several different MOF-based membranes and describe in detail their different synthesis methods, including solvent thermal method, ultrasonic method, microwave method, etc. Then, the physicochemical properties of MOF-based films are summarized in detail. The mechanism by which MOF-based films can separate oil-water mixtures is also explained. Finally, the modification of stainless steel mesh, sponge, aerogel and filtration membranes by MOF-based films, respectively, is emphasized and their applications in O/W separation are discussed.

Keywords: MOF, membrane, oil-water separation.

1. Introduction

Water pollution and major environmental issues are brought on by oily effluent from oil-based industry and regular oil spills into saltwater. Oil-water (O/W) emulsions are challenging to separate because they are extremely stable surfactants with tiny droplets. Even so, a variety of industrial-level procedures, including air and gravity-driven separation methods, centrifugal separation, and electrocoagulation, have been developed specifically to separate oil [1]. Nevertheless, they have lengthy recovery times, are difficult, require a lot of energy, and have low recovery rates. Although they often have limited adsorption capacities, poor repeatability, and the potential to create secondary contamination, porous large surface area adsorbents including flax, zeolite, and cotton have also been employed for oil water separation. Consequently, the use of membrane-based separation technologies is essential to addressing these issues.

A novel family of crystalline porous materials known as MOFs is made up of organic ligands bridging core metal ions. Their high porosity, light density, and specific surface area are their benefits. By adding a hydrophobic component to their pore structure, MOFs can become materials with unique wettability properties. It has been demonstrated in recent years that specific wettability MOFs are a useful technique for cleaning water tainted with oil. Materials with lipophilic qualities and hydrophobic MOFs are good for oil and water separation [2]. Furthermore, the creation of hydrophobic MOFs increases the stability, water-repellent qualities, and prospective uses of MOFs, as many of them are water-sensitive.

2. Synthesis of MOF-based membranes for O/W separation

A scattered filler phase and a continuous polymer phase make up mixed matrix membranes (MMMs). For MMMs with separation potential phases to grow smoothly, there should be an exact match between the polymer and filler phases. MOF fillers may be surface changed to create polymer-filler interfaces that are advantageous because their surface is rich in changeable sites. MOFs have a heterogeneous membrane structure, low thickness, tiny pore size, and high crystalline morphology.

Better selectivity and exceptional permeability are found in MOF-based polycrystalline membranes because of their ultra-microporous shape and outstanding chemical and thermal durability. A layer-by-layer method may be used to directly construct nanosheet-based membranes, and MOF nanosheets have gained attention as possible candidates for highly selective and hyperpermeable two-dimensional (2D) membranes [3]. The main factors to take into account while developing MOF-based membranes for separation are the choice of matrix, the stability and densification of the membrane, and the strength of the link between the membrane layers and matrix. Various techniques for creating MOF-based membranes have been reported now.

2.1. Solvothermal method

The Xie et al. prepared NH-MIL-88B with antifouling performance by solvothermal method and coated it on the surface of quartz fiber membrane; the test found that the retention rate of oil-in-water solution are above 99.4% and the flux of oil-in-water petroleum ether is up to 679L/m²-h, which has good performance of oil-water emulsion separation. The solvothermal method is a chemical reaction that occurs in organic/aqueous solution; the synthesis time of MOF is long, but the precision is high [4].

2.2. Ultrasonic method

The ultrasonic approach reduces the pace of heating and cooling by producing a localized high temperature and pressure using ultrasonic radiation. Zhai et al. effectively generated a new type of two-dimensional photocatalyst BiOCl/GO/MOF-5 using the ultrasound-assisted solvothermal approach, which is similar to the structure of MOF synthesized by microwave method. The novel catalyst has a photocatalytic effectiveness of up to 90.6%, which is substantially greater than that of pure BiOCl [5].

2.3. Microwave method

The primary mechanisms of the microwave approach include mutual friction to heat up the quick synthesis of small-sized MOFs and microwave heating to encourage molecular vibration. In contrast to the solvent heat technique, which offers the benefits of quick heating and efficient energy use. Jamshidifard et al. synthesized UIO-66-NH₂, which was then microwave heated and introduced into PAN/chitosan nanofibers. Pb(II), Cd(II), and Cr(II) ions were removed by membrane filtration and adsorption [6].

2.4. Mechanical synthesis method

Mechanical synthesis method destroys the chemical bond between molecules by physical means, and the synthesis reaction is completed in a very short time with a large amount of product. Generally mechanical grinding is used for synthesis.

2.5. Stirring method

Compared with other methods, stirring method has the advantages of room temperature, normal pressure, short time and high efficiency, which is one of the most widely used synthesis methods.

The structure and function of MOF-based membranes prepared by different methods are different, and the fields of application are also different. The solvent method is still the main preparation method for MOF-based membranes used for O/W separation.

3. Physicochemical properties of MOF-based membranes

3.1. Membrane surface wettability

The MOF base film has surface wettability, which plays a decisive role in its permeability to water and oil barrier properties. The permeation flux and rejection characteristics of the used membrane are positively impacted by its wettability. Oil interacts with molecules on the surface of conventional polymeric membranes, making them prone to contamination. Generally speaking, a membrane's wettability is determined by its chemical makeup and surface roughness. The wettability of a solid surface is determined by measuring the size of the contact angle formed between the edge of the droplet and the surface of the material. When the contact angle (WCA) is greater than 90° , the material is hydrophobic; when WCA is greater than 150° , the material is superhydrophobic; when WCA is less than 90° , the material is hydrophilic; when WCA is less than 10° , the material is superhydrophilic. According to the wettability of the material to water and oil, special wettability materials can be divided into super hydrophilic, super hydrophobic, super oleophilic and super oleophobic materials. When the same material exhibits completely opposite wettability to water and oil, it is selective for water and oil and can be used to separate oil-water mixtures. If the MOF-based membrane is lipophilic, it will only allow the oil phase to permeate away from the membrane surface. Conversely, if it has excellent hydrophilicity, it allows water molecules to pass through the film. Based on this, the membrane achieves the separation of the oil phase from the water phase.

3.2. Surface roughness and pore size

One important factor influencing the membrane's permeability and antifouling capabilities is surface roughness. It raises the membrane surface's adhesion capability, which influences the membrane's fouling properties [7]. The surface roughness of MOFs membranes is impacted by the incorporation of nanoparticles. This is due to the fact that nanoparticles can decrease the effective pore size and increase film roughness. However, the unequal dispersion of nanoparticles also causes local aggregation, which restricts the influence of the inserted nanoparticles, which might result in a decrease in the membrane's ultimate penetration flow.

3.3. Membrane surface charge

Another significant factor influencing the laminar flow membranes' rejection characteristics is their membrane surface charge. It is possible to improve the rejection capacity of laminar flow membranes by generating charge on their surface gradually and steadily. Therefore, some anionic and cationic functional groups can be introduced on the surface of the MOF membrane. These functional groups can interact with pollutants to achieve the effect of O/W separation.

4. Mechanism of O/W separation

O/W separation generally operates on the basis of hydrophilic and hydrophobic membranes being chemically functionalized. The usage of particular functional groups can limit the input of water or oil based on the membrane's specified wetting properties. Similar to this, MOF-based membranes, such as superhydrophilic/superoleophobic and superoleophilic/superhydrophobic membranes, offer distinct surfaces for separating substantial volumes of O/W emulsions. The two main factors that affect how well membranes conduct O/W separation are selectivity and permeability. The latter is influenced by the sieving principle in O/W separation, while the former is correlated with the membrane's pore size.

Because of its high wettability, the $\text{NH}_2\text{-MIL125 @PAA}$ composite membranes' water separation process was described by one research. It prevented oil droplets from making direct contact with the membrane by unfolding a water layer on it. This will successfully separate the O/W emulsion by allowing the water molecules to flow through the membrane and blocking the oil phase from penetrating through [8].

The dynamic action of O/W can greatly enhance the membranes' capacity for selective separation and separation efficiency. Water molecules spread over the membrane surface and enter the membrane holes when the membrane has a hydrophilic surface. O/W separation can therefore be accomplished if the membrane blocks the oil droplets, provided that the oil has a low affinity for the membrane's surface and a high contact angle with the oil phase.

Figure 1 illustrates a three-step (capture-demulsification-separation) method for O/W emulsions employing ZIF-71/PVDF-HEP membranes that was proposed in research. The water-in-oil droplets will be captured by ZIF-71 in the first stage because of its high porosity and lipophilicity. This is because the emulsion and ZIF-71 have lipophilic interactions that encourage the droplets to adsorb on the ZIF-71 surface. As a result of the lipophilic interactions that cause ZIF-71 to penetrate the emulsion's interface in the second stage, the O/W interface gradually twists and tears, disrupting the thermodynamic equilibrium and removing the surfactant's active ingredient [9]. Because of the superhydrophobic interface and increased oil density in the final stage, water droplets immediately separate from the heavy oil (density > 1), whereas lighter droplets rebound upon making direct contact with the membrane surface.

Another measure indicating the O/W separation process is intrusion pressure, which is the difference between two forces: the downward hydrostatic pressure and the upward capillary force. When the incursion pressure is positive, it signifies that more pressure is needed to allow the fluid to pass through the membrane; when it is negative, it shows that gravity is the method used.

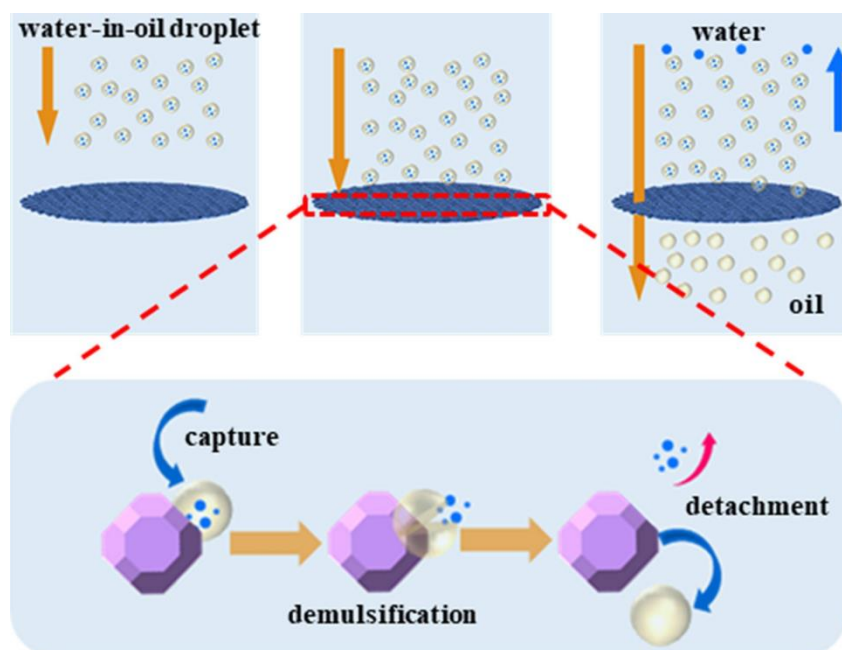


Fig. 1 Schematic diagram of ZIF-71/PVDF-HFP membrane separation mechanism [9].

5. Application of MOF in the field of O/W separation

The principal traditional processes for oil-water separation include agglomeration, air flotation, liquid-liquid cyclones, gravity settling, and adsorption. Although there is still no secondary damage to the environment, traditional oil-water separation technology concentrates more on cleaning the floating oil layer. It is certain that environmental damage from oil spills will draw increased attention, with the development of new technology for recovering from spills likely to become a new area of focus. Oil-water separation has been facilitated in recent years by the deployment of innovative and effective media, such as fat crystals, polymer films, and porous hydrophobic/lipophilic materials. This novel kind of separation material may be recycled during oil spill cleanup and uses its inherent hydrophobicity and lipophilicity to provide continuous oil-water separation in the event of an external pump. The adsorption capacity is constrained by the volume of the adsorbent material itself as the

conventional approach uses adsorbent materials to adsorb oil layers on the water's surface. This novel separation material won't lead to secondary contamination, has a high oil-water separation efficiency, and saves a significant amount of money.

Consequently, MOFs are part of an expanding class of porous materials that may be employed as adsorption material modifiers, giving researchers a fantastic and effective platform for removing contaminants from water.

5.1. Modification of stainless steel mesh

MOFs are applied on stainless steel mesh with extreme oleophobicity and extended service life; they are chemically stable. ZFCMs were created by Li depositing films of zeolite imidazolate backbone 8 (ZIF-8) onto stainless steel meshes (SSMs) by the processes of crystallization and crystal seeding. The films can produce outstanding O/W separation with superoleophobicity up to 161° and superhydrophobicity up to 153° . They also exhibit switchable surface wettability. The frontal mechanical strength of the film may be increased by choosing less costly SSMs, and the ZIF-8 film completely covers the SSMs' surface to prevent SSMs from affecting it. PVA is also added to the ZIF-8 film to further increase its hydrophilicity and, thus, the ZFCMs' dispersion characteristics. In addition, the density of the ZIF-8 films could be modulated by changing the time of crystallization to control the structure of the ZFCMs. For emulsions with flow rates exceeding $450 \text{ Lm}^{-2}\text{h}^{-1}$, the separation efficiency could reach more than 99%. Through gravity-driven emulsion separation tests, the researchers also tested the O/W separation efficiency of four different emulsions, and the film showed high separation performance in all of them [10].

5.2. Modification of sponge

Sponge reusability and oil/water separation efficiency can both be enhanced via MOF modification. Flexible polyurethane foams (FPUF) were surface modified with 3-mercaptopropyl trimethoxysilane (MTS) with low surface free energy by Hou et al. Additionally, the MTS coating offered a large number of active sites for additional FPUF modification. When FPUF was coated with biomimetic MOFs nanoparticles (FPUF@MOFs-NH₂), it exhibited superior oil absorption over pure FPUF. Furthermore, FPUF@MOFs-NH₂ has good fire resistance, strong cycle performance, and the ability to extrude away absorbed oil [11]. The preparation concept, recyclability, oil absorption, and fire safety are depicted in Figure 2.

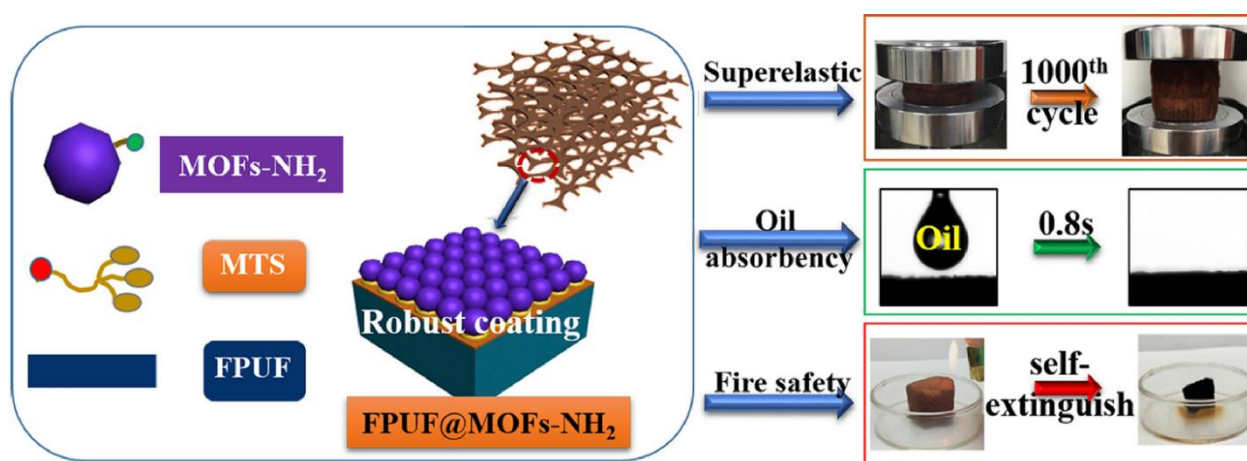


Fig. 2 FPUF@MOFs-NH₂ Preparation principle and performance [11].

5.3. Modification of aerogel

A lot of water is added to three-dimensional reticular hydrogels to modify nanostructured MOF. A significant chemical link is formed between the hydrogel's hydrophilic group and MOF, potentially contributing significantly to the process of oil-water separation. Li et al. produced multilayer porous ZIF-8 @ PLA composite aerogel by combining metal organic skeleton ZIF-8 nanoparticles with PLA aerogel matrix by physical mixing and thermally induced phase separation with the help of water. When compared to pure PLA aerogels, the produced aerogels exhibit better mechanical properties and increased oil wettability. Because ZIF-8 nanoparticles provide the aerogel a porous structure, PLA aerogel's pore size is significantly reduced while its pore volume and BET specific surface area are significantly increased. ZIF-8 additionally enhanced PLA aerogel's elongation at break and tensile strength. ZIF-8 @ PLA [12]. The composite aerogel performs exceptionally well in oil-water separation because it has superior oil wetting properties than pure PLA aerogel gel. Nevertheless, too much ZIF-8 in PLA aerogel will cause ZIF-8 particles to flocculate, which will lessen ZIF-8's effectiveness as a nano filler. therefore ZIF-8 @ PLA. Figure 3 shows ZIF-8 @ PLA Schematic diagram of the preparation process.aerogel.

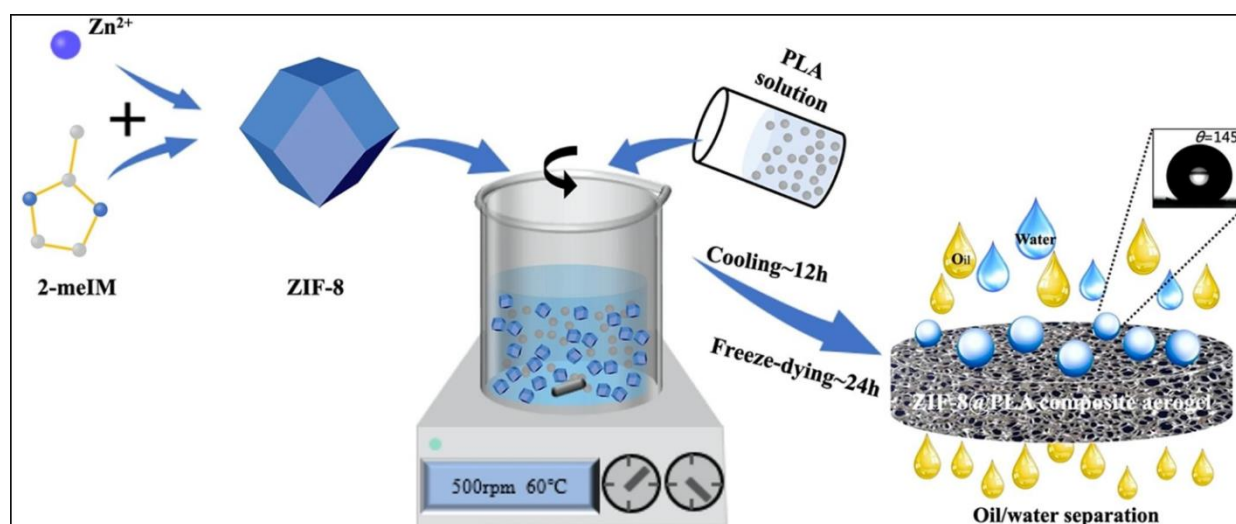


Fig. 3 Preparation of ZIF-8@PLA [12].

5.4. Modification of filtration membranes

Different base membranes, including inorganic ceramic membranes, organic polymer membranes, and innovative nano membranes, can be modified using MOFs. Interface polymerization (IP) technique was employed by Lee et al. to create a thin layer of polyamide (PA) on top of the polyethersulfone (PES) support layer. Fabricate a 1% composite membrane consisting of poly (N-2-methacryloxyethyl-N, N-dimethyl) and aminopropyl sulfonate (PMAPS). In the forward osmosis mode, the water flux is $(15.79 \pm 0.3) \text{ L/m}^2 \cdot \text{h}$, the traction liquid is 2mol/L NaCl, and the feed liquid is emulsified oil at a rate of 1000×10^{-6} . The flow rate of oil is $12.54 \pm 0.8 \text{ L/m}^2 \cdot \text{h}$. There is a 99% clearance rate of oil. A superhydrophobic ZIF-90 membrane with a self-healing feature was created by Cai et al. and successfully separated water from n-hexane with a 99.98% separation efficiency. During the cyclic testing process, superhydrophobicity can be maintained. It can be automatically restored and reused through heating [13].

6. Conclusion

The current focus on selective separation of different organic emulsions is a result of their deadly consequences for the environment, marine life, and human health. Different water-in-oil and oil-in-water emulsions may be efficiently separated using MOF-based membranes. These membranes have outstanding antifouling capabilities and a great promise for the selective separation of organic

emulsions. This article mainly introduces MOF based membranes used for O/W separation, including preparation methods, physicochemical properties, O/W separation mechanism, and specific applications.

Nevertheless, the majority of the research employing MOF-based oil-water separation membranes in the literature currently in publication has some limitations, necessitating the following actions to address wastewater's environmental issues: (1) MOF-based membranes' long-term performance has received less attention, particularly when it comes to the continuous oil-water separation process. Because of this, scientists may concentrate on finding methods to increase the membranes' long-term durability. Secondly, because most MOFs materials' organic and metal ligands don't coordinate well, they become unstable in humid settings. It is yet unknown how to increase MOF stability without changing their structural characteristics. (3) The environment surrounding wastewater is extremely complex and may include heavy metals, bacteria, organic compounds, and more. In complicated assemblies, membranes based on MOFs must be more stable and impervious to contamination. In light of this, scientists must develop materials with improved self-cleaning and stability. Furthermore, the absence of longitudinal comparison data on the contamination resistance, mechanical and chemical stability, and separation efficiency of MOF-based membranes based on complicated oil-water combinations would need further investigation by future investigators.

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