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MOF-5 Based Mesh for the Separation of the Oil-Water Mixture

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ABSTRACT

The petroleum industry inevitably produces large amounts of oily wastewater. Environmentally permissible treatment of oily wastewater is a major problem for the petroleum industry. Nowadays, the focus has been an awareness of the treatment methods of oily wastewater. Therefore, oil-water separation has become a recent problem, and it must be explored and resolved by petroleum Industries. The paper investigates and discusses the challenge of treating oily wastewater in the petroleum industry and the recent focus on oil-water separation methods. The study presents the development of a metal-organic framework (MOF) coated mesh for this purpose. The MOF-5 are prepared using a solvothermal method and characterized using XRD and SEM. The coated mesh exhibits superoleophobic properties with a contact angle exceeding 150º, making it promising for oil-water separation. The study employs a two-stage process involving a mesh to remove macro-sized droplets and polish to remove nanosized droplets. Gas chromatography - flame ionization detector (GC-FID) is used to characterize total petroleum hydrocarbons (TPHs) and separation efficiency. The results indicate a reduction of TPHs to 5 ppm and 98% separation efficiency after treatment.

شبكة مطلية بالأطر العضوية المعدنية (MOF-5) لفصل خليط الماء والزيت

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الكلمات المفتاحية:
الأطر المعدنية العضوية (MOFs)
المياه الزيتية
كفاءة الفصل
رهاب فائق
إجمالي الهيدروكربونات البترولية (TPHs)

الملخص

تنتج صناعة النفط حتماً كميات كبيرة من المياه الزيتية. تعد المعالجة المسموح بها بيئيًا للمياه الزيتية مشكلة كبيرة لصناعة النفط. في الوقت الحاضر، تم التركيز على الوعي بطرق معالجة المياه الزيتية. ولذلك فإن فصل الزيت عن الماء أصبح مشكلة حديثة، ويجب استكشافها وحلها من قبل الصناعات البترولية. توضح الدراسة الحالية تطوير شبكة مغلفة بأطر عضوية معدنية (MOFs) سهلة وقوية لفصل خليط الماء والزيت. يتم تحضير الأطر العضوية المعدنية (MOFs) عبر الطريقة الحرارية المكونة من خطوتين. تتميز الهياكل المعدنية العضوية المحضرة بحيود الأشعة السينية (XRD) والمجهر الإلكتروني الماسح (SEM). يتم قياس الخاصية القابلة للبلل للشبكة المطلية بالأطر العضوية المعدنية باستخدام تقنية قياسات زاوية التلامس. تُظهر الشبكة المطلية بالأطر المعدنية العضوية طبيعة كارهة للالتصاق مع زاوية تلامس تزيد عن 150º، مما يجعلها المرشح الواعد في الدراسة

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الحالية. تتضمن هذه الورقة أيضًا العملية المكونة من مرحلتين، والتي كانت مشابهة للعمل السابق لإزالة القطرات النانوية من الماء. يتضمن ذلك الشبكة التي تزيل القطرات ذات الحجم الكبير والتلميع الذي يزيل القطرات النانوية. يتميز إجمالي الهيدروكربونات البترولية (TPHs) وكفاءة فصل المياه المفلترة التي تم الحصول علها من الشبكة بالكروماتوغرافيا الغازية - كاشف تأين اللهب (GC-FID). يتم تقليل إجمالي الهيدروكربونات النفطية إلى 5 جزء في المليون ويتم تحقيق كفاءة فصل بنسبة 98% بعد العلاج.

1.Introduction

Metal-organic framework (MOFs) have appeared as a large class of crystalline materials with high porosity (more than 90%) and massive internal surface areas extending more than 6000 m^2/g [1]. Thus, these properties, degree of contrast and homogeneity in structures make MOFs of interest for potential applications in oil-water separation [2]. MOFs are also of great importance because of their work as storage media for gases such as hydrogen and methane and their high-absorbent capabilities to meet different separation needs [3]. Metal-organic framework are crystalline structures containing mineral ions and organic linkers; these components will form a tridimensional structure [4]. The content is known for its largest pore and high surface area. According to [5], these porous structures are constructed from the coordinative bonding between metal ions and organic linkers or bridging ligands [6]. The singular features of MOFs, such as their great surface-areas and variety of structures, will make the proper to a broad domain of industrial processes [7]. The metal-organic framework structure can be prepared to capture specific gases and chemicals while other substances pass through [8]. Therefore, metal-organic frameworks (MOFs) are well-suited for efficient separation processes [9]. Several methods are used to synthesise highly functional of the Metal-Organic Framework (MOFs) [10]. However, the most common process is called Solvothermal Batch Reaction, a procedure requiring a high temperature (160-250ºC), a long reaction period, and the use of solvents such as N, and N-Dimethylformamide [11]. Many MOFs synthesis is a liquid-phase synthesis where separate
metal and ligand solutions are mixed, or solvents are applied to a mixture of solid salt and ligand in a reaction vial [12]. The selection of solvent for these liquid-phase reactions can be based on different factors such as susceptibility to solubility, interactivity, susceptibility to oxidation, stabilization, etc. Therefore, the solvent plays a vital role in the determination of thermodynamics and activation power for a specific reaction [13]. Many researchers have concentrated on the pore size and pore surface of MOF-5 in order to enhance its efficiency for different applications [14]. Intense work has been carried out over the last two decades on MOFs, which have developed and increased the variety of porous materials [15]. According to [16], the separation efficiency of the mesh was 89% and after the polishing phase was more than 99%. Recently, the Nanomaterials of MOFs have become important due to their great properties such as high surface area and porous when compared with other materials [17].
Membrane filtration technology has gained widespread recognition as an effective method for treating oil-water mixtures, particularly in industrial settings. Its advantages include low cost, ease of operation, low energy consumption, and minimal potential for secondary pollution, making it a preferred choice for many applications. In recent years, there has been growing interest in the use of special wettability materials in membrane separation technology for oil-water separation. These materials offer high efficiency, suitable recoverability, and excellent oil-water selectivity. Moreover, special wett-abilities such as super-hydrophilicity, super-oleophilicity, super-hydrophobicity, and superoleophobicity can be achieved by adjusting the surface free energy and micro-nano structure of the materials [18,19]. Thus, the use of special wettability materials in membrane filtration technology offers promising prospects for improving the efficiency and effectiveness of oil-water separation processes, contributing to environmental sustainability and resource conservation [20].
However, has yet been available on the effective use of MOF-5 as a separator material for crude oil separation and removal from seawater, which is encouraging us for this study. The main objective of the current study is to discuss the potential use of laboratory-prepared MOF-5 for the separation and removal of crude oil spills from seawater. The influence of three factors (the wettable property of the MOFs coated mesh (contact angel), total petroleum hydrocarbons (TPHs), and the separation and removal efficiencies were studied on the oil-water mixture. Thus, the researchers identified the decanting & oily waste disposal/oil spill control strategies taken by the Memorial University of Newfoundland, St. John's, Canada in the study area.

2. Experimental procedure

MOF-5

Metal-organic frameworks have a porous structure where organic ligands coordinate with the metal ions (Fig. 1). MOFs act as model systems for the separation of oil/water mixture due to their highly porous nature. MOFs-based coating (MOF-5/PDDA) is developed via layer-by-layer deposition method for the separation of oil/water mixture. 1ml of MOF-5 (solution in deionized water) was deposited on stainless steel mesh (60 µm pore size). In continuation of this, 1ml of poly diallyl dimethyl ammonium chloride (PDDA) was further incorporated above that layer. This procedure was repeated three times.
However, the emulsion is created by adding 7 gm of NaCl and 200 µl of crude oil in 200 ml of water and mixed these ingredients with the high-speed homogenizer (10000 rpm) for 10 min of time. The emulsion was allowed to stabilize for 20 min before the separation experiments.

3. Results and Discussion

In this research, MOF-5 is synthesized via a two-step solvothermal method developed by Yaghi et al. [21,22].

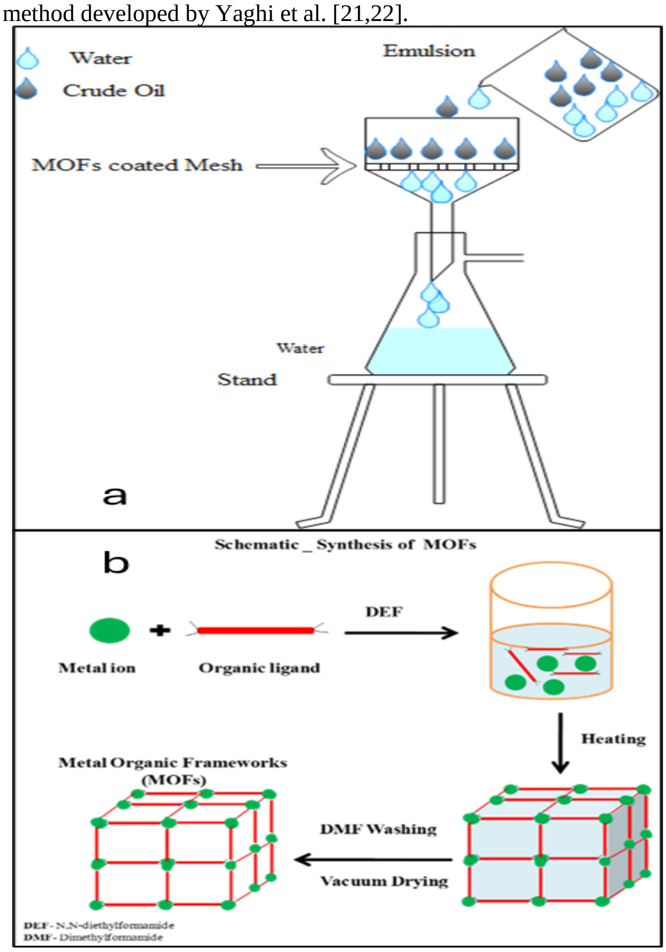

Fig. 1. (a) Schematic diagram of the separation process using the MOFs coated mesh (two-stage process mesh and polish). (b) Schematic diagram of the synthesis of the Metal-organic framework (MOFs).

Zn $(NO_3)_2 \cdot 6H_2O$ (336 mg),1,4-benzene dicarboxylic acid (BDC) (41.5 mg) and N, N-diethyl formamide (DEF) (5 ml) mixed at room temperature. Following this, 4-(dodecyloxy) benzoic acid DBA (76.6 mg) is added in the above mixture and stirred the solution for 24 h. After that, the solution is heated at 150 °C for 20 min the solution is turned into pale yellow color with precipitation of crystals. These crystals are then washed several times with DMF, and vacuum dried at 60 °C.

The structural characterization of the material is done by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The wettable properties of the material are measured through the contact angle measurement technique, where a homemade set up which includes a digital microscope camera, and ImageJ software, is used. The separation efficiency of the coating is also tested for previously developed two-stage processes, i.e., mesh and polish. Gas chromatography coupled to flash ion detector (GC-FID) was used to measure the total petroleum hydrocarbons (TPHs) and separation efficiency. Agilent 6890A GC equipped with an FID is used to measure the TPHs. For this process, samples were prepared by liquid extraction method with the help of hexane for the two processes, i.e., mesh and polish. The wettable characteristics of the coating are determined by the angle of contact. Therefore, homemade equipment for the measurement of the contact angle was manufactured. Hence, through Young's equation, the wetting of coating phenomenon is clarified [23].

$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

Where the contact angle, interfacial free energies of liquid-vapour, solid-vapour and solid-liquid are θ, γlv, γsv and γsl, respectively.

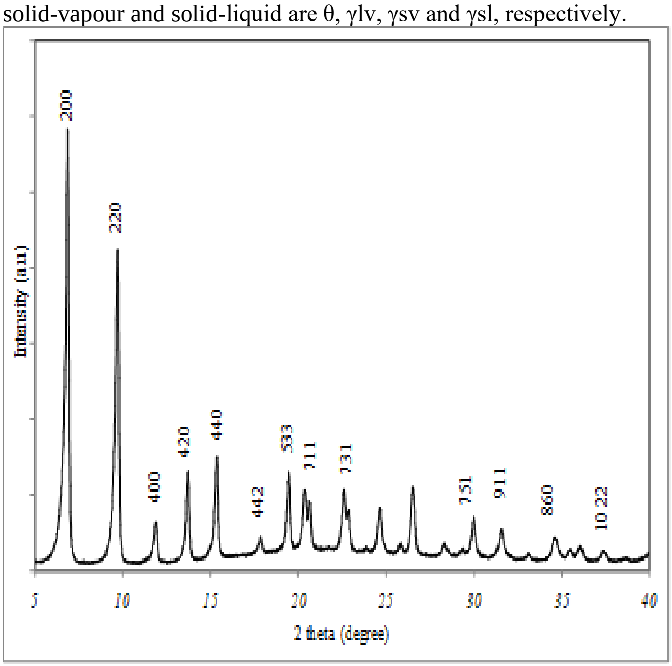

Fig. 2. X-ray diffraction pattern of the MOF-5

As you can see in Figure 2 the X-ray diffraction (XRD) pattern of the MOF-5. On the X-axis rotation angle, two thetas are projected, while on the y-axis, the intensity is given. All peaks of MOF-5 exist in the pattern. Here, some peaks of Zinc oxide also exist in the pattern. It means that zinc oxide also precipitates in the pores of the MOF-5.

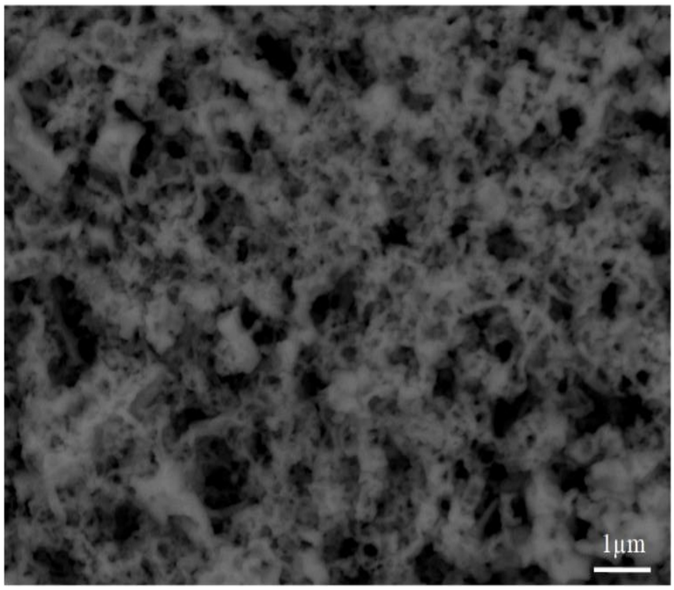

Fig. 3 Scanning electron microscope (SEM) micrograph of the MOF-5 and Mesh.

Figure 3 shows the scanning electron microscope image of the MOF-5. This micrograph shows the sponge-type structure of the MOF-5. This highly porous structure seems to be a good candidate for the separation of oil/water mixture.

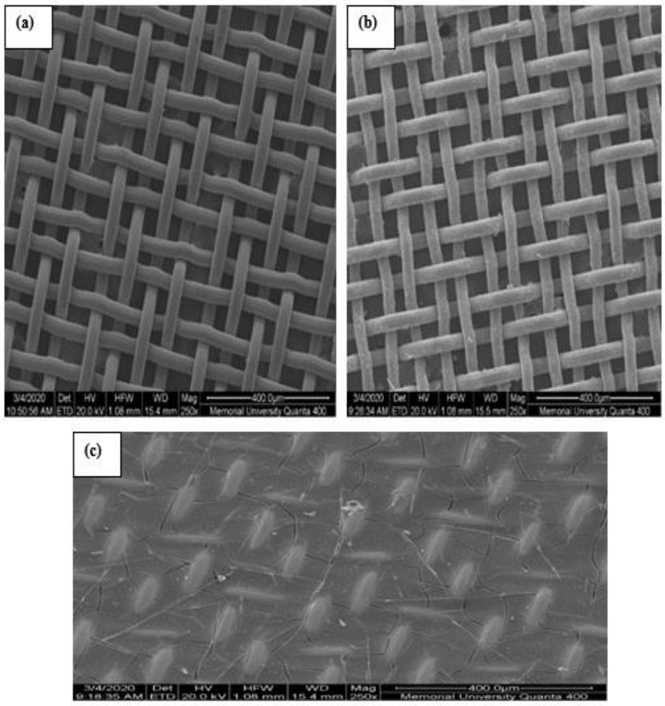

Fig. 4 (a) SEM image of the mesh, (b) SEM image of the mesh coated with MOF-5, and (c) SEM image of the mesh coated with MOF-5 and PDDA.

Figure 4(a) shows the scanning electron microscope image of the mesh. Figure 4(b) shows the scanning electron microscope image of the mesh coated with MOFs. Figure 4(c) shows the scanning electron microscope image of the mesh coated with MOFs and PDDA.

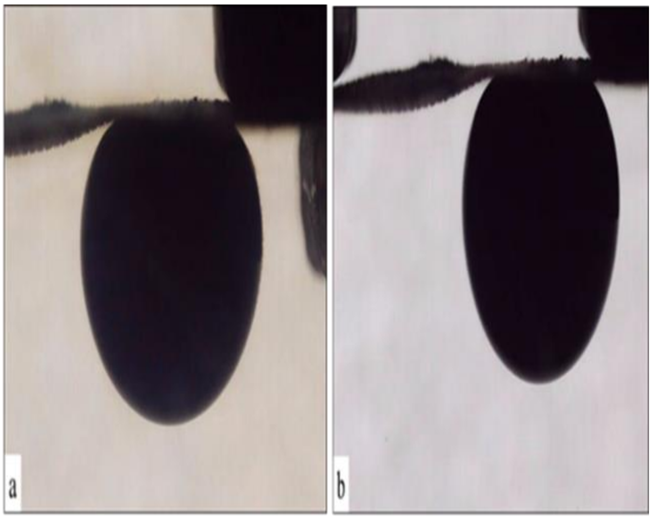

Fig. 5 (a) Contact angle of the crude oil on the mesh coated with MOFs, (b) Contact angle of the crude oil on the mesh coated with MOFs/PDDA.

Figure 5 (a) shows the contact angle measurement of the mesh coated with MOFs. The contact angle is 150º with crude oil, which makes it superoleophobic. Furthermore, Figure 5 (b) shows the contact angle of crude oil on mesh coated with MOFs/PDDA. The contact angle is 158º, which also makes it superoleophobic. This nature of the mesh is making it a promising candidate for the separation of oil-water mixture.

As a result of this process, the Total Petroleum Hydrocarbons (TPHs) are expected to reduce dramatically. Total Petroleum Hydrocarbons (TPHs) are determined by the (GC-FID) instrument. Thus, the separation efficiency is determined using the following equation number 2 [24]:

$$\text{Separation efficiency (\%)} = (1 - T_{\text{Mesh OR Polish}} / T_{\text{Emulsion}}) \times 100 \quad (2)$$

DEF	N, N-diethyl formamide
DFO	Department of Fisheries of Oceans
DMF	Dimethylformamide
GC-FID	Gas Chromatography - Flame Ionization Detector
MOFs	Metal-Organic Frameworks
MPRI	Multi-Partner Research Initiative
PDDA	Poly diallyl dimethyl ammonium chloride
PPM	Part Per Million
SEM	Scanning Electron Microscopy
TPHs	Total Petroleum Hydrocarbons
XRD	X-ray diffraction
γlv	interfacial free energies of liquid-vapour
γsl	interfacial free energies of solid-liquid
γsv	interfacial free energies of solid-vapour
θ	contact angle

Where TMesh/Polish is the TPHs after (Mesh or Polish prosses), and TEmulsion is the TPHs of the emulsion.

Figure 6 shows the separation efficiency of the MOFs/PDDA coating for two processes, i.e., mesh and polish. The total petroleum hydrocarbons (TPHS) of the emulsion were 290 ppm. After meshing, it became 30 ppm and 5 ppm for the sample obtained after the polish process. So, the separation efficiency for mesh is 89%, and after polish is 98 %.

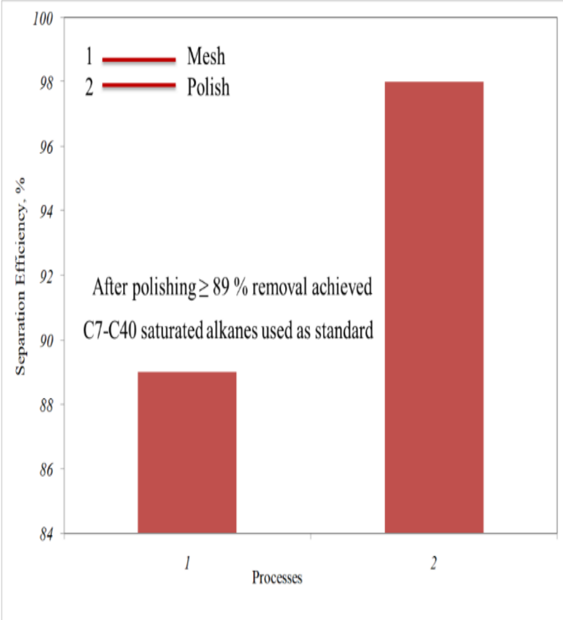

Fig. 6 Separation efficiency for two processes of MOF-5/PDDA coating.

4. Conclusions

Out of this study, the following conclusions are summarized:

- In this study, a brief discussion was held on the treatment of the oil-water mixture by using MOF-5, which could be considered as a new technology with its significant criticality for oil-water treatment.
- It has been shown through MOF-5's selection, material preparation, experimental procedure, and results obtained that the separation by MOF-5 is expected to be one of the most effective treatment methods for separating oil from water as per the provided experimental procedure and scale.
- Hence, a polymer/MOFs-based coating is fabricated by a layer-by-layer deposition method. This coating resulted in the contact angle of 158º, the separation efficiency of the coating reached 98%, and TPHs reduced to 5 ppm.

Future perspectives

- MOF-5 based mesh for the separation of oil-water mixtures holds significant promise for future applications in environmental remediation and industrial processes. The future perspectives in the development of this membrane technology include:
- Performing a multi measurement approach using the same samples presented in this research (e.g., 5-10 cycles) under the same consistent conditions for each measurement as well as using different instruments for TPHs to ensure the reliability and accuracy of data recorded and results obtained.
- Integrating with other surfactants to make the emulsion more stable.
- Scale-up of the experimental procedure, evaluate and repeat to confirm the repeatability.
- Due to the significance and the demand for oil-water separation materials, commercialization of MOF-5 is planned.
- Performing investigation on the economic analysis, environmental influence for the proposed up-scale setup and procedure of MOF-5 for optimal outcomes.
- Studying the impact of other types of wetting contact angles of the superhydrophobic/superoleophobic surface such as the tilt angle and contact angle hysteresis on the efficiency.

Nomenclatures

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