IJE TRANSACTIONS C: Aspects Vol. 37 No. 09, (September 2024) 1736-1745

International Journal of Engineering

Journal Homepage: www.ije.ir

Application of Polyvinyl Chloride- Halloysite Nanotubes/Uio66-NH_2 Mixed Matrix Membranes in Separation of Sunflower Oil from Water

N. Ghaedi, N. Nabian*, M. Delavar, M. Amid

Department of Chemical Engineering, University of Science and Technology of Mazandaran, Behshahr, Iran

PAPER INFO

Paper history:
Received 10 October 2023
Received in revised form 09 February 2024
Accepted 19 February 2024

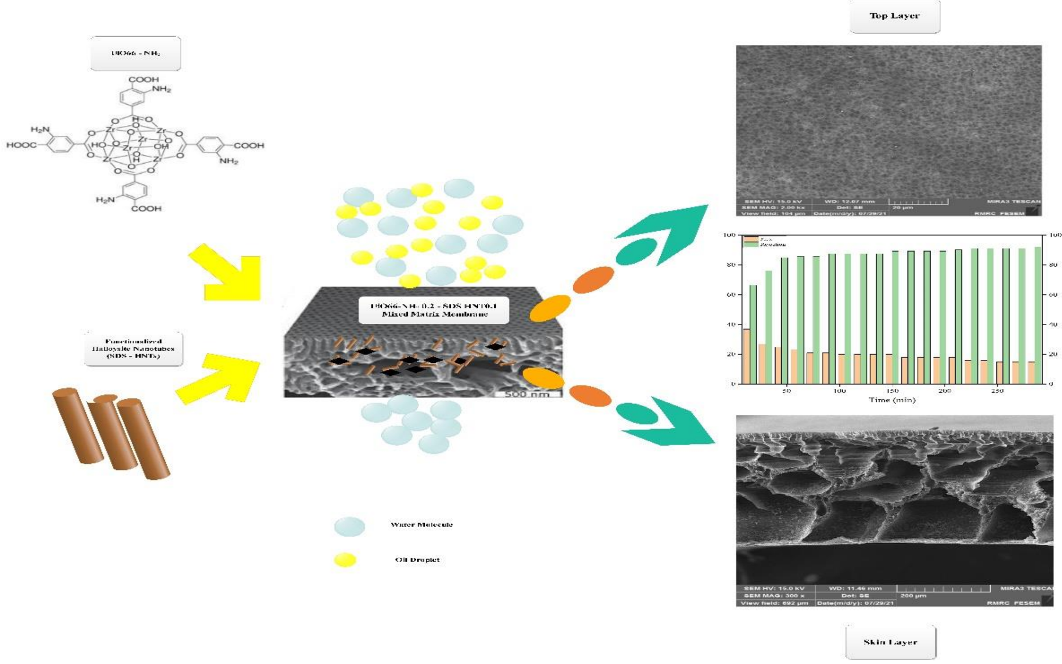
Keywords:
Ultrafiltration
Polyvinyl Chloride
Metal-organic Framework
Halloysite Nanotubes
Sodium Dodecyl Sulfate
Oil/Water Emulsion

ABSTRACT

Membrane technology is known as one of the most efficient and extensive methods for oily wastewater treatment. In this research, polyvinyl chloride (PVC)-based mixed matrix membranes containing Uio66-NH_2 nanoparticles and modified halloysite nanotubes (HNTs) were prepared using the phase inversion method. The synthesized membranes were characterized by field emission scanning electron microscope (FESEM), Fourier transform infrared (FTIR) and contact angle measurement analysis. Then, the effect of these nanoparticles was investigated for oil/water emulsion separation in the ultrafiltration process. To evaluate the prepared membranes, pure water flux, mean pore size, and oil separation ultrafiltration tests were performed. The results exhibited that addition of HNTs to the casting solution enhanced the pure water flux about up to 4 folds. Overall experimental results showed that due to the uniform distribution of halloysite nanotubes in sample 2, water contact angle decreased from 81° to 72°. UF results confirmed that sample 2 had the potential of rejecting 97% of sunflower oil.

***doi**: 10.5829/ije.2024.37.09c.03*

Graphical Abstract



---

*Corresponding Author Email: nimanabian@mazust.ac.ir (N. Nabian)

Please cite this article as: Ghaedi N, Nabian N, Delavar M, Amid M. Application of Polyvinyl Chloride- Halloysite Nanotubes/Uio66-NH_2 Mixed Matrix Membranes in Separation of Sunflower Oil from Water. International Journal of Engineering, Transactions C: Aspects. 2024;37(09): 1736-45.

1. INTRODUCTION

Oily effluents in many industries such as oil refineries, petrochemicals, food, and leather industries, are produced. These wastes effluents must be separated before reused the water in the process or discharge it into the surface water (1-4). Membrane technology is an extensive method for oily wastewater treatment. Ultrafiltration membrane is one of the membrane's categories, known as an efficient and effective method of oil separation from oil/water emulsion. The performance of polymeric membranes can be improved by various parameters such as the selection of suitable additives and methods. For example, addition of fillers such as nanoparticles, carbon nanotubes, and graphene oxide can improve the mechanical strength, permeability, and selectivity of the membranes. Also, surface modification of the membrane can enhance its hydrophilicity, antifouling properties, and stability. Moreover, the use of suitable fabrication methods such as phase inversion, electrospinning, interfacial polymerization, stretching, track-etching and electrospinning can control the morphology, pore size, and thickness of the membrane, which can affect its performance. Although there are different membrane fabrication methods, phase inversion is usually used in experimental scale due to its flexibility to control the synthetic parameters and can be done at ambient temperature (5).

Polyvinyl chloride polymer (PVC) is a hydrophobic plastic. Because of low cost, high chemical resistance and mechanical, thermal stability, and solubility in solvents like dimethylacetamide (DMAC), tetrahydrofuran (THF), dimethylformamide (DMF), N-methyl pyrrolidone (NMP)) for making membranes has received attention (6). Also, in recent years, metal-organic frameworks (MOF) have been widely used due to their high thermal stability and chemical, high porosity, adjustable pore size, and low density. In MOF, there are two structural components: secondary building units (SBU), clusters of metal ions, and organic binders that connect the secondary building units and create porous and regular structures (7). Uio66-NH_2 is a type of metal-organic framework (MOF) that has shown better performance compared to other MOFs, due to its high mechanical and chemical stability, and ease of regeneration. Halloysite nanotubes (HNTs) are a type of naturally occurring aluminosilicate mineral with a unique tubular structure that has been the subject of extensive research within various scientific fields. These nanotubes possess an inner diameter that ranges between 10-100 nm and an outer diameter that measures between 30-190 nm. Due to their unique structure, HNTs have numerous potential applications. They have been used in the development of high-performance polymeric membranes, which have shown great promise for use in gas separation, water treatment, and drug delivery. Additionally, HNTs have been explored for their potential as nanocarriers for targeted drug delivery, as well as for their use in tissue engineering and catalysis. Overall, the study of HNTs has proven to be an exciting area of research, with numerous potential applications in a variety of fields. HNTs have high mechanical strength, high thermal stability, and a high surface area, which make them attractive for a range of applications, including catalysis, drug delivery, and membrane technology. In membrane technology, HNTs have been used as fillers in polymeric membranes to improve their mechanical strength, permeability, and selectivity (8, 9). Halloysite nanotubes have received much attention because of mechanical resistance and the high contact surface, thermal stability, and economics (10, 11). Zhang et al. (12) prepared hydrophilic polyvinylidene fluoride composite membranes with dopamine, iron oxide, and modified halloysite nanotubes (HNT @ Fe3O4 / (DA + KH550/ PVDF)) as filler for separation of water and oil. The hydrophilicity and antifouling performance of the membrane was improved by adding nanoparticles. The prepared membrane performed well in oil separation with the highest oil removal rate of 97.2% (12). Kazemi et al. (13) used polyvinyl chloride membranes containing graphene oxide (Go) nanoparticles and modified ones in the process of treating oily wastewater. Their study results showed that by increasing the content of nanoparticles, the hydrophilicity of the membranes decreased. Also, all the membranes containing nanoparticles had a higher pure water flux compared to the base membrane (13). The main goal of this article is to fabricate the mixed matrix membrane-based polyvinyl chloride by mixing MOF and modified halloysite nanotubes.

2. MATERIALS AND METHODS

2. 1. Materials Polyvinyl chloride (PVC) from Abadan Petrochemical Company as basic of the polymeric membrane, N, N-dimethylformamide (DMF) produced by Daejung Korea as the solvent, polyvinyl pyrrolidone (PVP) and halloysite nanotubes (HNT) from Sigma - Aldrich (USA) as membrane additives, zirconium (IV) chloride, and 2-aminoterephthalic acid prepared from Sigma-Aldrich company for the synthesis of metal-organic framework Uio66-NH_2, sodium dodecyl sulfate (SDS- Merck company) as a surfactant, sunflower oil was used to prepare an oil/water emulsion separation.

2. 2. Feed Solution For this purpose, sunflower oil and sodium dodecyl sulfate as a stabilizer were mixed in a ratio of 3 to 1 in one liter of deionized water. The mixture was stirred at 3000 rpm by a mechanical stirrer for 5 hours. Finally, the oil is completely dispersed in the water and a stable milky emulsion is obtained.

2. 3. Surface Modification of Halloysite Nanotubes In this method, the surface of halloysite nanotubes was modified by SDS anionic modifier that was described in our previous work (14).

2. 4. Synthesis of Uio66-NH$_2$ The procedure involves stirring the mixture of 2-amino terephthalic acid, zirconium chloride and DMF for 30 minutes, transferring it to an autoclave, and heating it at 120 °C for 24 hours. The resulting solid is then washed several times with DMF and methanol, followed by drying at room temperature and then in an oven at 150 °C for 4 hours (15).

2. 5. Preparation of Ultrafiltration Membranes To fabricate mixed matrix membranes (MMMs), the phase inversion method was used. This method has been fully described in our previous studies (14, 16). Table 1 shows the composition of the casting solutions of the MMMs. Furthermore, for better interpretation of the process, the UF setup is shown in Figure 1.

2. 6. Characterization of Synthesized Membranes In order to analyze the surface morphology of the membranes in detail, a field emission scanning electron microscope (FESEM) was used. This microscopy technique is known for its high resolution, and it allowed for imaging of surface features at the nanoscale. Fourier transform infrared (FTIR) spectroscopy was employed to investigate the functional groups of the membranes. FTIR works by measuring the absorption or transmission of infrared radiation by a sample, which can provide detailed information about the molecular bonds and functional groups present in the material. Furthermore, the surface hydrophilicity of the mixed matrix membranes was evaluated with a contact angle meter. This device measures the angle between a liquid droplet and a solid surface, providing information about the wettability of the surface and its ability to interact with different liquids. In addition, X-ray diffraction (XRD) was used to observe the crystal structure of the synthesized Uio66-NH$_2$ metal-organic framework. XRD works by measuring the diffraction pattern of X-rays as they interact with the crystal lattice of a material, which can provide detailed information about its crystal structure. BET analysis was used to determine the pore size distribution, pore volume, and specific surface area of the synthesized Uio66-NH$_2$ metal-organic framework. This involved measuring the amount of gas adsorbed onto a material at different pressures, providing in-depth information about its porosity and surface area. Finally, to further characterize the synthesized membranes, tests were conducted on water flux and oil rejection, mean pore size, and porosity. These tests likely involved measuring the rate of water or oil flow through the membranes, as well as the size and distribution of the pores within the material (14, 16).

TABLE 1. Composition of membrane casting solution

Sample	MOF (wt%)	PVP (wt%)	PVC (wt%)	SDS-HNT (wt%)	DMF (wt%)
1	0.2	1	8	-	90.8
2	0.2	1	8	0.1	90.7
3	0.2	1	8	0.2	90.6
4	0.2	1	8	0.3	90.5

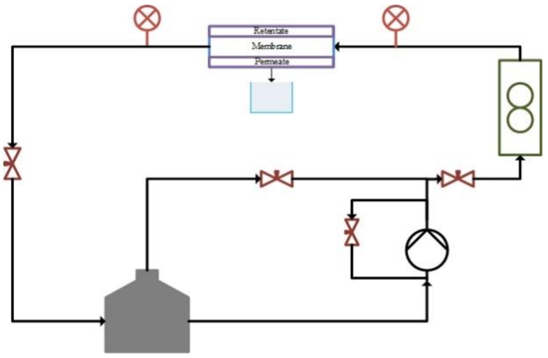


Figure1. UF Experimental setup

3. RESULTS AND DISCUSSION

3. 1. Characterization of synthesized Uio66-NH$_2$ To investigate the crystalline structure of the synthesized metal-organic framework, X-ray diffraction (XRD) patterns of the synthesized nanostructures were prepared and the results are shown in Figure 2. The observed peaks in region 2θ around 7 to 10 degrees indicate the cubic crystal structure of Uio66-NH$_2$. The two main peaks observed at 2θ = 7.4° (111) and 2θ=8.3° (200) are related to the crystalline structure of Uio66-NH$_2$ and crystal planes, respectively (17, 18). BET test for surface area, total pore volume, and average pore diameter of the synthesized material has showed values of 371.71 m^2/g, 3.7248 nm, and 0.3461 cm^3/g, respectively.

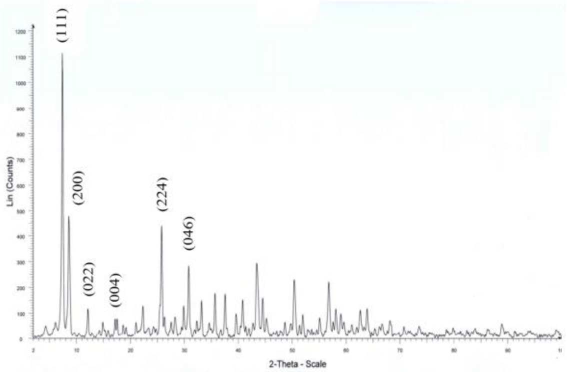


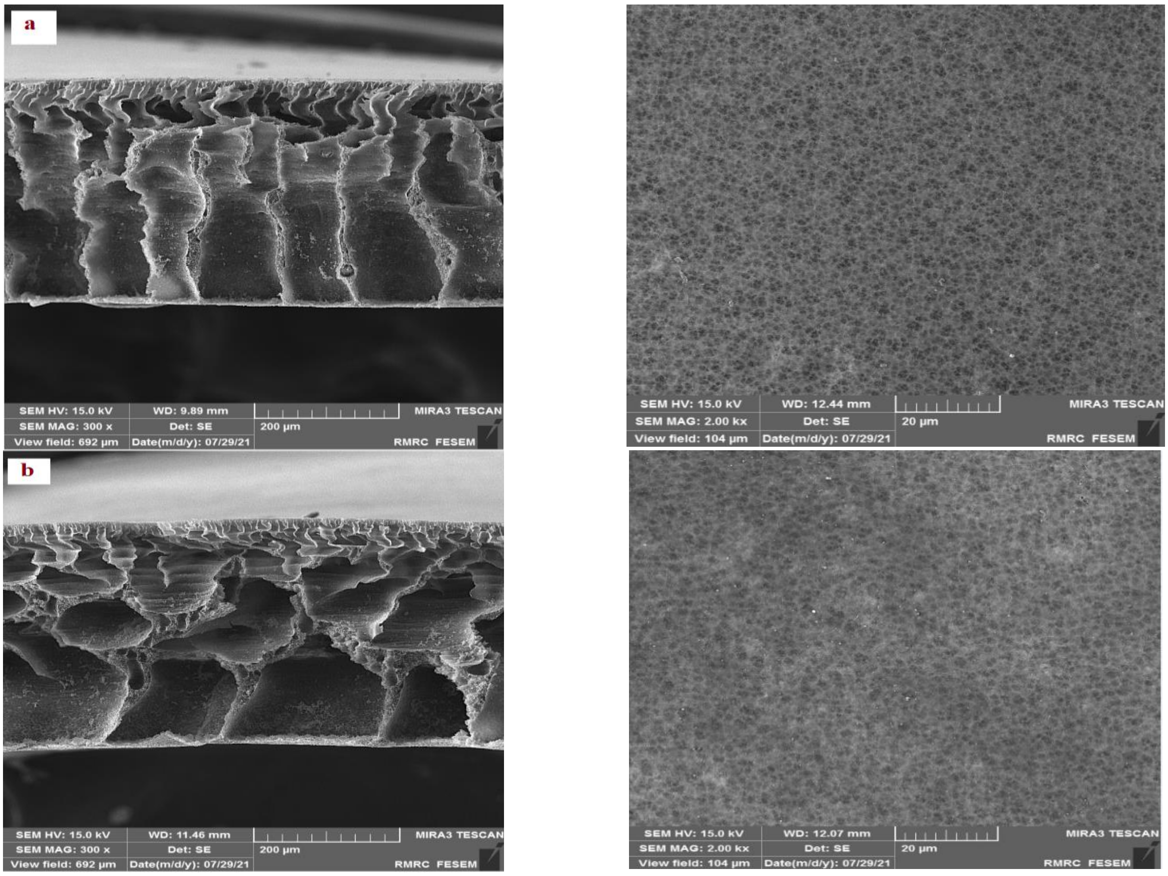
Figure 2. XRD pattern of synthesized Uio66-NH$_2$

3. 2. Characterization of Fabricated Membranes

3. 2. 1. FESEM Image FESEM analysis was used to check the morphology and surface structure of the synthesized membranes. For this purpose, the picture of the cross sections and upper surfaces of the samples have shown in Figure 3.

As can be seen, sample 1 has a finger-like structure. The macro pores of the bottom layer have grown by adding nanoparticles to the casting solution. Also, the addition of Uio66-NH_2 creates the largest macro pores in the membrane of sample 1, which can cause the passing of water through the mixed matrix membrane. In sample 2, the pores of the membrane have become larger than in sample 1. The FESEM images show that the ores in the layer of sample 2 are larger than the other ones. In other words, after the addition of modified halloysite nanotubes, hydrophilicity increases and water penetration occurs faster in the phase separation. In sample 3 narrow and short pores and large finger ores have been created. Increasing hydrophilicity makes the addition of water permeation, and as a result, the surface porosity also increases (19). As can be seen, in samples 2 and 3, the porosity increases compared to sample 1 as a result of the pure water flux. In sample 4, there are many elongated long finger-like structures.

Based on Figure 3, it was found that incorporating modified halloysite nanotubes into the membrane matrix resulted in a significant reduction in the formation of finger-like structures. This effect was attributed to the increase in viscosity of the casting solution, which can be explained by the larger size and altered surface characteristics of the modified nanotubes (20, 21). The study also explored the role of sodium dodecyl sulfate surfactant in the membrane formation process and found that it can further increase the viscosity of the casting solution. By applying the surfactant on the surface of the nanoparticles, it creates a uniform layer that promotes better dispersion of the nanoparticles in the casting solution (22). Moreover, the study investigated the distribution of nanoparticles in the prepared membrane using FESEM images. The images revealed that samples 1 and 2 exhibited a uniform distribution of nanoparticles in the membrane matrix, while samples 3 and 4 showed accumulation of nanoparticles in certain areas of the membrane matrix. This suggests that the addition of modified halloysite nanotubes, in combination with the appropriate surfactant, can enhance the uniformity and integrity of the membrane structure (23).



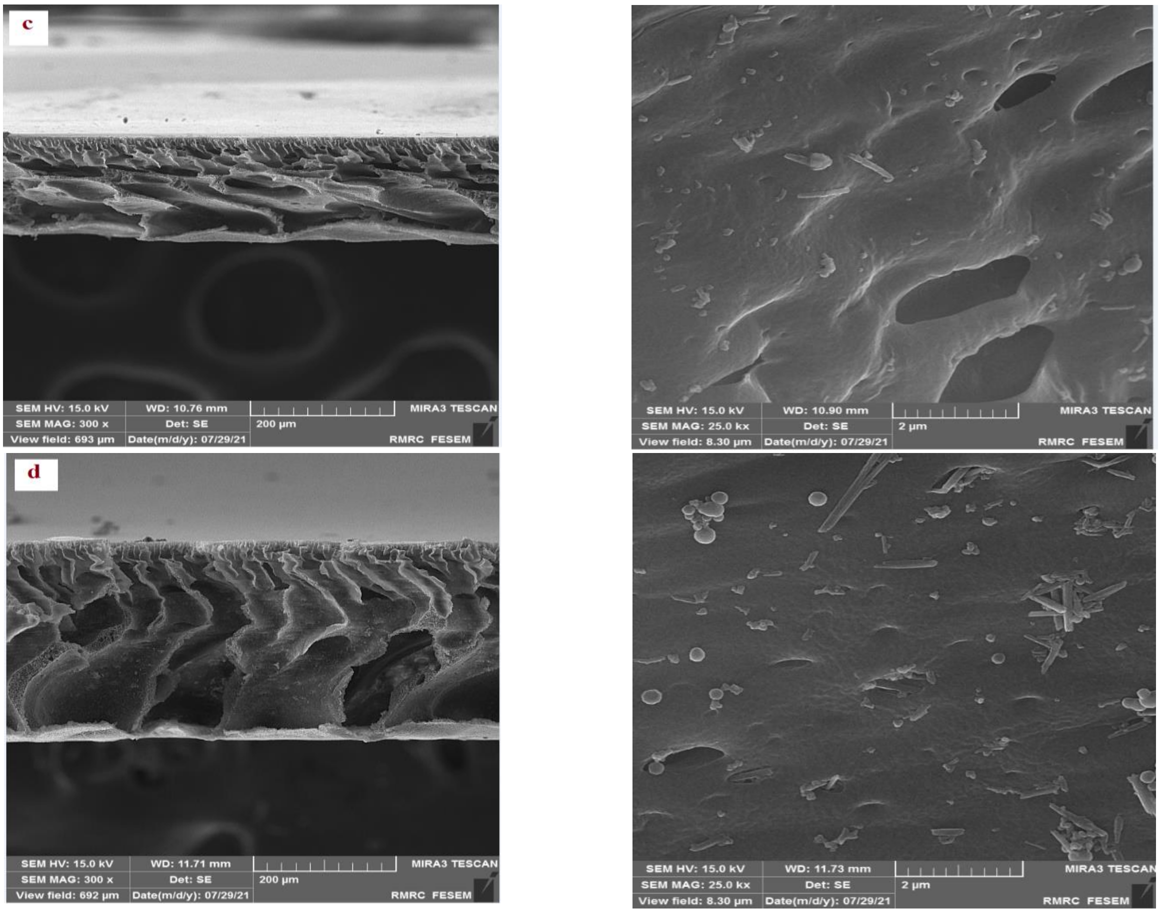


Figure 3. FESEM images of prepared mixed matrix membranes a: sample 1, b: sample 2, c: sample 3, d: sample 4

3. 2. 2. FTIR Pattern

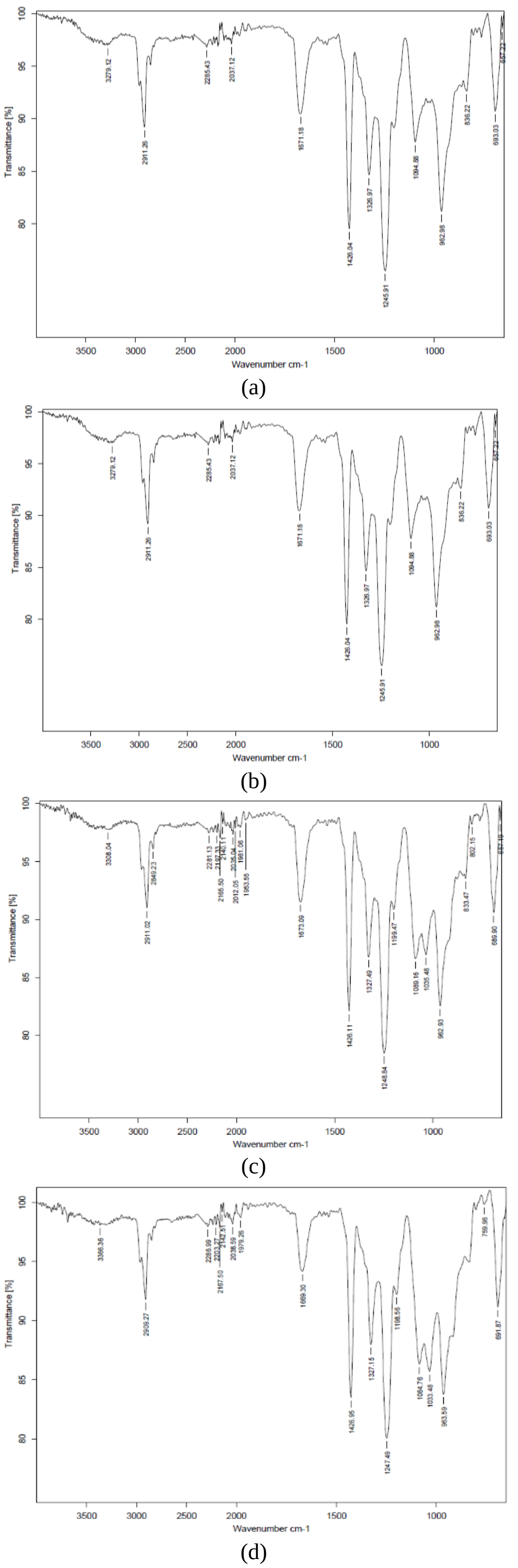
The fabricated membranes were analyzed using FTIR spectroscopy, and the results are presented in Figure 4 and the peaks attributed to PVC matrix were listed in Table 2. The FTIR spectrum displays peaks that correspond to different functional groups present in the material. The peak appearing at 3279 cm^{-1} is related to the vibrations of the NH_2 functional group, which confirms the presence of Uio66-NH_2 nanoparticles in the membrane. The vibrations of the N-H bond can be seen at the wavelength of 1671 cm^{-1}, which also supports the presence of the NH_2 functional group. The peak observed at 1426 cm^{-1} can be attributed to the stretching vibrations of the C-N bond, and it could also be related to the presence of the NH_2 functional group. The peak at 1326 cm^{-1} may be caused by the stretching vibrations of the hydroxyl functional group, which suggests the presence of modified halloysite nanotubes in the membrane. The peak at 1199 cm^{-1} can be attributed to the stretching vibration of the S=O bond, which may be related to the presence of other functional groups or impurities in the material. The peak appearing at the wavelength of 3454 cm^{-1} is due to absorbed water on the surface of halloysite nanotubes, which could indicate the presence of moisture in the sample or adsorbed water on the surface of the nanotubes. Finally, the weak peak created at the wavelength of 2850 cm^{-1} could be caused by the vibrations of the aliphatic or aromatic C-H bonds in the solvent. This peak may be related to residual solvent in the sample or to the presence of other organic compounds in the material (24-29).

3. 2. 3. Properties of Membranes

Table 3 provides detailed information on the synthesized membranes' properties, namely their mean pore size

TABLE 2. The paeks of PVC matrix

Wavenumber (cm^{-1})	Assignment	Ref.
2910-2912	C-H stretching vibration	
1427	CH_2-Cl angular deformation	
1327	CH_2 deformation group	
1245	CH-Cl out of plane angular deformation	(30)
1093	C-C stretching bond vibration	
961-963	C-H out of plane trans deformation	
689-693	C-Cl stretching vibration	



(a)

(b)

(c)

(d)

Figure 4. FTIR analysis of fabricated mixed matrix membranes A: sample 1, B: sample 2, C: sample 3, D: sample 4

(MPS), contact angle, and porosity, after the addition of modified halloysite nanotubes. The data shows that the mean pore size of the membranes increased with the addition of nanoparticles, reaching the maximum value in sample 2. Thereafter, it gradually decreased with the increasing nanotube loading due to the displacement rate of nonsolvent and solvent during the membrane formation process. This phenomenon can cause larger pores on the membrane surface. However, the mean pore size reduced upon increasing halloysite nanotube loading at 3%, which could be due to the increase in the viscosity of the casting solution. The contact angle of the membranes decreased with the addition of nanoparticles, indicating an increase in hydrophilicity. This could be due to the presence of hydrophilic functional groups on the surface of nanoparticles that enhance the membrane's wettability. However, in samples 3 and 4, the contact angle increased due to the agglomeration of nanotubes, which reduced the hydrophilicity of the membrane. Furthermore, the porosity of the membranes increased with the addition of nanoparticles. This is likely because the presence of nanoparticles can increase the number of voids or pores in the membrane, leading to an increase in overall porosity.

3. 3. Ultrafiltration Tests

3. 3. 1. PWF The experiment involved measuring the pure water flux (PWF) of the synthesized membranes and presenting the results in Figure 5. It was observed that the addition of nanoparticles to the casting solution had a positive impact on the PWF of the membrane. The improvement in PWF is attributed to the hydrophilic properties of the Uio66-NH_2 nanoparticles and modified halloysite nanotubes, which can enhance the membrane's ability to transport water. The hydrophilic properties of the nanoparticles increase the surface energy of the membrane and attract water molecules, which ultimately leads to enhanced PWF. However, it was also noted that at the highest loading of modified halloysite nanotubes, the PWF decreases. This is most likely due to the agglomeration of the nanotubes, which leads to the formation of larger pores and a decrease in the hydrophilicity of the membrane. It is important to note that the optimal loading of nanoparticles is dependent on various factors, such as the specific application of the membrane and the desired properties of the material. The

TABLE 3. Properties of resulting membranes

Sample	Porosity (%)	Mean pore size (nm)	Contact angle (°)
1	92.233	13.801	**81**
2	91.981	25.550	**72.6**
3	92.040	23.653	**76.4**
4	92.484	22.222	**90.6**

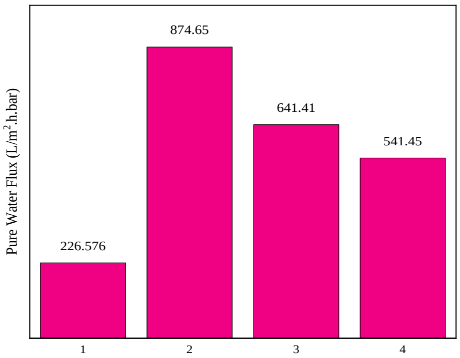


Figure 5. Pure water flux of resulting membranes

increase in PWF with an increase in nanoparticle loading is not linear, and there is an optimum concentration at which the highest PWF is achieved. Beyond this optimal concentration, the PWF decreases, as observed in the experiment. Therefore, it is important to optimize the nanoparticle loading for the specific application of the membrane to achieve the best possible results (30).

3. 3. 2. Ultrafiltration Experiments on Sunflower Oil Removal

The separation of sunflower oil/water emulsions was done by selected membranes (samples 1 and 2) at 1 bar and ambient temperature. For this purpose, the feed solution is prepared at different concentrations of 120 mg/L, 80 mg/L, 40 mg/L, and selected membranes are examined for sunflower oil removal.

In the context of oil/water emulsion separation experiments, it has been observed that the percentage of oil rejection increases as the duration of the ultrafiltration process is prolonged. After approximately two hours, this percentage reaches a steady value. The increase in the amount of oil removal can be explained by the formation of an oily cake layer on the surface of the membrane, which can block some of the surface pores or reduce their size. This ultimately leads to a reduction in the permeation flux of the membrane, thereby negatively impacting its overall performance. The study has shown that the selected membranes exhibited an increase in removal efficiency with the gradual increase of time in the ultrafiltration tests, while the permeation flux decreased due to the blockage of pores. This is indicative of the fact that the membrane's efficiency in oil/water emulsion separation improves significantly with time. However, the reduction of the permeation flux caused by the deposition of the oily cake layer can be mitigated by reducing the membrane's tendency to adsorb oil on its surface. This can be achieved by reducing the contact angle and improving the hydrophilic properties of the membrane, which in turn can help to mitigate the reduction in permeation flux caused by the deposition of the oily cake layer. Overall, the results highlight the importance of balancing oil rejection performance and permeation flux to develop high-performance membranes for oil/water emulsion separation applications. This is particularly important because the oily cake layer formation is a natural consequence of the separation process, and it can negatively impact the overall performance of the membrane in terms of both oil rejection and permeation flux. Therefore, any strategy to improve the performance of the membrane must address this issue (31). Figure 6 shows the rejection efficiency and permeate volume of the selected membranes at 40 ppm feed concentration. Figures 7 and 8 illustrate the rejection efficiencies and permeate volumes of the selected membranes at 80 ppm feed concentrations of 80 and 120 ppm, respectively.

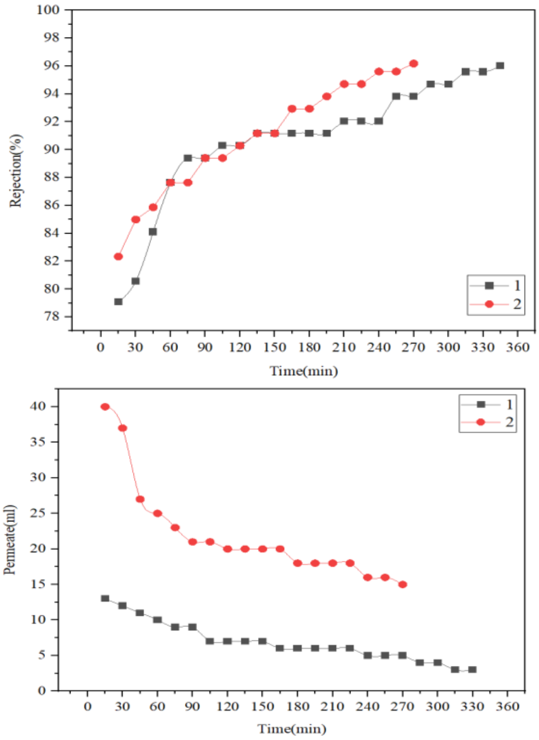
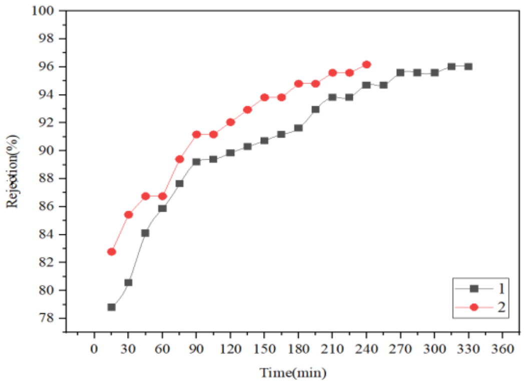


Figure 6. Rejection efficiency and permeate volume of selected membranes at 40 ppm feed concentration



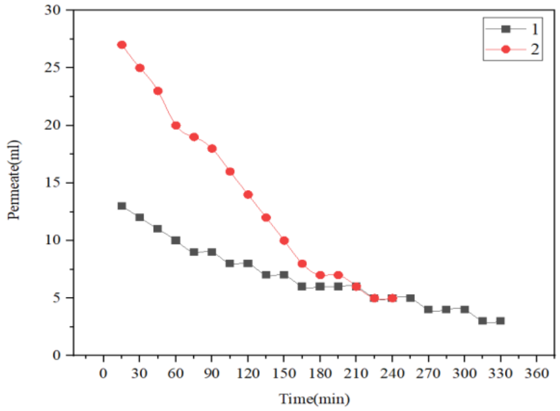


Figure 7. Rejection efficiency and permeate volume of selected membranes at 80 ppm feed concentration

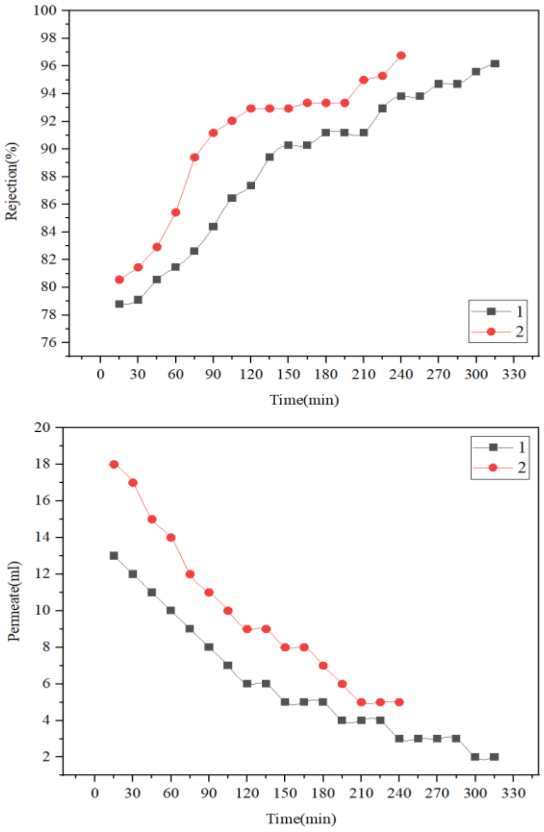


Figure 8. Rejection efficiency and permeate volume of selected membranes at 120 ppm feed concentration

4. CONCLUSIONS

PVC-based membranes comprising Uio66-NH2 were synthesized by the method of phase inversion and were subsequently modified with halloysite nanotubes to improve their performance and properties for separating sunflower oil/water emulsion. The following general results were observed: FTIR and SEM results confirmed the presence of MOF and modified halloysite nanotubes in the membrane structure. FESEM images of the membranes showed that the membrane structure became finger-like. The membrane with 0.1% loading of modified halloysite nanotubes had larger macropores, and samples 1 and 4 had a longer finger-like structure than other samples, which can affect factors such as the mean pore size, PWF, and separation rate. Sample 2 had the lowest contact angle and the highest hydrophilicity, indicating that it had the best water-wettability. By adding nanoparticles to the mixed matrix membranes, the PWF, hydrophilicity, and mean pore size of the membranes increased. Based on these results, membrane sample 2 was considered as the optimal membrane for the separation of sunflower oil/water emulsions. It is worth mentioning that these results verifies the application of low-cost membranes like PVC in membrane separation processes. Furthermore, the optimum fabricated membrane can be recognized as a good candidate in sunflower production industry. It is clear that the membrane performance is strongly dependent on the area of mixed matrix membrane that was assembled in the module. In this work, only one sheet of MMM with effective surface of about 36 cm^2 was used for the oil removal process in an experimental scale whereas for industrial separation processes, a number of membrane modules can be combined to form a membrane stack that increases the effective area of MMM. Therefore, by increasing the effective area of the applied MMM using some individual membrane modules in the stack form, this fabricated membrane can be applied in industrial wastewaters.

5. REFERENCES

1. Salahshoori I, Seyfaee A, Babapoor A. Recent advances in synthesis and applications of mixed matrix membranes. Synthesis and Sintering. 2021;1(1):1-27. https://doi.org/10.53063/synsint.2021.116
2. Grylewicz A, Mozia S. Polymeric mixed-matrix membranes modified with halloysite nanotubes for water and wastewater treatment: A review. Separation and Purification Technology. 2021;256:117827. https://doi.org/10.1016/j.seppur.2020.117827
3. Wang L, Huang J, Li Z, Han Z, Fan J. Review of synthesis and separation application of metal-organic framework-based mixed-matrix membranes. Polymers. 2023;15(8):1950. https://doi.org/10.3390/polym15081950
4. Abuhantash F, Abuhasheesh YH, Hegab HM, Aljundi IH, Al Marzooqi F, Hasan SW. Hydrophilic, oleophilic and switchable Janus mixed matrix membranes for oily wastewater treatment: A review. Journal of Water Process Engineering. 2023;56:104310. https://doi.org/10.1016/j.jwpe.2023.104310
5. Lalia BS, Kochkodan V, Hashaikeh R, Hilal N. A review on membrane fabrication: Structure, properties and performance relationship. Desalination. 2013;326:77-95. https://doi.org/10.1016/j.desal.2013.06.016
6. Akhair S, Harun Z, Basri H, Ahmad R, Rashid A, Azhar FH. Hydrophobicity properties of graphite and reduced graphene

oxide of the polysulfone (PSf) mixed matrix membrane. International Journal of Engineering, Transactions B: Applications, . 2018;31(8):1381-8. 10.5829/ije.2018.31.08b.29

7. Gholami F, Zinadini S, Zinatizadeh A, Noori E, Rafiee E. Preparation and characterization of an antifouling polyethersulfone nanofiltration membrane blended with graphene oxide/ag nanoparticles. International Journal of Engineering, Transactions A: Basics. 2017;30(10):1425-33. 10.5829/ije.2017.30.10a.02
8. Aripin H, Priatna E, Dedi D, Sudiana I, Sabchevski S. Characterization of Ceramic Membrane based on Calcium Carbonate from Onyx Stone and Its Application for Coconut Sap Treatment. International Journal of Engineering, Transactions B: Applications,. 2022;35(2):300-6. 10.5829/IJE.2022.35.02B.05
9. Lee W, Goh P, Lau W, Ong C, Ismail A. Zwitterion Embedded Thin Film Composite Membrane for Oily Wastewater Treatment. International Journal of Engineering, Transactions B: Applications. 2018;31(8):1464-72. 10.5829/ije.2018.31.08b.39
10. Tuswan T, Sari E, Ismail A, Prabowo A. Experimental evaluation on palm oil and sesame oil-based resin properties as core sandwich material for lightweight ship structure. International Journal of Engineering, Transactions C: Aspects. 2022;35(9):1690-8. 10.5829/ije.2022.35.09c.03
11. Rakhshani N, Hassanzadeh Nemati N, Ramezani Saadatabadi A, Sadrnezhaad S. Fabrication and evaluation of controlled release of Doxorubicin loaded UiO-66-NH2 metal organic frameworks. International Journal of Engineering, Transactions B: Applications,. 2021;34(8):1874-81. 10.5829/IJE.2021.34.08B.08
12. Zhang R, Liu Y, Zhu X, Cai Y, Li Y, Han Q, et al. A modified, mussel-inspired method to fabricate polyvinylidene fluoride membranes filled with halloysite nanotubes modified with dopamine, iron oxide, and silane for oil–water separation. Journal of Plastic Film & Sheeting. 2019;35(3):260-80. https://doi.org/10.1177/875608791881779
13. Kazemi F, Jafarzadeh Y, Masoumi S, Rostamizadeh M. Oil-in-water emulsion separation by PVC membranes embedded with GO-ZnO nanoparticles. Journal of Environmental Chemical Engineering. 2021;9(1):104992. https://doi.org/10.1016/j.jece.2020.104992
14. Amid M, Nabian N, Delavar M. Fabrication of polycarbonate ultrafiltration mixed matrix membranes including modified halloysite nanotubes and graphene oxide nanosheets for olive oil/water emulsion separation. Separation and purification technology. 2020;251:117332. https://doi.org/10.1016/j.seppur.2020.117332
15. Tambat SN, Sane PK, Suresh S, Varadan N, Pandit AB, Sontakke SM. Hydrothermal synthesis of NH2-UiO-66 and its application for adsorptive removal of dye. Advanced Powder Technology. 2018;29(11):2626-32. https://doi.org/10.1016/j.apt.2018.07.010
16. Amid M, Nabian N, Delavar M. Performance evaluation and modeling study of PC blended membranes incorporated with SDS-modified and unmodified halloysite nanotubes in the separation of oil from water. Journal of Environmental Chemical Engineering. 2021;9(4):105237.
17. Zhang W, Huang H, Zhong C, Liu D. Cooperative effect of temperature and linker functionality on CO 2 capture from industrial gas mixtures in metal–organic frameworks: a combined experimental and molecular simulation study. Physical Chemistry Chemical Physics. 2012;14(7):2317-25. https://doi.org/10.1039/C2CP23839J
18. Cavka JH, Jakobsen S, Olsbye U, Guillou N, Lamberti C, Bordiga S, et al. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. Journal of the American Chemical Society. 2008;130(42):13850-1. https://doi.org/10.1021/ja8057953
19. Behboudi A, Jafarzadeh Y, Yegani R. Preparation and characterization of TiO2 embedded PVC ultrafiltration membranes. chemical engineering research and design. 2016;114:96-107. https://doi.org/10.1016/j.cherd.2016.07.027
20. Bakeri G, Ismail A, DashtArzhandi MR, Matsuura T. Porous PES and PEI hollow fiber membranes in a gas–liquid contacting process—A comparative study. Journal of Membrane Science. 2015;475:57-64. https://doi.org/10.1016/j.memsci.2014.09.037
21. Ren J, Zhou J, Deng M. Morphology transition of asymmetric polyetherimide flat sheet membranes with different thickness by wet phase-inversion process. Separation and purification technology. 2010;74(1):119-29. https://doi.org/10.1016/j.seppur.2010.05.014
22. Yang Y, Chen Y, Leng F, Huang L, Wang Z, Tian W. Recent advances on surface modification of halloysite nanotubes for multifunctional applications. Applied Sciences. 2017;7(12):1215. https://doi.org/10.3390/app7121215
23. Vermoortele F, Ameloot R, Vimont A, Serre C, De Vos D. An amino-modified Zr-terephthalate metal–organic framework as an acid–base catalyst for cross-aldol condensation. Chemical communications. 2011;47(5):1521-3. 10.1039/C0CC03038D
24. Kandiah M, Usseglio S, Svelle S, Olsbye U, Lillerud KP, Tilset M. Post-synthetic modification of the metal–organic framework compound UiO-66. Journal of Materials Chemistry. 2010;20(44):9848-51. 10.1039/C0JM02416C
25. Embaby MS, Elwany SD, Setyaningsih W, Saber MR. The adsorptive properties of UiO-66 towards organic dyes: A record adsorption capacity for the anionic dye Alizarin Red S. Chinese journal of chemical engineering. 2018;26(4):731-9. https://doi.org/10.1016/j.cjche.2017.07.014
26. Molavi H, Eskandari A, Shojaei A, Mousavi SA. Enhancing CO2/N2 adsorption selectivity via post-synthetic modification of NH2-UiO-66 (Zr). Microporous and Mesoporous Materials. 2018;257:193-201. https://doi.org/10.1016/j.micromeso.2017.08.043
27. Mahdiani M, Sobhani A, Ansari F, Salavati-Niasari M. Lead hexaferrite nanostructures: green amino acid sol–gel auto-combustion synthesis, characterization and considering magnetic property. Journal of Materials Science: Materials in Electronics. 2017;28:17627-34. https://doi.org/10.1007/s10854-017-7701-0
28. Albdiry M, Yousif B. Morphological structures and tribological performance of unsaturated polyester based untreated/silane-treated halloysite nanotubes. Materials & Design. 2013;48:68-76. https://doi.org/10.1016/j.matdes.2012.08.035
29. Wypych F, Schreiner WH, Richard Jr E. Grafting of phenylarsonic and 2-nitrophenol-4-arsonic acid onto disordered silica obtained by selective leaching of brucite-like sheet from chrysotile structure. Journal of colloid and interface science. 2004;276(1):167-73. https://doi.org/10.1016/j.jcis.2004.03.022
30. Mohammadipour E, Nabian N, Delavar M. Novel PVC-melamine mixed matrix membranes for the Sirius Red removal from aqueous solutions: Experimental study and RSM modeling. Journal of Water Process Engineering. 2022;47:102752. https://doi.org/10.1016/j.jwpe.2022.102752
31. Amid M, Nabian N, Delavar M. Functionalized halloysite nanotubes and graphene oxide nanosheets fillers incorporated in uf membranes for oil/water separation. International Journal of Engineering, Transactions A: Basics. 2023;36(7):1201-10. 10.5829/IJE.2023.36.07A.01

Persian Abstract

چکیده

تکنولوژی غشایی به عنوان یکی از روش های کارآمد برای تصفیه فاضلاب روغنی شناخته شده است. در این تحقیق، غشاهای ماتریس مخلوط برپایه پلی وینیل کلرید (PVC)حاوی ترکیبات Uio66-NH_2 و نانولوله های هالوسیت اصلاح شده با استفاده از روش وارونگی فاز تهیه شدند. غشاهای سنتز شده توسط آنالیزهای FESEM، FTIR و اندازه‌گیر زاویه تماس مشخصه‌یابی شدند. سپس اثر این نانوذرات برای جداسازی امولسیون روغن/آب در فرآیند اولترافیلتراسیون بررسی شد. برای ارزیابی غشاهای سنتز شده، آزمایش‌های اولترافیلتراسیون فلاکس آب خالص، میانگین اندازه حفرات و جداسازی روغن انجام شد. نتایج نشان داده که تمام غشاهای ماتریس مخلوط ساخته شده دارای شار آب خالص خوبی هستند. نتایج تجربی کلی نشان داده که به دلیل توزیع یکنواخت نانولوله‌های هالوسیت، نمونه ۲ دارای میانگین اندازه حفرات، تخلخل و شار آب خالص بالاتری نسبت به نمونه‌های دیگر است. همچنین نمونه ۲ زمان جداسازی کمتر و بازده حذف روغن بالاتری نسبت به غشای PVC خالص داشته است.