Development of low-pressure polymeric membrane incorporated with powdered activated carbon and nanosilica for groundwater applications

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Abstract. Groundwater has become a vital alternate supply of freshwater, which has now frequently been contaminated with high iron and lead levels that are harmful to human health and agriculture. Hence, various modifications on membrane surfaces are fabricated in this study to improve the membrane's performance. Low-pressure PES polymeric membranes are made by combining polyether sulfone (PES) as the polymer, N-methyl-2-pyrrolidone (NMP) as the solvent, and nano-silica (SiO_2) and powdered activated carbon (PAC) as additives. The membranes' performance is tested multiple times to evaluate for their pure water permeation, groundwater filtration flux, the effectiveness of groundwater turbidity, colour, chemical oxygen demand (COD), iron, and lead removal. Results showed that the 5.0 wt.% PES-PAC membrane has the best filtering permeate and flux volume along with the highest removal efficiency for turbidity, colour, COD iron, and lead removal, which are 99.33%, 96.15 %, 96%, 100%, and 100%, respectively. All low-pressure membrane systems successfully reduced the iron concentration in groundwater to the irrigation water standards. Whereas, the 5.0 wt% PES-PAC and 5.0 wt% PES-SiO2 membranes can meet the lead requirements for agricultural water. The membrane with 5.0 wt% PES-PAC fulfils the lead content requirement after treatment for drinking water quality showing the membrane with PAC incorporation as an alternative water treatment technology to ensure water safety.

1 Introduction

Water scarcity, exacerbated by climate change, population growth, and inadequate resource management, affects billions globally, hindering social and economic development [1]. To mitigate this challenge, exploring alternative water sources like groundwater is crucial. Groundwater, vital for agriculture and drinking, provides a dependable, year-round supply, particularly beneficial for small-scale farmers [2]. However, its utilisation varies across countries due to factors like surface water availability and contamination issues, such as heavy metals, which impede its use for irrigation and drinking. Despite its potential,

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groundwater usage remains low in some regions like Malaysia due to abundant surface water and heavy metal contamination [3]. Among these contaminants, iron and lead pose significant health and agricultural risks purposes. To address this, various techniques including membrane technology, offer efficient removal solutions. Advancements in membrane technology, particularly through blending with additives like PAC and SiO_2, show promise in enhancing heavy metal removal, paving the way for more sustainable water treatment methods with lower costs and energy consumption. This research aims to develop innovative membranes tailored focuses on iron and lead removal, as they have distinctive prevalence and will damage the sprinkle water designed by farmer during irrigation activities as well as health impacts.

2 Material and methods

2.1 Membrane fabrication

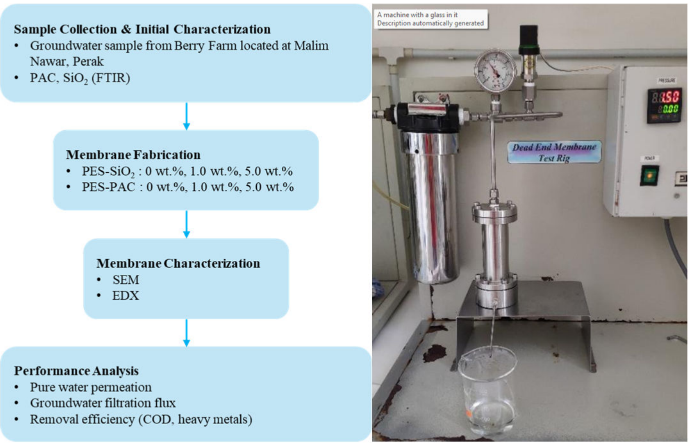

Fig. 1. (Left) Experimental flow chart. The chemical functional groups of PAC and SiO_2 were identified using Fourier transform infrared spectroscopy (FTIR). (Right) Set-up of dead-end membrane test rig.

Figure 1 shows the experimental flow and the setup of the study. PES low-pressure polymeric membrane was fabricated using the dry/wet phase inversion technique, NMP as the solvent, with SiO_2 and PAC as the additives. The mass of SiO_2 and PAC was manipulated to investigate its effects on the membrane performance in treating groundwater. Table 1 shows the mass ratio of polymer (PES), solvent (NMP), nano-silica and PAC required for each membrane fabrication. The particles size of SiO_2 used in this study was 95 nm – 188 nm. PAC applied in the membrane fabrication is from ChemPur®. All the materials (PES, PAC and SiO_2) were dried overnight at 60°C in the oven before membrane dope preparation. Then, 87 g of NMP solvent was heated to a range of 55°C to 65°C, and then polymer was added slowly to ensure complete dissolve in the solvent through mixing. The mixture was let to cool down to ambient temperature before adding an additive (SiO_2 or PAC) coupled with 8 hours of sonication for a well-mixed dope. The sonicated dope was poured evenly onto a glass plate and proceeded with the casting stage where the thickness was set to 10µm. It was then submerged into tap water where the flat sheet membrane will be formed and separated from the glass plate. The formed membrane will be left in the water for 24 hours, followed by 8 hours post treatment in methanol solution. After drying at room temperature, the membrane is now ready for filtration process.

Table 1. Quantity of PES, NMP and additives (PAC, SiO_2) for membrane fabrication in this study.

Membrane	SiO_2 additive concentration (%)	PAC additive concentration (%)	SiO_2 (g)	PES (g)	NMP (g)
0 wt. % of PES-SiO_2	0	0	0.00	13.00	87.00
1 wt. % of PES-SiO_2	1	0	0.13	12.87	87.00
5 wt. % of PES-SiO_2	5	0	0.65	12.35	87.00
1 wt. % of PES-PAC	0	1	0.13	12.87	87.00
5 wt. % of PES-PAC	0	5	0.65	12.35	87.00

2.2 Membrane characterisation

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) were performed on the membranes to analyze their surface morphology and elemental composition, respectively. For SEM analysis, the membranes were immersed in liquid nitrogen to enhance structural visibility, followed by sputter-coating with a Pt/Pd layer to prevent surface charging by electrons. Similarly, the membranes for EDX analysis were also sputter-coated to ensure accurate detection of elemental substances on the surface. As reported by Ha et al. (2020), the average particle size distribution and surface area are 0.6 mm and 956 m^2 g^{-1}, respectively [4].

3 Results and discussion

3.1 Characterisation of PAC and SiO_2

The FTIR spectrum for PAC (Figure 2 (a)) shows the adsorption bands around 2300 - 1600 cm^{-1} indicating the presence of C=O, a carbonyl group, typically found in PAC, proving the formation of active carbon. The band at 1636 cm^{-1} and 1300 – 1100 cm^{-1} indicates the vibration of the aromatic C=C group [5]. Moreover, the company of Si-O-Si vibrations aligns with the band observed at 542 $cm^{-1.}$ The FTIR spectrum for SiO_2 in Figure 2 (b) shows absorption band at 777 cm^{-1} indicates the O-Si-O bending vibration characteristic. The band corresponding to vibration bending can be noticed at 1637 cm^{-1} to 1617 cm^{-1}, proving an O-H stretching bond. The adsorption band at 2921 cm^{-1} and 2023 cm^{-1} indicates the buckling vibration of Si-O, whereas the band at 3551 cm^{-1} to 3241 cm^{-1} indicates the presence of the OH-group of Si-OH [6, 7].

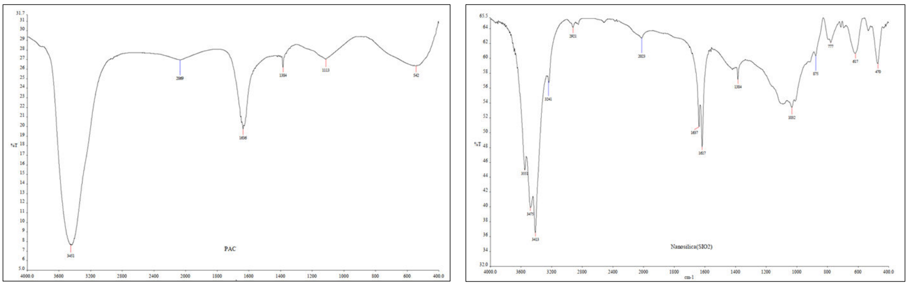

Fig. 2. (a) FTIR spectrum of PAC (b) FTIR spectrum of SiO_2.

3.2 Characterisation of low-pressure membrane

3.2.1 Morphology analysis

The cross-sectional results (Figure 3 (a)) showed that the 0 wt.% pristine polymers have the least porosity and lacks strong connectivity to the underlying sublayer, leading to reduced permeability. 5.0 wt.% PES-PAC membrane exhibits larger macrovoids with greater porosity. As the additive concentration rises, the formation of larger voids and the connection between layers become more pronounced and uniform. The additives in the polymer binder can reduce the interactions between polymer molecules, forming sizable micro-voids [8].

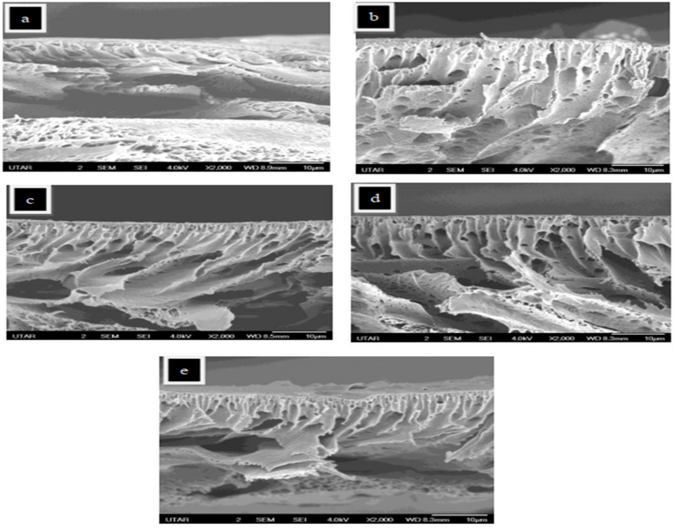

Fig. **3.** (a)-(e) SEM images of cross section morphology of (a): 0 wt.% Pristine membrane; (b): 1.0 wt.% PES-SiO_2 membrane; (c): 5.0 wt.% PES- SiO_2 membrane; (d): 1.0 wt.% PES-PAC membrane; (e): 5.0 wt.% PES-PAC membrane.

3.2.2 EDX analysis

The data presented in Table 2 shows that the membrane surface retains a higher concentration of iron ions than lead ions. This observation underscores the selective affinity of the membrane surface for iron ions, further emphasizing the effectiveness of the membrane in capturing and retaining these heavy metal ions during the filtration process. Overall, the 5.0 wt.% PES-PAC membrane can represent the optimal additive concentration for generating the highest iron retention and lead rejection within the membrane [9].

Table 2. The concentration of iron and lead remains on the surface by different wt.% of membrane.

Membrane	Weight Percentage (%)	
	Iron (Fe)	Lead (Pb)
0 wt. % of pristine	89.33	10.67
1 wt. % of PES-SiO_2	51.22	48.78
5 wt. % of PES-SiO_2	84.04	15.96
1 wt. % of PES-PAC	82.69	17.31
5 wt. % of PES-PAC	92.38	7.62

3.3 Membrane performance analysis

Produced membranes were tested on their pure water permeation, groundwater filtration flux, and the removal ability on COD, Fe and Pb as shown in Figure 4. All test was repeated three times, and an average value was taken for analysis. In pure water permeation test, 5.0 wt% PES-PAC membrane has the highest pure water permeation, which ranges from 411.04 L/m^{2}h to 813.61 L/ m^{2}h. The second highest pure water permeation ranges from 349.52 L/ m^{2}h to 739.91 L/ m^{2}h, by the 1.0 wt% PES-PAC membrane, followed by 5.0 wt% PES-SiO_2 membrane (293.59 L/ m^{2}h to 685.06 L/ m^{2}h), and 1.0 wt% PES-SiO_2 membrane (285.44 L/ m^{2}h to 610.94 L/ m^{2}h). While the 0 wt.% Pristine membrane has the lowest permeation from 217.71 L/ m^{2}h to 411.04 L/ m^{2}h. Better permeation of hybrid membrane due to amplified permeability and enlargement of pore dimensions within the resulting membrane structure [10]. The appearance of the OH functional group of both membranes, proves the increased hydrophilic property of the membrane, thus reducing hydraulic resistance and enhancing the water permeation [11]. Figure 4 shows that the water permeation is directly proportional to the increase in pressure. Notably, membranes infused with SiO_2 and PAC individually demonstrate substantial improvements in membrane permeability when contrasted with the unmodified pristine membrane. This enhancement can be attributed to the amplified permeability and enlargement of pore dimensions within the resulting membrane structure [10].

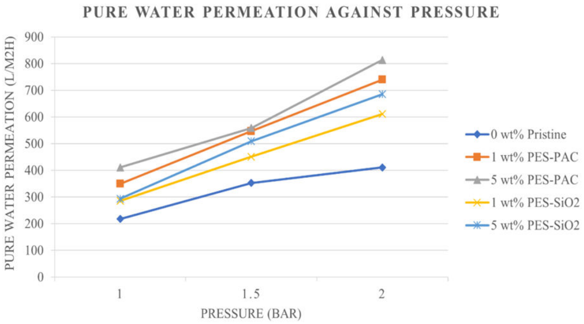

Fig. 4. Relationship between pure water permeation of different wt.% membranes and pressure.

For groundwater filtration flux, the 5.0 wt.% PES-PAC membrane exhibited the highest initial groundwater filtration flux at 458.31 L/m^{2}h, followed by the 5.0 wt.% PES-SiO2 membrane (304.17 L/m^{2}h), 1.0 wt.% PES-SiO_2 membrane (262.04 L/m^{2}h), 1.0 wt.% PES-PAC membrane (131.53 L/m^{2}h). The 0 wt.% Pristine membrane had the lowest initial filtration flux at 115.09 L/m^{2}h. The larger macro voids in the modified membrane enable enhanced water adsorption and elevated flow rates of substances through the pores. This, in turn, leads to a quicker accumulation of pollutants at the pores, subsequently contributing to membrane fouling at an accelerated rate [3]. Similar phenomena in study by Mulyati et al. (2020) where higher concentration of silica generated higher water flux [10].

In COD removal analysis, the 5.0 wt.% PAC achieved the highest COD removal efficiency at an impressive 96 %. Following closely behind was the membrane with 5.0 wt.% SiO_2, with a COD removal efficiency of 94%. The 1.0 wt% PES-PAC membrane exhibited an efficiency of 82.14%, and the 1.0 wt% PES-SiO_2 with 78.95 % COD removal. Notably, the 0 wt% Pristine membrane achieved a COD removal efficiency of 71.43%. This enhancement in removal efficiency can be attributed to nanoparticles, which act as exceptional molecular sieves with highly effective separation capabilities, as demonstrated in the study by Kusworo et al. (2017) [12]. As reported by Taghavi et al. (2021), COD removal efficiency of 68% was achieved in treating leachate wastewater [13].

Fe and Pd metal removal tests showed that all hybrid membranes incorporating additives exhibit a consistent iron removal efficiency, ranging from 98.04 % to 100 %. In lead removal, only the 5.0 wt% PES-SiO_2 and 5.0 wt% PES-PAC membrane exhibit significant removal efficiency, achieving 96.05% and 100%, respectively. All the low-pressure membrane systems produced are effective in reducing iron and lead concentrations in groundwater to meet the acceptable limits for irrigation water. It was observed that the lead removal efficiency is lower than the iron removal efficiency. This phenomenon is because lead has a smaller ionic radius and higher charge density than iron. Consequently, lead ions encounter greater resistance when attempting to traverse the membrane's pores, leading to diminished removal efficiency [14]. The modified membranes' effective removal of heavy metal ions can likely be attributed to the electrostatic exclusion mechanism suggested by Dadari et al. (2022) [15]. It is proven by this study, as stated in Table 2, the membrane added with different types of additives led to negative surface charges, thus leading to the ability of electrostatic repulsion for heavy metals.

4 Conclusion

Flat sheet asymmetric membranes with varying concentrations of additives (nano-silica or PAC) were successfully produced using various additives concentration. Addition of both additives was found to be effective in permeability, solute filtration flux, COD, and the removal efficiency of iron and lead. The 5.0 wt.% PES-PAC membrane exhibited the largest, most uniform pore sizes and greatest lead rejection, indicating the highest pure water permeation and groundwater filtration flux. The 5.0 wt.% PES-PAC membrane was proven most effective in removing COD, iron, and lead, demonstrating superior heavy metal removal efficiency compared to other membranes in this study. As this research is a preliminary study on this collaboration work, more future analysis is needed to explore the feasibility, reusability and cleaning of the membrane.

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