Nanotechnology Perceptions
ISSN 1660-6795
www.nano-ntp.com

Enhancing Wastewater Treatment Efficiency: A Comparative Analysis of Fabricated PES and PES/GO Nanomembranes

Noura Al Balushi , Marwan Al-Sahbani, Ghaydah Al-Abri, Aryam Al Uraimi

[1]*National university of science and technology, Muscat, Oman*
Email: nouraalbalushi@nu.edu.om

This study focuses on tackling challenges in petroleum and oil extraction wastewater treatment, particularly the separation of heavy crude oil from water and membrane fouling. The project aims to enhance wastewater treatment efficiency by developing a nanomembrane that improves selectivity, efficiency, and filtration performance. The proposed solution involves modifying polyethersulfone (PES) membranes with graphene oxide (GO) nanoparticles. Analysis reveals that the fabricated membrane consists of 75.3% carbon (C), 13.8% oxygen (O), and 10.3% sulfur (S), indicating the presence of carbon-based materials, organic compounds, and oxygen-containing functional groups. The incorporation of GO enhances hydrophilicity, resulting in improved water permeability with values of 31.467 L/m².hr for the PES/GO membrane and 25.525 L/m².hr for the pure PES membrane. Both membranes effectively remove salts, with salt rejection values of 14.5% and 12.5% for PES/GO and pure PES membranes, respectively. These findings contribute to sustainable wastewater management solutions.

Keywords: Petroleum wastewater treatment, Nanomembrane, Graphene oxide, Polyethersulfone (PES) membrane, Membrane fouling.

1. Introduction

The treatment of wastewater generated from petroleum and oil extraction processes is a significant challenge faced by the industry. This wastewater, often referred to as produced water, contains various contaminants, including heavy crude oil and other pollutants, making it difficult to separate and treat effectively. The accumulation of oil and contaminants on the membranes used in the treatment process further exacerbates the issue, leading to membrane fouling and reduced treatment efficiency. Therefore, there is a critical need to develop innovative and efficient wastewater treatment technologies to overcome these challenges. The objective of this report is to address the challenges associated with petroleum and oil extraction wastewater treatment and explore the potential of using polyethersulfone (PES) and

PES/graphene oxide (GO) membranes to enhance the efficiency of the treatment process. These membranes are designed to improve selectivity, efficiency, and filtration performance, ultimately leading to improved wastewater treatment in crude oil extraction operations. Petroleum and oil extraction wastewater contains heavy crude oil, which poses a significant challenge in the treatment process. Traditional treatment methods struggle to effectively separate the oil from water due to the complex nature of the emulsions formed [1]. Additionally, the presence of other contaminants further complicates the treatment process. Membrane-based filtration is a promising technology for treating such wastewater, as it offers high efficiency and selectivity. However, the fouling of membranes due to the accumulation of oil and contaminants hinders their performance and necessitates frequent cleaning and replacement, leading to increased operational costs [2]. To address these challenges, the proposed solution involves the development of a fabricated nanomembrane using PES and graphene oxide nanoparticles. Graphene oxide, derived from graphene through a series of chemical processes, offers unique properties such as high surface area, mechanical strength, and chemical stability. By incorporating graphene oxide nanoparticles into the PES membrane, its performance can be enhanced, specifically in terms of pollutant removal from wastewater and resistance to membrane fouling [3]. The methodology for this project includes the synthesis of graphene oxide nanoparticles, fabrication of the nanomembrane, and subsequent testing and characterization. Fourier Transform Infrared Spectroscopy (FTIR) analysis confirms the presence of the PES membrane and graphene oxide nanoparticles, validating the successful modification of the membrane. Scanning electron microscopy (SEM) analysis further reveals a uniform structure with a homogeneous distribution of particles throughout the fabricated membrane, indicating consistent composition across the sample. Elemental composition analysis using Energy Dispersive X-ray (EDX) demonstrates the presence of carbon-based materials, organic compounds, and oxygen-containing functional groups within the membrane [4]. The incorporation of graphene oxide into the PES membrane enhances its hydrophilicity, as evidenced by the presence of hydroxyl (O-H) and carbonyl (C=O) functional groups in the FTIR spectrum. This improved hydrophilicity leads to enhanced water permeability and flux, as demonstrated by water flux measurements. Moreover, the PES/GO membrane exhibits effective salt rejection, indicating its ability to remove salts from the wastewater. These findings highlight the potential of the PES/GO membrane as a sustainable solution for managing industrial and domestic effluents [5]. In conclusion, the treatment of wastewater generated from petroleum and oil extraction operations presents significant challenges due to the difficulty of separating heavy crude oil from water and the issue of membrane fouling. The utilization of PES and PES/GO membranes offers a promising approach to enhance the efficiency of wastewater treatment by improving selectivity, filtration performance, and resistance to fouling. The fabricated nanomembrane, incorporating graphene oxide nanoparticles, demonstrates improved hydrophilicity and water permeability, as well as effective salt rejection. These advancements contribute to the development of sustainable solutions for managing industrial and domestic effluents, addressing the challenges associated with membrane fouling and pollutant removal from wastewater.

2. METHODOLOGY

1. Hummer Method (synthesis of graphene oxide):

The synthesis of graphene oxide (GO) from graphene involves several steps. Initially, a mixture of 175ml HNO3 and 525ml H2SO4 in a 1:3 ratio is prepared in a beaker and cooled in an ice bath. Then, 1.5g of graphene is added to the acid mixture and continuously stirred for 1 hour. Subsequently, 4.5g of KMnO4 is added, and the stirring process is continued for an additional 2 hours. The resulting mixture is transferred to a larger beaker containing 3.5L of deionized water and stirred for 5 minutes, followed by a 24-hour rest period. The GO particles are separated from the solution using a centrifugal device, and subsequent washing with deionized water ensures acid removal. The GO particles are then dried in an oven at 105°C for 2 hours to remove most of the water content, followed by further drying under sunlight. The final product obtained is GO nanoparticles, which can be utilized as sheets or crushed into smaller particles like powder [6].

2. Phase inversion method (membrane Solution):

Table 1: Membrane Samples Ratios.

Material	Sample #	Chemicals			
		PES (g)	PEG (g)	GO (g)	NMP (ml)
PES	Sample 1	4.4	2	0	16
PES/GO	Sample 2	4	2	0.4	16

To prepare a membrane solution, several steps are involved. For sample 1 (Pure PES) a mixture of 4.4 g PES (polyethersulfone), 2g PEG (polyethylene glycol), and 16ml NMP (N-methyl-2-pyrrolidone) is dissolved in one beaker. For sample 2 (PES/GO) initially, 0.4g of graphene oxide (GO) particles is dissolved in 3ml of NMP (N-methyl-2-pyrrolidone) in the first beaker. In another beaker, a mixture of 4g PES (polyethersulfone), 2g PEG (polyethylene glycol), and 13ml NMP (N-methyl-2-pyrrolidone) is prepared. The solutions from both beakers are then combined in a single beaker for sample 2. For both samples, using a magnetic stirrer, the mixture is continuously stirred for a minimum of 24 hours at a temperature of 60°C. Finally, the solution is cast onto a flat glass surface using a glass rod, forming a membrane for further processing or application [7].

3. RESULTS AND DISCUSSION:

- FTIR Test Results:

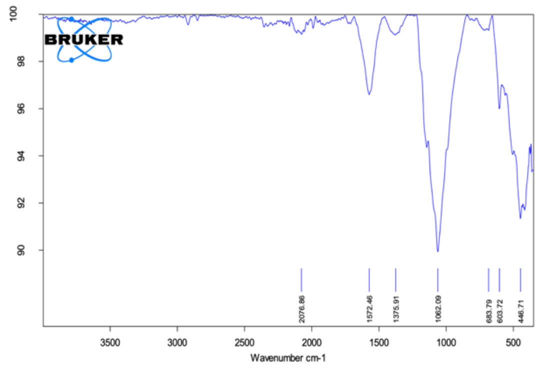

Figure 1: GO NPs FTIR Result.

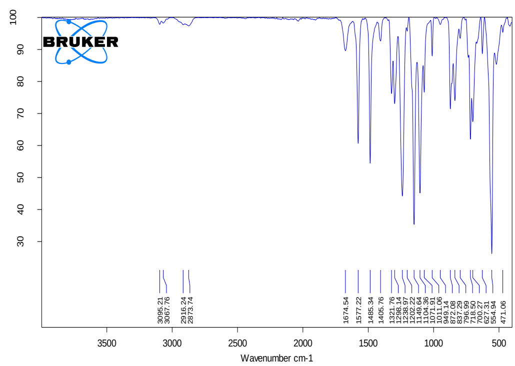

Figure: PES/GO Membrane FTIR Result.

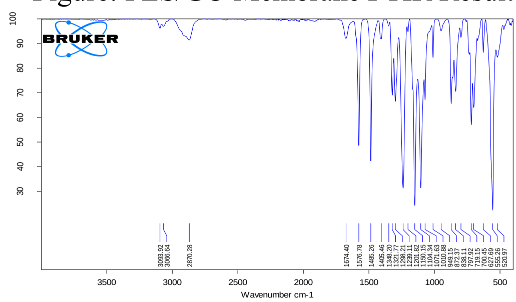

Figure 2: PES Membrane FTIR Result.

The FTIR analysis of graphene oxide (GO) nanoparticles revealed specific peaks at certain wavenumbers, indicating the presence of distinct functional groups. These peaks included 446.71 cm-1 (C-O bonds), 603.72 cm-1 (C-OH bending vibrations), 683.79 cm-1 (C=C out-of-plane bending vibrations), 1062.09 cm-1 (C-O stretching vibrations), 1375.91 cm-1 (C-H bending vibrations), 1572.46 cm-1 (C=C stretching vibrations), and 2076.86 cm-1 (C≡C triple bonds). These results provided evidence of successful oxidation and functionalization of the graphene structure in the GO nanoparticles. Furthermore, the FTIR analysis confirmed the presence of a polyethersulfone (PES) membrane by identifying absorption peaks associated with its composition. The PES Pure membrane exhibited absorption bands that indicated the presence of an aromatic ring (1485.26-1576 cm-1), ether groups (1298.23-1239.11 cm-1), sulfone groups (1010.88-1201.82 cm-1), and aromatic C−H groups (627.96-872 cm-1), providing strong support for the existence of the membrane. When GO was introduced into the PES membrane, the FTIR analysis revealed changes in chemical composition and functional groups. The incorporation of GO increased the hydrophilicity of the membrane, which could be attributed to the presence of hydroxyl (O–H) functional groups. The FTIR spectrum of GO exhibited functional groups such as hydroxyl (O–H) at 3067 cm-1 and carbonyl (C=O) groups. The enhancement of hydroxyl groups in the PES with GO membranes was evidenced by increased peak intensities in the range of 2873–3095 cm-1. The presence of characteristic peaks related to C=O stretching vibrations at 1674 cm-1 confirmed the formation of GO nanosheets, which was consistent with XRD analysis. These findings demonstrate the impact of GO on the chemical and functional properties of the PES membrane, particularly through the enhancement of its hydrophilicity [8], [9].

- SEM and EDX Test Results:

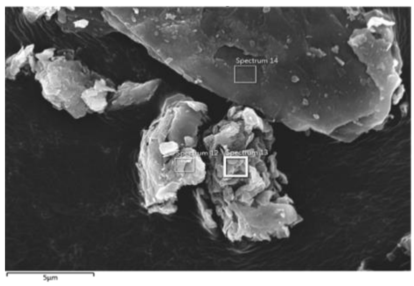

Figure 3: GO NPs EDX Result 1

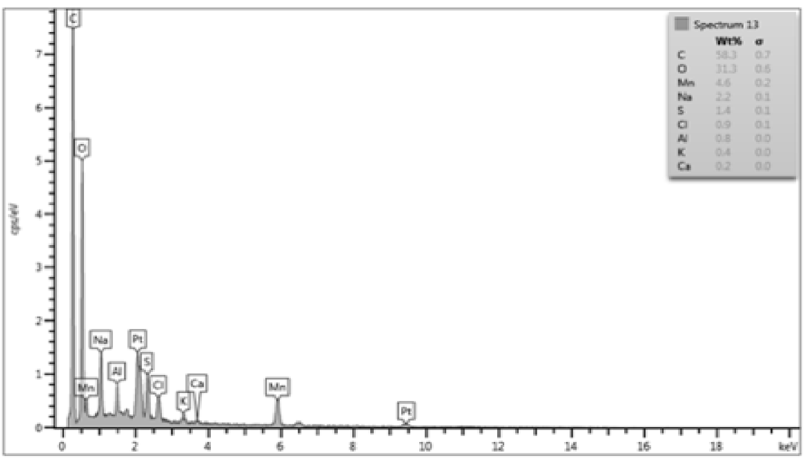

Figure 4: GO NPs EDX Result 2

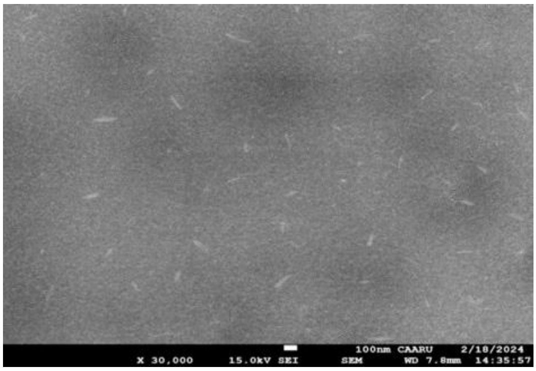

Figure 5: Pure PES Membrana SEM Result.

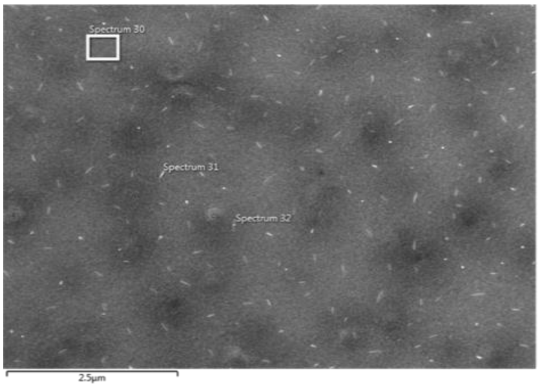

Figure 6: Membrane EDX Result 1.

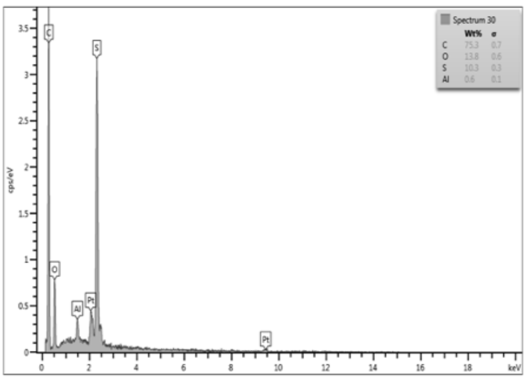

Figure 7: Pure PES Membrane EDX Result 2.

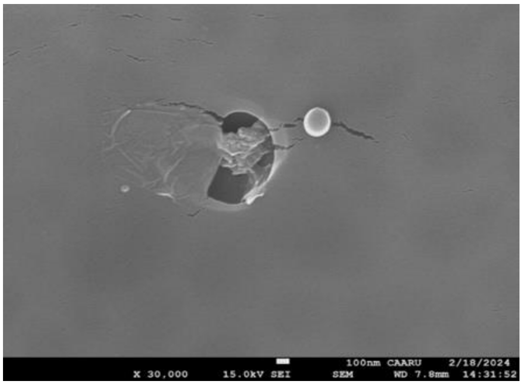

Figure 8: PES/GO Membrana SEM Result.

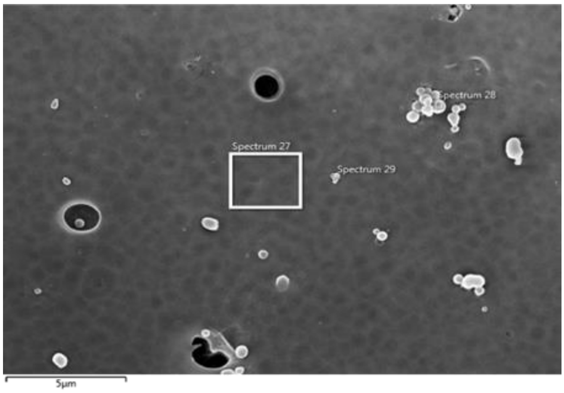

Figure 9: PES/GO Membrane EDX Result 1.

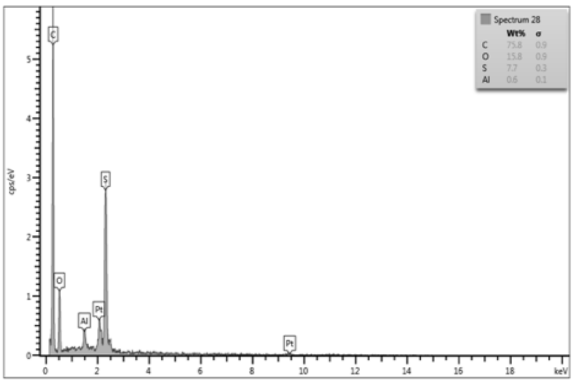

Figure 10: PES/GO Membrane EDX Result 2.

The EDX analysis of GO (Graphene Oxide) nanoparticles revealed significant elemental percentages. Carbon (C) and oxygen (O) were found to be the major constituents, constituting 58.3% and 31.3% respectively. These values are crucial as they confirm the presence of the graphene oxide structure in the nanoparticles. Manganese (Mn), present at 4.6 %, suggests the potential presence of impurities. The trace amounts of sodium (Na), sulfur (S), aluminum (Al), chlorine (Cl), potassium (K), silicon (Si), and calcium (Ca) indicate the presence of minor elements or contaminants. These values highlight the importance of assessing the purity and potential impurities in GO nanoparticles, ensuring their suitability for desired applications. The SEM analysis of the PES membrane showed a uniform distribution of particles, indicating a homogeneous structure. The EDX analysis revealed that the membrane consists of 75.3% carbon (C), 13.8% oxygen (O), and 10.3% sulfur (S), suggesting the presence of carbon-based materials, oxygen-containing functional groups, and sulfur-based compounds. These findings provide insights into the composition and characteristics of the PES membrane. Similarly, the SEM analysis of the PES/GO membrane exhibited a uniform surface structure, although some damage was observed due to the sensitivity of the surface to the SEM light beam. The EDX analysis showed that the membrane contains 75.8% carbon (C), 15.8% oxygen (O), and 7.7% sulfur (S). Despite the surface damage, these results provide valuable information about the composition of the PES/GO membrane.

- Membrane Performance:

Table 2: Water Analysis.

Parameter	Feed (Before filtration)	Product (After filtration)	
		Sample 1 (Pure PES)	Sample 2 (PES/GO)
pH	7.43	8.38	7.95
Salt (ppt)	1.92	1.68	1.64
TDS (ppt)	2.59	2.33	2.28
Conductivity (ms)	3.65	3.28	2.53
COD (mg/L)	2624	5557	7287

Table 3: J Flux.

Sample	Type of water	Time	Volume (ml)	Membrane Area (m^2)	J flux=V/(A.t) (L/ m^2.hr)
Sample 1 (Pure PES)	Distill water	10 min 22 sec	10	0.0023	25.525
	Waste produced water	12 min 24 sec	10		21.312
Sample 2 (PES/GO)	Distill water	8 min 29 sec	10	0.0023	31.467
	Waste produced water	10 min 36 sec	10		25.181

Table 4: Water Permeability.

Sample	Type of water	J flux=V/(A.t) (L/ m^2.hr)	$W_p = J_w/P$ (Pressure= 5 bar) (L/ m^2.hr.bar)
Sample 1 (Pure PES)	Distill water	25.525	5.105
	Waste produced water	21.312	4.2624
Sample 2 (PES/GO)	Distill water	31.467	6.2934
	Waste produced water	25.181	5.0362

Table 5: Salt Rejection & COD Reduction

Salt rejection% $= \left(1 - \frac{C_P}{C_F}\right) \times 100$		COD Reduction% $= \frac{(COD_{in} - COD_{out})}{COD_{in}} \times 100\%$	
Sample 1 (Pure PES)	Sample 2 (PES/GO)	Sample 1 (Pure PES)	Sample 2 (PES/GO)
12.5%	14.5%	51.2%	53.8%

The discussion focuses on the results presented in tables related to water flux, water permeability, salt rejection, and COD reduction. In the water flux table, two samples were tested using different water types and membrane materials. Sample 1, with a pure PES membrane, exhibited a water flux of 25.525 L/m².hr, while Sample 2, with a PES/GO (graphene oxide) membrane, showed a higher water flux of 31.467 L/m².hr. These results indicate that the addition of graphene oxide to the PES membrane enhances water permeability, allowing for a greater flow rate. The waste produced water had a lower water flux compared to the feed water, suggesting solute retention by the membrane during filtration. The water permeability table supports the water flux findings, with Sample 2 (PES/GO membrane) exhibiting higher water permeability (6.2934 L/m². hr.bar) compared to Sample 1 (pure PES membrane) (5.105 L/m². hr.bar). These results suggest that the incorporation of graphene oxide nanoparticles improves the membrane's water permeability, enabling higher filtration rates. Moving on to the salt rejection and COD reduction table, both samples demonstrated the effectiveness of the filtration process in removing salts and reducing chemical oxygen demand (COD) from the feed water. Both samples achieved significant COD reductions, with Sample 1 (Pure PES) at 51.2% and Sample 2 (PES/GO) at 53.8%. This indicates the membranes' capability to effectively remove organic compounds from the water. Regarding salt rejection, both samples showed similar performance, with Sample 1 and Sample 2 achieving salt rejections of 12.5% and 14.5% respectively. These values indicate that a portion of the salts present in the feed water was rejected by the membranes, resulting in lower salt concentration in the product water.

- Water Angle Test Results:

The pure PES membrane demonstrates moderate hydrophilicity, indicating an affinity for water and potentially better water permeability. However, it may have reduced fouling resistance. In contrast, the PES/GO membrane exhibits higher hydrophobicity, suggesting improved fouling resistance, which is advantageous in industrial wastewater treatment. However, higher hydrophobicity may decrease water permeability. Comparing the two membranes, the PES/GO membrane shows stronger hydrophobic behavior, indicating enhanced fouling resistance, while the pure PES membrane is more hydrophilic, potentially offering better water permeability. These water angle test results provide initial insights, but further analysis considering specific wastewater characteristics, filtration efficiency, fouling potential, and long-term stability is crucial in selecting the most suitable membrane for industrial wastewater treatment.

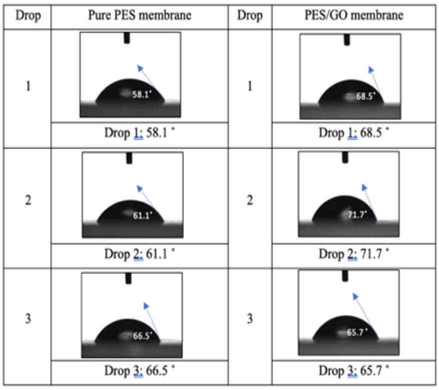

Figure 11: Water angle test results.

4. CONCLUSIONS:

In conclusion, this study focused on addressing challenges in petroleum and oil extraction wastewater treatment, specifically the separation of heavy crude oil from water and membrane fouling. The project aimed to enhance wastewater treatment efficiency by developing a nanomembrane that improves selectivity, efficiency, and filtration performance. The proposed solution involved modifying polyethersulfone (PES) membranes with graphene oxide (GO) nanoparticles. Analysis revealed that the fabricated membrane consisted of 75.3% carbon (C), 13.8% oxygen (O), and 10.3% sulfur (S), indicating the presence of carbon-based materials, organic compounds, and oxygen-containing functional groups. The incorporation of GO enhanced hydrophilicity, resulting in improved water permeability with values of 31.467 $L/m^2.hr$ for the PES/GO membrane and 25.525 $L/m^2.hr$ for the pure PES membrane. Both membranes effectively removed salts, with salt rejection values of 14.5% and 12.5% for PES/GO and pure PES membranes, respectively. These findings contribute to sustainable wastewater management solutions in petroleum and oil extraction.

References

1. N. Al Balushi, S. Al Rashdi, S. M. Rizwan, G. Patil, and A. M. Saravanan, "Development of a Noble Fouling-Resistant Membrane for Wastewater Treatment," Int. J. Membr. Sci. Technol., vol. 9, no. 2, pp. 55–60, 2022, doi: 10.15379/2410-1869.2022.09.02.04.
2. E. O. Ezugbe and S. Rathilal, "Membrane technologies in wastewater treatment: A review," Membranes (Basel)., vol. 10, no. 5, 2020, doi: 10.3390/membranes10050089.
3. X. Chen, Z. Qu, Z. Liu, and G. Ren, "Mechanism of Oxidization of Graphite to Graphene Oxide by the Hummers Method," ACS Omega, vol. 7, no. 27, pp. 23503–23510, 2022, doi: 10.1021/acsomega.2c01963.
4. N. I. Zaaba, K. L. Foo, U. Hashim, S. J. Tan, W. W. Liu, and C. H. Voon, "Synthesis of Graphene Oxide using Modified Hummers Method: Solvent Influence," Procedia Eng., vol. 184, pp. 469–477, 2017, doi: 10.1016/j.proeng.2017.04.118.
5. Bauer, "NIMR Water Treatment Project TREATMENT USING WETLANDS – REDUCING," 2014.

6. A. Marjani, A. T. Nakhjiri, M. Adimi, H. F. Jirandehi, and S. Shirazian, “Effect of graphene oxide on modifying polyethersulfone membrane performance and its application in wastewater treatment,” Sci. Rep., vol. 10, no. 1, pp. 1–11, 2020, doi: 10.1038/s41598-020-58472-y.
7. N. N. R. Ahmad, W. L. Ang, C. P. Leo, A. W. Mohammad, and N. Hilal, “Current advances in membrane technologies for saline wastewater treatment: A comprehensive review,” Desalination, vol. 517, no. April, p. 115170, 2021, doi: 10.1016/j.desal.2021.115170.
8. S. A. Speakman, “Introduction to X-Ray Powder Diffraction Data Analysis,” Mater. Sci., p. 20, 1902, [Online]. Available: https://www.researchgate.net/file.PostFileLoader.html?id=58d22df3dc332d06c7245969&assetKey=AS%3A474618730422273%401490169331513
9. A. B. D. Nandiyanto, R. Oktiani, and R. Ragadhita, “How to read and interpret ftir spectroscope of organic material,” Indones. J. Sci. Technol., vol. 4, no. 1, pp. 97–118, 2019, doi: 10.17509/ijost.v4i1.15806.