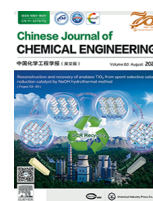




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Full Length Article

Graphene oxide/hydrotalcite modified polyethersulfone nanohybrid membrane for the treatment of lead ion from battery industrial effluent

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ABSTRACT

In the present study, polyethersulfone based nanohybrid membranes were effectively fabricated by incorporating graphene oxide (GO) and hydrotalcite (HT) nanosheets into the membrane structure. HT was prepared to overcome the irreversible agglomeration behavior of GO at a high concentration which affects the performance of the membranes. In particular, the shedding of HT in formamide provides a two-dimensional nanosheet with a higher positive charge density to prevent the restacking of GO nanosheets. Here, exfoliated GO and HT with different combinations (1:1, 1:2 and 1:3) were infused in the membrane matrix to treat lead-acid battery effluent effectively. Finally, the hybrid membranes were characterized for hydrophilicity, mechanical strength and pure water flux. In combination with the superior properties of GO and HT, the prepared hybrid membranes can be used as effectively to improve the separation and permeation performance. The phase inversion process eliminated the leaching of nanoparticles from the membrane matrix. The reusability of the hybrid membrane was achieved using 0.1 mol·L⁻¹ NaOH solution and reused without significant reduction in lead removal efficiency. The cost analysis of the membrane was also estimated from the lab study. Therefore, the present study suggested the selective and sustainable treatment of lead from a real-life effluent.

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1. Introduction

The pollution problem and environmental concerns have recently emerged as one of the main government concerns. In this esteem, finding solutions to environmental challenges is the fundamental strategy used to accomplish environmental and economic targets [1]. The rapidly increasing global population and industrialisation are the main contributors to the pollution problem. A considerable amount of water is used in the manufacturing plants from the production stage to the final recycling stage and the process water becomes heavily contaminated. The cardinal source of such pollution is heavy metal issues, especially lead, mercury, cadmium, chromium and nickel [2,3]. With applications ranging from lead acid batteries to safety systems in aircraft and radiotherapy equipment in hospitals, the world depends on the special qualities of lead ion every day. Almost 86% of total consumption of lead is used for the production of lead acid batteries. As a result, the battery production facilities produce a sizable amount of waste that contains lead. In battery production unit, water is used as a major

transport medium and surface cleaning agent and it generates wastewater having lead ion concentration of 15 mg·L⁻¹, which is 150 times higher than the permissible limit of lead ion in water course according to Central Pollution Control Board India. Thus, the effluent should be treated to make their discharge possible or regenerated for the washing and cleaning process. The conventional purification techniques are not sophisticated and result in waste and complex effluents harmful to the environment, demanding more advanced purification systems [4]. Manufacturers must overcome the critical obstacle of developing an effective and affordable technology for treating wastewater that contains metal ions.

A non-destructive separation, known as membrane separation, is a well-established technique for treating wastewater containing heavy metal ions and producing high-quality treated effluent [5]. Polymeric membranes are of primary interest, as they can be easily modified and made compatible with different materials like polymers and nano additives to improve membrane performance [6,7]. Polyethersulfone (PES) is preferred as membrane-forming polymer material attributed of its excellent film-forming property, cost-effectiveness, exceptional thermal and mechanical stability, and commendable chemical resistance [8,9]. However, several challenges are still restricted, such as hydrophobic nature and

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the trade-off between selectivity and permeability [10]. In addition, its inherent hydrophobicity primes to irreversible fouling, which weakens the performance and membrane life span [11]. Recently, incorporating functionalized nanoparticles has been considered an excellent choice to render them hydrophilic, thus reducing membrane fouling and enhancing membrane flux [12–14]. During the past few years, several investigators have studied the incorporation of graphene oxide (GO) into PES polymer to develop antifouling nanocomposite membranes [15–18]. However, the homogenous dispersion of GO sheets in the solution is restricted due to their strong tendency towards aggregation. An irreversible agglomeration may occur due to the inter-structural affinity of GO sheets [19,20]. Thus, the retention of the layered structure is vital for GO sheets because most of their unique properties are principally connected with individual layers. To overcome this problem, hybridizing graphene with substrates like metal oxides are being trained for several applications. Mg–Al based layered double hydroxide (LDH or hydrotalcite (HT)), is a positively charged membrane additive, exhibits relatively small adequate pore size and excellent hydrophilicity with high rejection for multivalent cations. In addition to that, exfoliation of HT provides a 2-dimensional nanosheet with a higher positive charge density known as exfoliated HT (EHT) [21]. EHT made a stable bridge between GO and PES polymer.

This work designs and incorporates the combination of oxidized nanoparticles such as coupled GO-EHT into the PES matrix by a simple blending method. Here, the superior properties of GO and EHT are combined at various combinations and can be infused into the membrane matrix. GO and EHT combination brought an excellent membrane characteristic and performance with cost-effectiveness as EHT is cheaper. The study of GO-EHT based nanohybrid membrane brings about the importance of dispersion of additives in nanofiltration (NF) applications. Based on the nanofiltration performance analysis, PES based hybrid membrane was proposed for the treatment of lead containing wastewater.

2. Materials and Methods

2.1. Chemicals and reagents

The membrane polymer, polyethersulfone (Veradel, 3000 P) was purchased from Solvay Process. Solvent, *N,N*-dimethyl formamide (DMF) was purchased from Merck, India Ltd. Polyvinylpyrrolidone (PVP) from Sigma Aldrich was selected as the porogen. Graphite powder (Alfa Aesar, crystalline, 99%) was used to prepare graphene oxide. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were bought from Merck India Ltd. Potassium permanganate (KMnO_4 ; 99%), hydrogen peroxide (H_2O_2 ; 30%), sodium hydroxide (NaOH), sulphuric acid (H_2SO_4 ; 98%), nitric acid (HNO_3 ; 68%) and hydrochloric acid (HCl ; 37%) were purchased from Merck India Ltd, and used as received. Lead nitrate (PbNO_3) was procured from Merck India Ltd. to prepare a feed solution.

2.2. Synthesis and characterization of nanoparticles

GO was successfully synthesized by the modified-Hummers' method [19,22,23] and HT were synthesized by the co-precipitation method. Our earlier works provide the precise steps and characterization of nanoparticles [15,21].

2.3. Development of PES nanohybrid membrane

The simple conventional preparation method, such as non-solvent induced phase inversion (NIPS), fabricates the GO-EHT

modified PES hybrid membrane. The flat sheet membrane is cast with the help of the Elcometer 4340 motorized film applicator by fine-tuning a thickness of 200 μm and a length of 20 cm. A simple blending method successfully infused these GO and EHT nanoparticles in different ratios in the dope solution. The membranes are prepared at various weight combinations, as in Table 1. Fig. S1 (Supplementary Material) depicts the development of the total dope solution and the subsequent membrane fabrication.

2.4. Characterization of PES hybrid membranes

The infusion of modifiers on the produced membranes was established by attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectroscopy (Agilent Cary 630) examination in the range of 400–4000 cm^{-1} . It was conducted for both unmodified (M0) and modified membranes (MH) via 630 1 B diamond ATR modules and average scans were taken. Membrane hydrophilicity was determined using static and dynamic contact angle values according to a sessile drop method employing automated goniometer equipment (Kyowa Interface Science Co. Ltd. DMS-401) coupled by a software-controlled DI water dosing system. Contact angles were taken at three points for each membrane coupon to estimate an average contact angle value. The surface and cross-sectional images of the dehydrated membrane samples were pictured using field emission–scanning electron microscopes (FE-SEM Model JEM 19 2100). The elemental composition of the M0 and modified membranes was observed using energy dispersive spectroscopy (EDS) (JEOL JSM–7600F FEG-SEM). An atomic force microscope (AFM APER 100 SPM) with non-contact mode was used to examine the surface roughness and morphology of the prepared membrane. The mechanical strength of the membranes was quantitatively estimated with the help of a universal testing machine (UTM) of Shimadzu AG-X plus at 10 kN and a cross-head speed of 5 $\text{mm} \cdot \text{min}^{-1}$.

The classical gravimetric technique was used to calculate the overall membrane porosity and percentage of water uptake at an ambient temperature according to Eqs. (1) and (2).

$$\text{Porosity } (\varepsilon) = \frac{W_1 - W_2}{\rho_w A} \quad (1)$$

$$\text{Water uptake} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (2)$$

where ρ_w is the mass density of water at ambient temperature (0.997 $\text{g} \cdot \text{cm}^{-3}$), A is the active area of the membrane (cm^2). An electronic micrometer (Mitutoyo, Tokyo, Japan) with 1 μm precision measured the membrane thickness. Each sample had three repeated measurements, which were reported as the average membrane porosity.

2.5. Membrane performance

A membrane sample of area 42 cm^2 was fixed into the cross-flow cell (CF042D) and the cell was operated in a total recycle mode (Fig. S2). Primarily, the membranes were compacted at 1.2 MPa pressure to lessen compaction effects. Afterward, the pure water flux was measured till it accomplishes a steady state, after which all experiments were performed at 0.4 MPa and 298.15 K. The pure water flux was calculated by the following Eq. (3).

$$J_w = \frac{Q}{A \times \Delta t} \quad (3)$$

where J_w is the pure water flux in $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, Q is the permeate volume in L, Δt is the sampling time in h.

The retention studies of hybrid membrane samples were conducted in the same cross-flow cell using a 30 $\text{mg} \cdot \text{L}^{-1}$ synthetic

Table 1
Combination of GO and EHT in PES nanohybrid membrane

Membrane	PES/% (mass)	GO/EHT ratios	PVP/% (mass)	GO/% (mass)	EHT/% (mass)	DMF/ml
M0	18	—	—	—	—	82
MP3	18	—	1	—	—	81
MG3	18	—	1	0.5	—	80.5
ME2	18	—	1	—	0.5	80.5
MH1	18	1:1	1	0.25	0.25	80.5
MH2	18	1:2	1	0.25	0.5	80.25
MH3	18	1:3	1	0.25	0.75	80

lead nitrate solution. The solute retention was estimated from the concentration of the feed (C_f) and permeate (C_p) using Eq. (4).

$$\text{Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (4)$$

The same operating circumstances were used to explore the applicability of an optimised hybrid membrane for industrial wastewater. Real-life battery industry effluent was collected from an automotive and tubular battery manufacturing industry. The effluent was put through a cross-flow filtration cell at a pressure of 0.8 MPa and a flow rate of 100 L·h⁻¹ without any prior treatment. The industrial effluent was characterized in terms of heavy metal concentration like Pb²⁺, Zn²⁺, Fe²⁺, chemical oxygen demand (COD), pH, total hardness (TH) as CaCO₃ and total suspended solids (TSS) before and after the membrane treatment by APHA test method.

2.6. Membrane reusability

The best-performed membrane was chosen for the cleaning test. Alkali wash (0.1 mol·L⁻¹ NaOH) was conducted for 3 h to remove the fouled components in the membrane surface and pores. Afterward, the treated membrane was cleaned with adequate DI water three times, dried at 60 °C and further recovered for the filtration test.

2.7. Antifouling studies

Bovine serum albumin (BSA) was chosen for this investigation as a model foulant since it was found to have a high fouling potential. BSA solution with a concentration of 100 mg·L⁻¹ was made in phosphate buffer saline (PBS solution) to uphold the pH at 7. The fouling-resistant ability of membranes was assessed by calculating the flux recovery ratio (FRR), irreversible resistance (R_{ir}), reversible resistance (R_{ir}) and total resistance (R_t) after fouling by BSA solution through the subsequent expressions.

$$\text{FRR} = \frac{J_2}{J_0} \times 100\% \quad (5)$$

$$R_r = \frac{J_2 - J_1}{J_0} \times 100\% \quad (6)$$

$$R_{ir} = \frac{J_0 - J_2}{J_0} \times 100\% \quad (7)$$

$$R_t = \frac{J_0 - J_1}{J_0} \times 100\% \quad (8)$$

where J_0 is the pure water flux of the sample membrane before fouling, J_1 is the BSA solution flux and J_2 is the water flux after the backwashing (after the BSA permeation).

2.8. Economic analysis of the system

Economic analysis of any system is vital for its commercialization purpose [24,25]. Clearwater production cost mainly depends on equipment costs (membrane and cross-flow system), operation and maintenance costs. In this study, a small-bench scale membrane system comprises a feed tank of 4 L, a high-pressure pump of 1.5 kW, and a membrane housing of 42 cm² effective area. The feed flow rate (100 L·h⁻¹) was kept constant and the system pressure was adjusted using a valve and monitored by a pressure gauge. For the cross low filtration cell, an average lifespan of 5 to 7 years is presumable with 8 to 10 h of daily operation. With a table size of 305 mm × 225 mm, the Elcometer 4340 motorised film applicator (Up to 15 years of standard use) was utilised for the manufacturing of membranes. The cost of electricity was taken into account based on electrical energy consumption and electricity costs, and as of March 2020, the unit price in the Indian market was 5.43 INR·(kW·h)⁻¹. Capital cost expenditure was primarily considered in this study to predict the system's feasibility. 98.5% of the total cost was impacted by the capital cost of the cross-flow filtration system. Once the filtration system is installed, it is again reused with different membranes for different applications. Hence, the higher capital cost of the system is substantiated by the number of usages. Here, we have also estimated the divisions of the capital cost that determine the feasibility of our lab study.

3. Results and Discussion

3.1. Membrane characterizations

3.1.1. Fourier transform infrared spectroscopy (FTIR)

The chemical nature of the neat and modified membrane was studied using FTIR spectroscopy. It is represented in Fig. S3, in which MP3 (1% (mass) PVP), MG3 (0.5% (mass) GO) and ME2 (0.5% (mass) EHT) represented the PVP and optimized GO and EHT modified membranes. All membranes exhibited the corresponding characteristics of FT-IR peaks of the PES membrane. The PES structure included a benzene ring, an ether bond and a sulphone structure. The C—H stretching peak of benzene ring was situated at 3097 cm⁻¹. The three peaks between the 1600 cm⁻¹ and 1400 cm⁻¹ were attributed to aromatic skeletal vibration. The C—O—C stretching peaks were located at 1324 cm⁻¹ and 1239 cm⁻¹. The S=O stretching peaks were present at 1151 cm⁻¹ and 1105 cm⁻¹. There was a rise in OH⁻ stretching vibration (~3500 cm⁻¹) intensity for modified membranes, representing the hydrophilicity enhancement due to hydrophilic additives in the membrane structure [26].

3.1.2. Membrane hydrophilicity

The relative concentration of GO and EHT inside the membrane matrix, the ratio of the two additives, and the degree of agglomeration all had an impact on the hydrophilicity of the produced membranes. The modified membranes' porosity and water uptake capacity were measured using a simple gravimetric method. The variation of porosity and water uptake with the additive

Table 2
Hydrophilicity enhancement of modified membrane

Type of membrane	M0	MG3	ME2	MH1	MH2	MH3
Porosity /% (± 0.85)	27.01	73.01	67.99	81.67	83.46	81.32
Water uptake /% (± 1.4)	34.08	78.69	80.56	84.18	86.54	83.95
Contact angle/ ($^{\circ}$) (± 1.5)	79.62	69.12	53.90	54.90	51.52	53.94

concentration was obtained and presented in Table 2. The effect of the combination (optimized) of GO-EHT such as MG3 and ME2 was considered in our previous studies.

All modified membranes showed good porosities and were more significant than 65%. The MH2 hybrid membrane showed greater porosity than neat M0, which created a better channel for water molecules as the voids were the provinces for the water molecules. The increase in porosity could be explained by the mass transfer rate between solvent and non-solvent during the NIPS method, confirming higher sorption of water molecules. Similarly, the surface hydrophilicity had also enhanced with the incorpora-

tion of GO-EHT nanoparticles. According to Table 2, the average contact angle value of the M0 membrane was 79.62 ± 1.5 , which reduced on membrane modification to a lower value of 51.52 ± 1.5 , indicating increased hydrophilicity.

3.1.3. Morphological analysis

To observe the effect of EHT/GO on the hybrid membrane structure, the SEM images of the top surface and cross-section morphologies of the dried and fractured membrane were shown in Fig. 1. Comparing the top surface pore size of M0 and modified membranes, the average pore size of MH2 was 9.3 nm. Thus, the

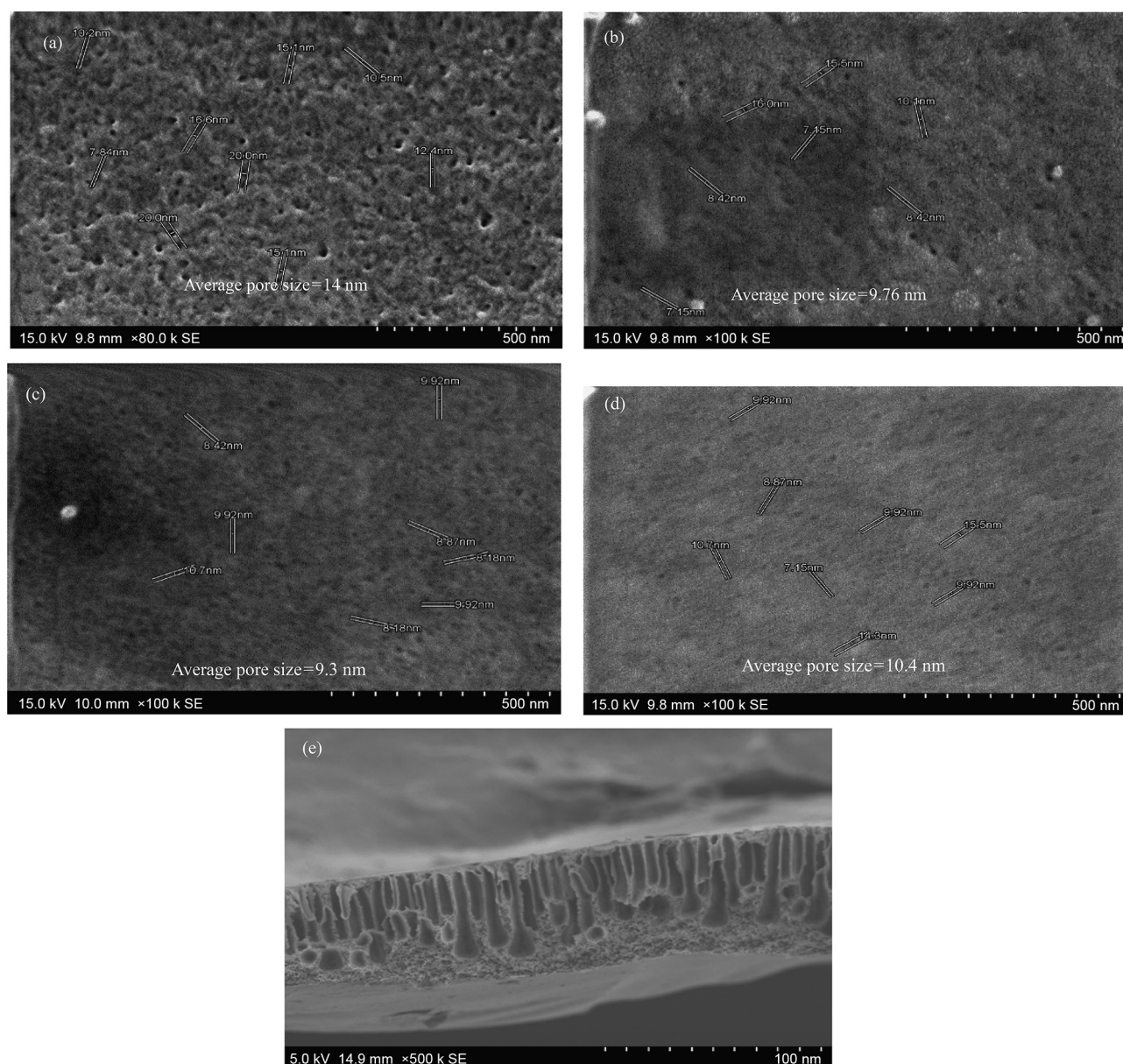


Fig. 1. Surface images (a) M0, (b) MH1, (c) MH2, (d) MH3 and C/S images (e) M0, (f) MH2 membranes using SEM analysis.

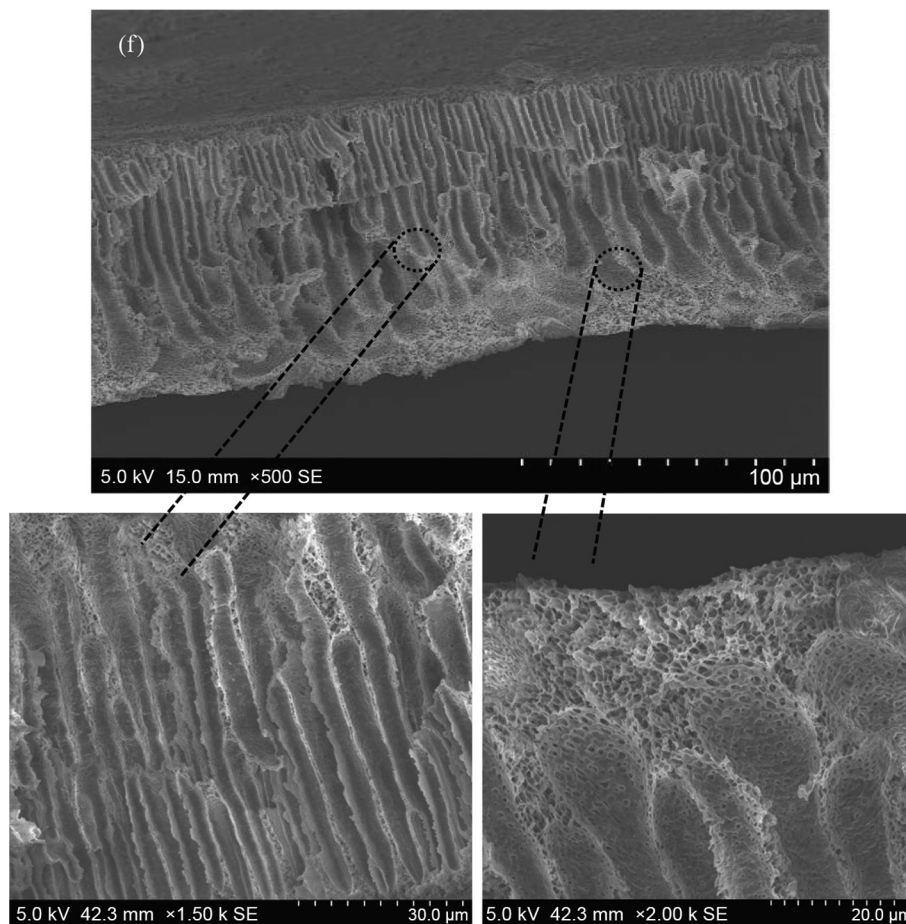


Fig. 1 (continued)

surface pore size was successfully tuned by adding GO-EHT nanoparticles.

Fig. 1(b) represents the cross-section morphology of the M0 and MH2 membrane, which indicates that unmodified and modified membranes showed a distinctive asymmetric structure with a skinny sieving top layer, which was supported by a finger-like substructure. The thickness of the top surface was detected to be the supreme for the M0 membrane, which reduced as the mass fraction of GO-EHT. This reduction in top layer thickness could be responsible for the enhancement in the pure water flux.

The substructure of the M0 membranes exhibited larger macro voids, while fully developed, long-thin pores were looked on as the GO-EHT nanoparticles were introduced. A greater number of pores were produced as the nanosheet's percentage increased, which led to better interconnectivity between the pores. As per the EDS analysis, Table S1 represents the elemental composition in M0 and MH2 membranes. It can be seen that the mass fraction of C, O, and S were changed from M0 to MH2 concerning the GO addition. Similarly, elements such as Mg and Al were introduced into the membrane structure due to the infusion of EHT nanoparticles. These results would confirm the successful formation of hybrid membranes from GO and EHT on PES polymer. As shown in Fig. S4, C, O, and S elements appeared on EDS mapping for the outer surface of the M0 membrane, indicating C, O, and S as component elements in the membrane structure. Similarly, the EDS mapping of MH2 showed all the dominant elements in the GO and EHT materials.

The surface roughness of the prepared membranes was investigated using 3D atomic force microscopy (AFM). The images are shown in Fig. 2.

The roughness parameters of each membrane were also presented. As shown in Figure, the M0 membrane displayed an inflated surface roughness value than all other membranes. The brightest regions represent the highest points or nodules on the membrane surface, whereas the darkest regions represent troughs or membrane pores [27,28]. The roughness parameter value for the M0 membrane was 29.45 nm, while it was 17.09 nm, 12.33 nm, and 24.56 nm for the MH1, MH2, and MH3 membranes, respectively, *i.e.* the surface roughness decreased to a lower value of 12.33 nm (MH2 membrane). This could be clarified as ensuing from improved miscibility of organic and aqueous phases due to hydrophilic nanoadditives during the NIPS method. In addition to that the membrane has smoothed out after the inclusion of nanoparticles. Because the foulants collect in the valleys on the membrane surface, smooth surfaces are less likely to foul [29]. Thus, the modified membrane's smooth surface has increased water permeability [30], which was proven by water flux measurements (Fig. 3(a)). More nanoparticles (MH3 membrane) increased the surface roughness due to the agglomeration of nanoparticles in the membrane matrix.

3.1.4. Mechanical strength

The mechanical properties of the prepared membranes with different GO-EHT nanofiller loading were investigated and elongation, tensile strength and Young's modulus of the fabricated membranes were reported in Table S2. According to the results, the M0 membrane with ultimate stress of $5.36 \text{ N}\cdot\text{mm}^{-2}$ showed the lowest tensile strength. Furthermore, the tensile strength and Young's modulus of the fabricated MH1, MH2 and MH3 membranes were increased continuously with increasing GO-EHT ratios. Similarly,

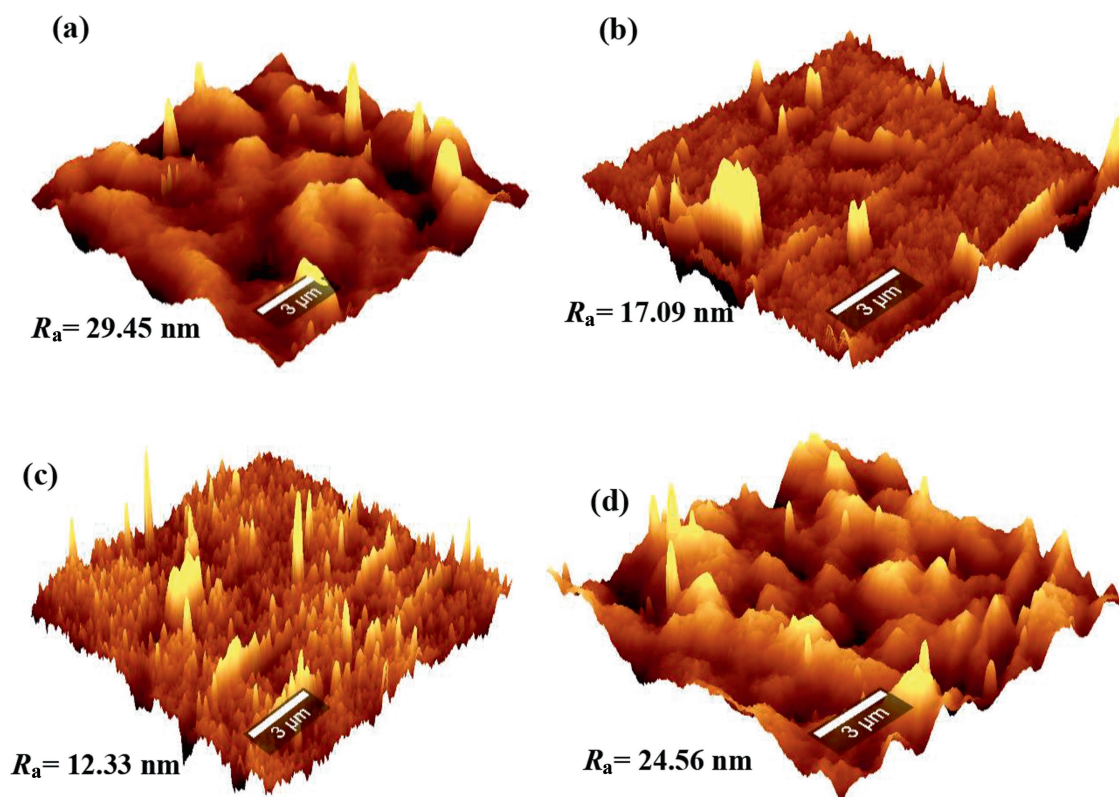


Fig. 2. AFM images of prepared membranes: (a) M0 (b) MH1 (c) MH2 and (d) MH3.

the elongation was gradually decreased, indicating the strong interfacial hydrogen bonds between hydroxyl and carboxyl groups of nanoadditives and oxygen atoms of PVP and PES matrix.

3.2. Membrane performance studies

The pure water flux is one of the key characteristics used to evaluate the effectiveness of produced membranes. The water flux of the membrane was seen to progress with nanoparticle addition into the PES structure. MH2 presented a higher water flux value of $(198.12 \pm 3.5) \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ against a lower flux of $(32.14 \pm 4.2) \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, as shown in Fig. 3(a).

The rise in hydrophilicity of the hybrid membrane resulted from the oxygen-rich functional groups in the GO-EHT material, which had relocated to the membrane's front surface through the NIPS method. The oxygen-containing functional group weakened the water masses and smoothed the passage across the membrane pores. This could be the reason for the enormous increase in pure water flux value. In addition, the presence of GO-EHT in dope solution intensified the solvent-nonsolvent exchange rate, causing an improved porosity which grew the area of the domain for water molecules.

Rejection studies of synthetic lead nitrate solution for M0 and hybrid membranes were conducted (Fig. 3(b)). When tested with $30 \text{ mg}\cdot\text{L}^{-1}$ synthetic lead nitrate solution, an impressive lead rejection of 96.3% with a permeate flux value of $193.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ was noticed for the MH2 membrane. However, a reduction in rejection and permeate flux value was obtained at a higher ratio of GO-EHT. This was due to the agglomeration of nanoparticles in higher mass content and a consequent reduction in the active membrane pores. It could be said that an optimal loading (GO-EHT ratio of 1:2) of nanoparticles tuned the hybrid membrane to obtain a high solute rejection with permeate flux.

3.3. Antifouling studies

Furthermore, all hybrid membranes were tested to ensure antifouling behavior, and the results are represented in Fig. 4. An increase in the flux recovery ratio (FRR) was attributed to the better antifouling property of the prepared membrane. Hence, the FRR of the MH2 membrane showed a better antifouling nature related to the membrane hydrophilicity.

The outstanding antifouling nature was also confirmed by an 80-min examination on the fouling propensity of MH2. Meanwhile, most of the proteins and other foulants were hydrophobic; the enhancement of hydrophilicity of the membranes resulted in lower adhesion of foulants on the membrane.

3.4. Study on real-life lead-containing battery industry effluent

The actual battery effluent was passed through the optimized MH2, housed in the same cross-flow cell, using a high-pressure diaphragm pump at an operating pressure of 0.8 MPa and a flow-rate of $100 \text{ L}\cdot\text{h}^{-1}$ without any pre-treatment. The detailed characterization of effluent before and after treatment is presented in Table S3. It was observed that most of the initial characteristics were slightly improved in terms of treated water quality. However, the higher removal percentage of Pb^{2+} ions concerning other metal ions proved the membrane's selectivity towards the lead. The nanofiltration performance of the MH2 membrane for synthetic and real wastewater is depicted in Fig. 5. The filtration study on battery industry effluent found that the rejection of MH2 (94.63%) decreased compared to the synthetic solution (96.31%).

Similarly, a reduced water flux value ($193.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) was observed for battery wastewater ($174.31 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) compared with synthetic water. As a result, it was suggested that MH2 membrane be used for the treatment of lead-acid battery effluent

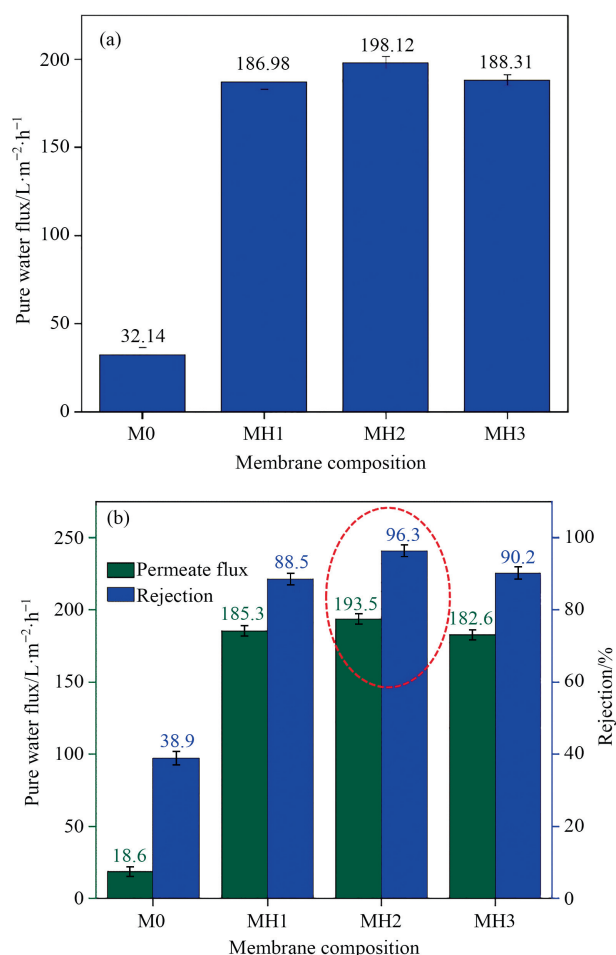


Fig. 3. (a) Pure water flux studies; (b) Rejection studies.

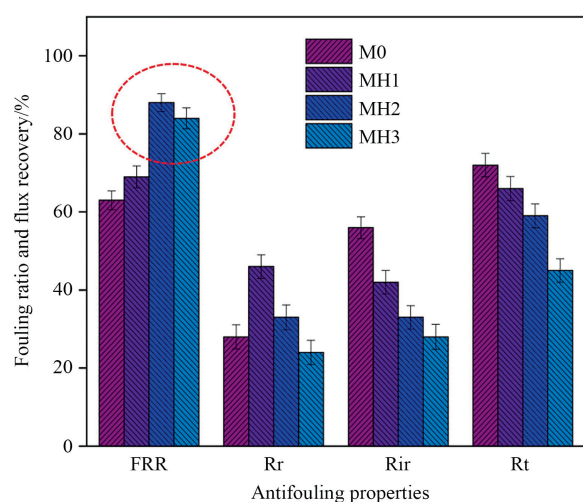


Fig. 4. Antifouling studies.

based on this study's successful experiment with real battery wastewater.

3.5. Membrane reusability studies

To ensure membrane reusability and waste minimization, regeneration efficiency and performance of regenerated

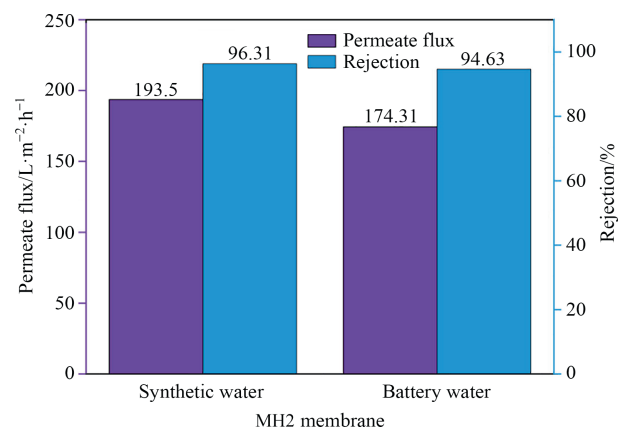


Fig. 5. NF performance of MH2 with synthetic and real wastewater.

membranes were crucial. After treating actual wastewater, the MH2 membrane was cleaned with an alkali ($0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH) in the same filtration cell. Then the membrane was subjected to pure water flux and rejection studies using lead-acid wastewater, and the results are represented in Table S4.

The surface SEM images of the used MH2 membrane before and after cleaning with water are represented in Fig. S5. According to Fig. S5, the regeneration of the used membrane was effectively carried out by $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution following washing with DI water. The regenerated membrane could be reused successfully with an almost equal rejection rate. However, the water flux was decreased to a lower value of 169.28 from 198.54 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

3.6. Cost analysis

A detailed spreadsheet of the estimate and the operation and maintenance costs of the present study are presented in Tables S5 and S6, respectively. In the current work, the capital investment for a $2 \text{ L}\cdot\text{h}^{-1}$ capacity has been projected to be INR 2.3 Lakh (3011 USD). A detailed spreadsheet of this estimate and the wastewater characteristics, operation and maintenance costs are presented in Tables S4, S5 and S6. The cost of membrane cleaning could add up to 3%–5% of total operational costs. Moreover, the costly additive GO was combined with a comparatively cheaper additive, namely EHT, and developed GO-EHT modified PES nanohybrid membrane for the treatment of lead containing effluent.

3.7. Comparison with literatures

PES is well suited for use in separation membranes because of its high mechanical properties and overall chemical stability. Both of these functions are derived from the polymer's chemical structure. These features helps to increase the flow rate and the efficiency of filtration operations in PES separation membranes. Table 3 lists some of the published research that has attempted to remove heavy metal ions using various polymer membranes.

It can be seen that various polymer membranes were used for Pb^{2+} removal from an aqueous environment. CA membranes were used to remove Pb^{2+} ions from industrial wastewater and removal efficiency was not more than 75% [31,32]. Another membrane known as PVDF established maximum removal efficiencies of Pb^{2+} , Cd^{2+} and Cu^{2+} ions of about 68%, 77% and 78%, respectively [35,39]. In addition, PTFE membrane was also used to remove Pb^{2+} , Cu^{2+} and Zn^{2+} and a removal of 76%, 85% and 86% were

Table 3

Comparison of polymeric membranes for lead metal removal

Process	Material	Heavy metal ion	Pb ²⁺ concentration/mg.L ⁻¹	Removal/%	Ref.
NF	CA	Pb ²⁺ , Cd ²⁺ , Cu ²⁺	5–200	72, 85, 80	[31]
NF	CA	Pb ²⁺ , Cd ²⁺ , Cr ⁶⁺	10	68, 47, 10	[32]
NF	CA/PMVEA	Pb ²⁺ , Cd ²⁺ , Cr ⁶⁺	50	75, 72, 27	[33]
UF	PVDF/PANI	Pb ²⁺ , Cd ²⁺	20	68, 77	[34]
UF	PVDF	Cu ²⁺ , Pb ²⁺	30	78, 70	[35]
MF	PTFE	Pb ²⁺ , Cu ²⁺ , Zn ²⁺	50	76, 85, 86	[36]
NF	PSF	Cd ²⁺ , Pb ²⁺	30	85, 66	[37]
UF	PES	Pb ²⁺ , Cu ²⁺ , Cd ²⁺	20	>68	[38]
NF	PES/EHT	Pb ²⁺	30	50	[21]
NF	PES/GO	Pb ²⁺	30	80	[15]
NF	PES/GO-EHT	Pb ²⁺	30	96	This study

obtained respectively. Sulfone polymers (PSF and PES) were also used for Pb²⁺ removal. Han and Nam [37] reported 85% and 66% removal for Cd²⁺, Pb²⁺ ions respectively. Poolachira and Velmurugan [21], 2020 prepared an EHT modified PES membrane and removed 50% lead ions. They were also modified PES membrane with GO nanoparticles and obtained a higher removal rate of 80%. This study represents 96% lead removal rate.

4. Conclusions

A nanohybrid membrane with a respectable rejection rate was obtained by incorporating the superior properties of GO and EHT materials in the PES membrane matrix. The combined features of GO and EHT were accountable for the perceptible effects on membrane functionality. GO-EHT/PES nanohybrid membranes were prepared using the same NIPS method at various weight combinations. Different ratios of GO-EHT were tried, and more relevant results were obtained with 1:2 MH2. FTIR and EDAX analysis confirmed the successful formation of the PES nanohybrid membrane. Morphological analysis by SEM confirmed the practical pore size tuning, which resulted from the inclusion of additives. A minimal pore size of 9.3 nm was obtained for the MH2 membrane. Hence, the expected mechanism for heavy metal removal was size exclusion. Similarly, the lower roughness value from AFM analysis and contact angle of MH2 represented its antifouling nature. The cross-flow filtration experiments obtained a higher rejection rate of 96.31%, with a permeate flux value of 193.5 L.m⁻².h⁻¹ for the MH2 membrane. This result showed the applicability of the MH2 membrane for lead-acid battery effluent treatment. The actual battery effluent was collected and analyzed using the same cross-flow filtration experiment with a flow rate of 100 L.h⁻¹. The wastewater analysis after the treatment revealed the applicability of PES nanohybrid as it resulted in a Pb²⁺ removal rate of 94.63%. The membrane regeneration was completed by 0.1 mol.L⁻¹NaOH solution. Hence, the developed nanohybrid membrane promoted its applicability in lead wastewater treatment.

Contributions

All authors contributed to the study conception and design. Sinu Poolachira carried out experimental works, data analysis and interpretation and drafting the manuscript. Sivasubramanian Velmurugan supervised the work and conducted the critical revision of the article. All authors read and approved the final manuscript.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2023.01.021>.

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