Enhanced Performance of Graphene-Oxide Polyethersulfone Nanocomposite Membrane Wastewater and its Fouling Mechanism

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Abstract. Membrane fouling is still a great challenge in filtration process for wastewater treatment which limits its technical and economic performance. To prevent and control on fouling it is important to understand the filtration behaviour and fouling mechanism. In this study, a new graphene oxide-polyethersulfone nanocomposite (GPN) membrane is fabricated and later the performance and rejection of heavy metals removal were studied using a dead-end filtration system. The performance of the fabricated GPN membrane was measured by evaluating pure water flux, salt and heavy metals removal. Fouling mechanisms are investigated for lead-containing wastewater using pore blocking models. From the results, cake filtration was found to dominate all other filtration mechanisms with the highest R^2 at all the applied transmembrane pressure. Furthermore, the experimental results confirmed that adding GO to the membrane improved pure water flux, and heavy metals removal, and can be used as a novel method for preparing high performance membranes in wastewater treatment.

Keywords: graphene oxide-polyethersulfone; nanocomposite; membrane; fouling mechanism; wastewater treatment.

INTRODUCTION

Wastewater pollution related to heavy metals contamination is one of the major problems that led to environmental and health concerns worldwide which occur as a result of both natural and human activities [1, 2]. Heavy metals were identified as one of the inorganic pollutants found in significant amounts in industrial effluents discharges. The most common hazardous heavy metals such as arsenic, lead, copper, cadmium, chromium silver and other chemical pollutants need to be removed from wastewater effluent. Among those heavy metals, lead (Pb) is one of the common and most toxic pollutants in natural waters. Lead contaminations present in water sources are usually associated with mining industries such as petroleum mining, smelting, lead-acid battery manufacturing, fabrication of semiconductors and incineration of solid wastes [3]. In addition, according to Malaysia Environmental Quality Report (DOE, 2017), lead is one of the highest contaminants' concentrations found in tested water and it falls under Class II risk of toxicity.

Accumulation of lead in wastewater streams and long-term exposure of human bodies to lead makes them susceptible to a variety of infections and diseases including rising in blood pressure, kidney damage, brain damage, and behavioural disruption in children [4, 5]. Therefore, the treatment is necessary for lead removal from wastewater which can be used as part of a reuse and reclamation strategy or to help achieve the requirement of process water quality.

The reuse of treated wastewater is the key access to discover new water resources. There are many ways to treat wastewater including adsorption, membrane filtration, chemical precipitation, ion exchange and electrodialysis [6, 7]. One of the widely used technology in treating wastewater is by using a membrane. Membrane technology was developed in the mid of 1980s and it is functioning as a physical barrier that allows wanted materials (permeate) to pass through while the unwanted constituents (retentate) to be retained on the membrane surface based on the molecular and pore sizes of the components and membrane, respectively [8]. The development of membrane technology plays a significant role in water/wastewater treatment due to its simplicity in operation, cost-effectiveness, high productivity, high removal capacity and scale-up easiness [9]. Moreover, membrane technology is an attractive approach for heavy metal removal due to the dual function of membrane adsorption and filtration [8]. To date, the incorporation of nanomaterials in membrane fabrication has proven to improve membrane performance. Thus, the integration of membrane technology and nanotechnology has further increased the effectiveness of adsorbent materials providing innovative systems to novel adsorptive/filtration membranes for improving wastewater treatment.

Polymeric membranes have shown great promise in the separation and purification process in wastewater treatment due to their biocompatibility, structural flexibility and versatile surface chemistry [10]. However, the major limitation of conventional polymeric membrane technology in wastewater treatment is membrane fouling [11]. Moreover, the information on the fouling mechanism of heavy metals in the filtration behaviour of the modified membrane have not yet been elucidated. Therefore, by studying the fouling mechanism through pore blocking models, the gap in the membrane's fouling propensity knowledge can be fulfilled. Hence, highly motivated to contribute a subsequent new and robust method for modified membrane fabrication and its effective application, this study investigates the ability of the new graphene oxide polyetehrsulfone nanocomposite (GPN) membrane to remove heavy metals from wastewater and analyze their fouling mechanisms.

MATERIALS AND METHOD

Materials

All reagents used for fabrication were analytical grade. Lead nitrate ($PbNO_3$; 99%), iron sulfate ($FeSO_4$: 98%) were purchased from R&M Chemicals. Copper sulfate ($CuSO_4$; 98%) were supplied from Ajax Finechem and aluminium sulfate ($Al_2(SO_4)_3$) were purchased from HmbG Chemicals. Deionized water was used as the nonsolvent for polymer precipitation and sample preparation. The synthesized graphene oxide was used throughout the experiment.

Experimental and Methodology

Filtration experiments were conducted using a hand-made dead-end membrane filtration set-up which was fabricated specifically for this work, with variation of transmembrane pressure (TMP) and filtration time. The compaction step was carried out for 15 min at a pressure of 3 bars to obtain steadier solution flux and to remove residual chemicals. Membrane pure water flux was conducted for 20 min at a pressure of 3 bars. The permeate flux and permeability were calculated using Equations 1 and 2:

$$J_w = \frac{\Delta V}{A \Delta t} \tag{1}$$

$$J_p = \frac{\Delta V}{A \Delta t \Delta P} \tag{2}$$

where J is the measured permeate flux (L/m^2 h), ΔV is the permeate cumulative volume (L), A is the effective membrane surface area (m^2), Δt is the filtration duration (h) and ΔP is the pressure (bar). Then, analysis of filtration blocking mechanism was investigated according to the complete blocking, standard blocking, intermediate blocking and cake filtration models for the GPN membrane. The permeate volume at different filtration time data was recorded at each TMP, and the flux–time plots were used to evaluate the fouling propensity of the feedwater. The linearized version of the models was employed for evaluation of the pore blocking mechanism. From the models, the dominant model in the mechanisms with the best linearity with the experimental data was observed.

To validate the applicability of GPN membrane, the simulated wastewater containing heavy metals were used in the treatment. In general, industrial effluent contains a variety of pollutants which is more than one of heavy metals. As a result, incorporating other heavy metals would serve as simulated real-world wastewater, allowing the hindrance of other metal ions to be determined utilizing the GPN membrane. In this study, the simulated industrial wastewater was prepared based on the real waste content as reported previously [12] and tested for the applicability of the GPN. The components of simulated wastewater from industrial wastewater were tabulated as in Table 1 which were according to previous findings from mining and semiconductor industries pertaining to the multi-metal ions system. The lead (Pb) ion concentration was mixed with other metals including iron (Fe), copper (Cu) and aluminium (Al). Then, the dead-end filtration was conducted as described above using the prepared simulated wastewater. Finally, the final concentration of the multi-metal elements was determined using Inductively coupled plasma mass spectrometry (ICPMS) and the removal efficiency were observed.

TABLE 1 : Components of simulated wastewater containing heavy metals

Component of heavy metal	Pb	Fe	Cu	Al
Concentration (mg/L)	1.5	3.5	2	3

RESULTS AND DISCUSSION

The membrane performance was evaluated in terms of clean water flux, permeability and flux recovery ratio. The results are explained in the following sections.

Membrane mean pore radius

The mean pore radius of the membranes was measured since pore size distribution plays a crucial influence in membrane performance and permeability. The results are demonstrated in Figure 1 below. Based on the results of mean pore radius of the membranes presented in the Figure 1, GPN membrane showed an increase mean pore radius when compared to neat PES membrane, which is 47.5 nm and 31.1 nm for GPN and PES membranes, respectively.

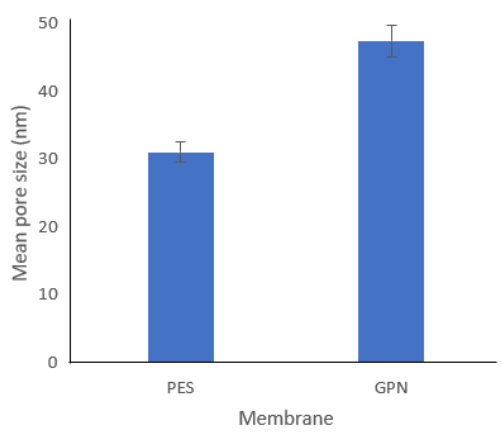

FIGURE 1: Mean pore radius of bare PES and GPN membranes.

The value of mean pore radius for PES membrane is comparable with other studies in the range of 22.7- 32 nm (Dizge et al., 2017; Najjar et al., 2019). Meanwhile, the value of mean pore radius for GPN membrane in this study is higher than other GO-PES composite membranes which were 21.92 nm [13] and 24.1 nm [14]. The pore radius of the fabricated GPN membrane revealed that the addition of GO increases the pore radius [15, 16]. The addition of hydrophilic nanoparticles (GO) to the casting solution can decrease the thermodynamic stability of the casting solution (weakening the van der Waals interaction between the polymer and solvent molecules). This enabled the solvent molecules to diffuse rapidly from the polymer matrix to the coagulation bath and thus resulted in the formation of larger pore size and porosity structure of the polymer membrane [17]. In addition, other factors that controlled the pore size and pore distribution were the type and molecular weight of polymers, composition of polymer and phase inversion kinetics (evaporation time after casting) [18]. The mean pore radius of GPN membrane is favorable to membrane permeability; that membrane with higher porosity recorded higher water flux [15, 17, 19] as discussed in the next section.

Clean water flux and permeability

Clean water flux (CWF) was determined for both bare PES and GPN membrane at three different transmembrane pressure (TMP) which are 2, 2.5 and 3 bar. This was done to determine the level of fouling in the membranes in relation to the feedwater. Furthermore, these parameters are frequently required in filtration modelling and simulation based on the Hermia's pore blocking and Darcy's cake filtration models. From the graph shown in Figures 2 and 3, constant fluxes were obtained at each TMP in relation with filtration time for both PES and GPN membranes. This suggests that the deionized water employed in this research was devoid of particles that might have blocked the membrane pores. Furthermore, it was discovered that as TMP increased, the permeate volume of water increased, in accordance with Darcy's law of fluid flow through a porous medium (membrane).

From the plotted graph (Figure 2), the recorded water fluxes for bare PES membrane were 478, 442 and 338 L/m^2h at TMP of 2, 2.5 and 3 bar, respectively. Meanwhile, water fluxes for GPN membrane (Figure 3) were 766, 718 and 681 L/m^2h at 2, 2.5 and 3 bar of TMP, respectively. The clean water permeability (CWP) is also measured for both membranes indicating GPN membrane has higher permeability compared to bare PES membrane. At 3 bar of TMP, the CWP are 1851 and 2150.36 $L/m^2h.bar$ for PES and GPN membranes, respectively. Therefore, it was suggested that the latter result exhibited higher water flux and permeability due to increased porosity and more hydrophilicity as reported from previous studies [16, 20].

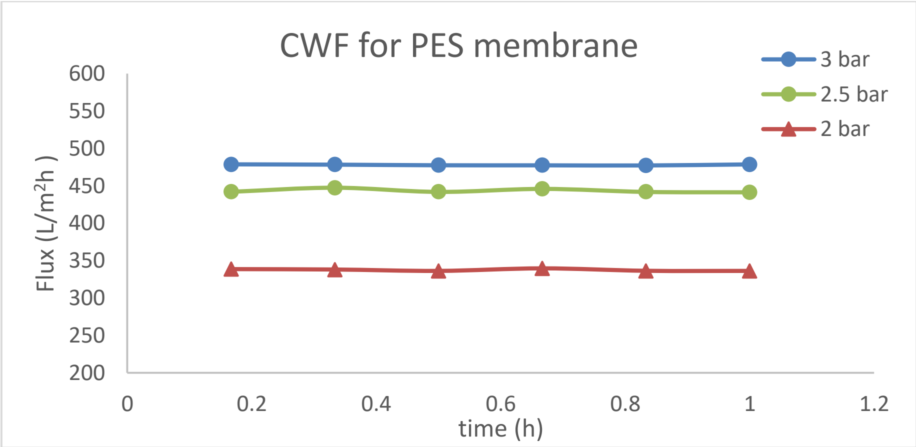

FIGURE 2: Clean water flux graph for PES membrane at different TMP

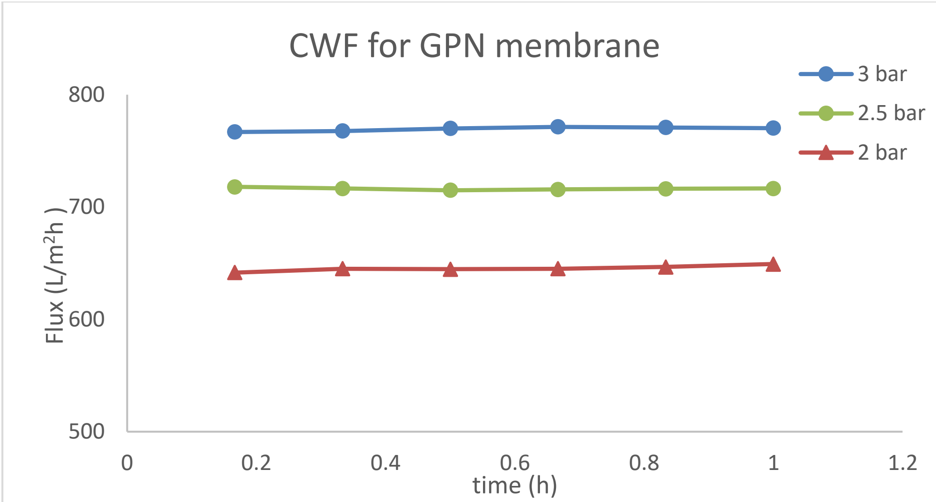

FIGURE 3 : Clean water flux graph for GPN membrane at different TMP

In addition, the low pure water flux value is obtained for pure PES membrane due to membranes very tight polymer matrix is formed, thus the pores formed on the membrane surface will be in smaller size. When the GO is added in the membrane, CWF showed an increased value. Increase in the CWF could be due addition of nanoparticles GO, has been confirmed to systematically increase the average pore size of the membrane [21, 22].

Removal of Pb by GPN membrane

The filtration process was then conducted GPN membrane at different TMP utilizing 100 ppm of lead solution as inlet feed using dead-end filtration system to investigate the GPN membrane permeation performance. The experiments were triplicated, and the average values of the flux vs time were plotted. From the graphs, it was observed that higher TMP generated higher fluxes for the whole filtration time. The permeation flux of GPN membrane (Figure 4) sharply decreased with time at the onset of the filtration, but the flux gradually attained stability and was almost constant after 40 min.

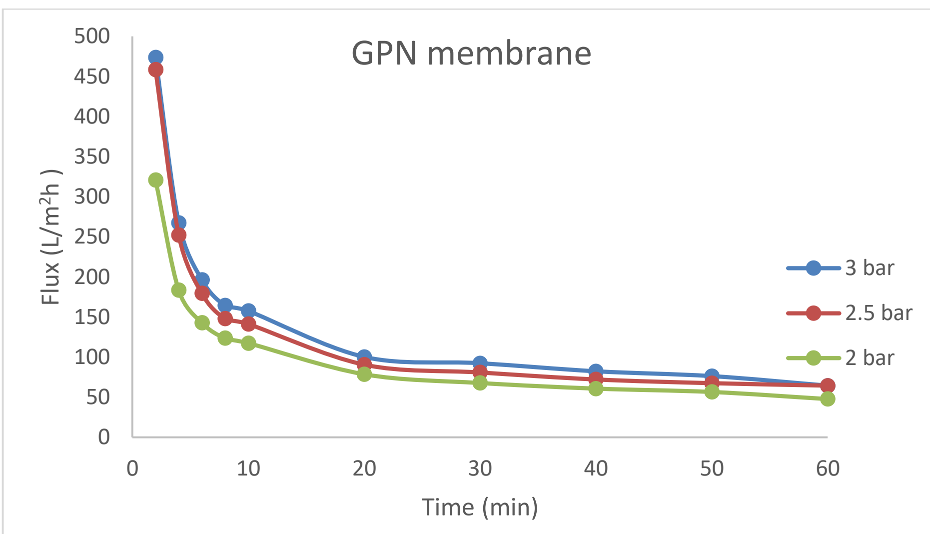

FIGURE 4: Effect of TMP of permeation flux of PES membrane

Fouling Mechanism Analysis

The phenomenon of decreasing flux with time is commonly used to describe membrane fouling. However, the flux–time plots of the filtration tests do not adequately depict the fouling tendencies of the feed on the membranes. Thus, the fouling mechanism of the feed on the GPN membrane was further analyzed using the improved Hermia law of blocking filtration. Four models were used to investigate the filtration blocking mechanisms of the membrane which were complete blocking, standard blocking, intermediate blocking and cake filtration models and the linearized models follow the mathematical relation as in Equations 1 to 4, respectively [23–25]:

$$\boldsymbol{Q = Q_i - K_b V} \qquad (3)$$

where Q is the volumetric permeate flow rate (L/h), Qi is the initial volumetric permeate flow rate (L/h), V represents the permeate volume (L) and K_b is the filtration constant for complete blocking model.

$$\boldsymbol{\sqrt{Q} = \sqrt{Q_i} - \left(\frac{K_s\, V \sqrt{Q_i}}{2}\right)} \qquad (4)$$

Where K_s in the equation represents the model constant for standard pore blocking which is derived from the slope of the plot and the value of Q_i, the volumetric flow rate of eluent is represent by the intercept of the plot.

$$\boldsymbol{\frac{1}{Q} = K_i t + \frac{1}{Q_i}} \qquad (5)$$

where t is the filtration time, and K_i represents the intermediate blocking model constant which is derived from the slope and Q_i is the intercept of the experimental plot.

$$\boldsymbol{\frac{1}{Q} = \frac{1}{Q_i} + K_c V} \qquad (6)$$

where K_c is the constant for cake filtration model which is derived from the slope of linearized plot and Q_i is the intercept of the graph. The constant-pressure filtration blocking models were fitted to each of the filtration experiments performed at constant TMP of 2, 2.5 and 3 bar for GPN membrane used in this study. The linearized plot for all models were shown in Figures 5, 6 and 7.

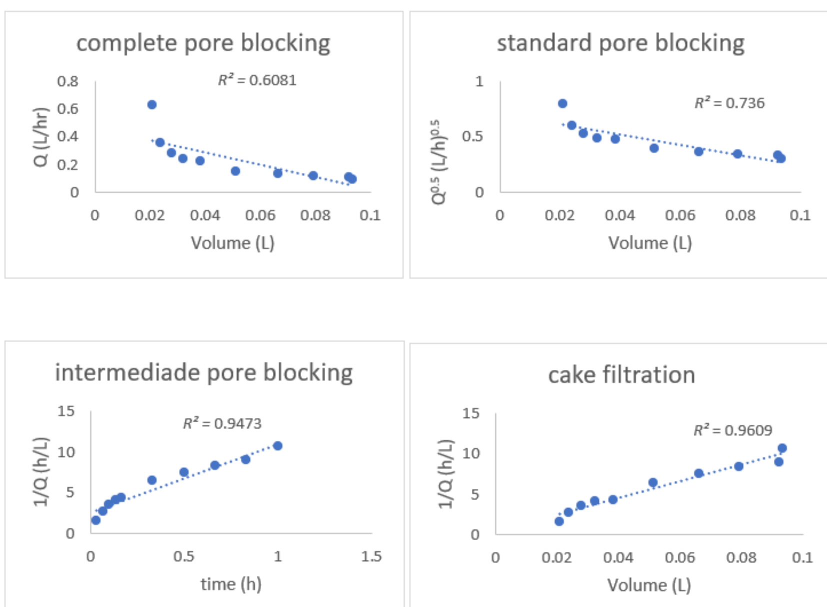

FIGURE 5: Pore blocking models plot for GPN membrane at 2 bar

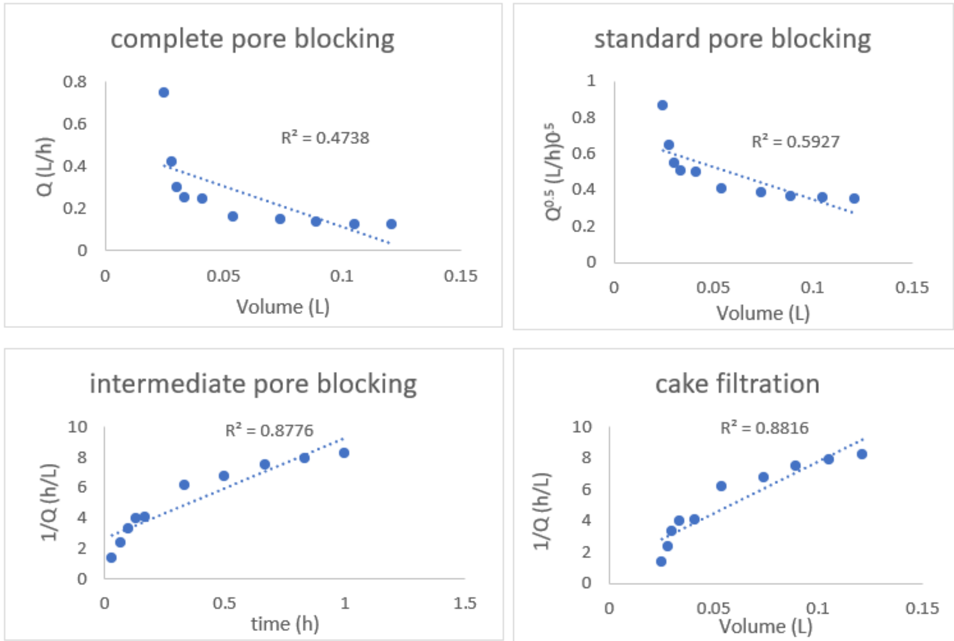

FIGURE 6: Pore blocking models plot for GPN membrane at 2.5 bar.

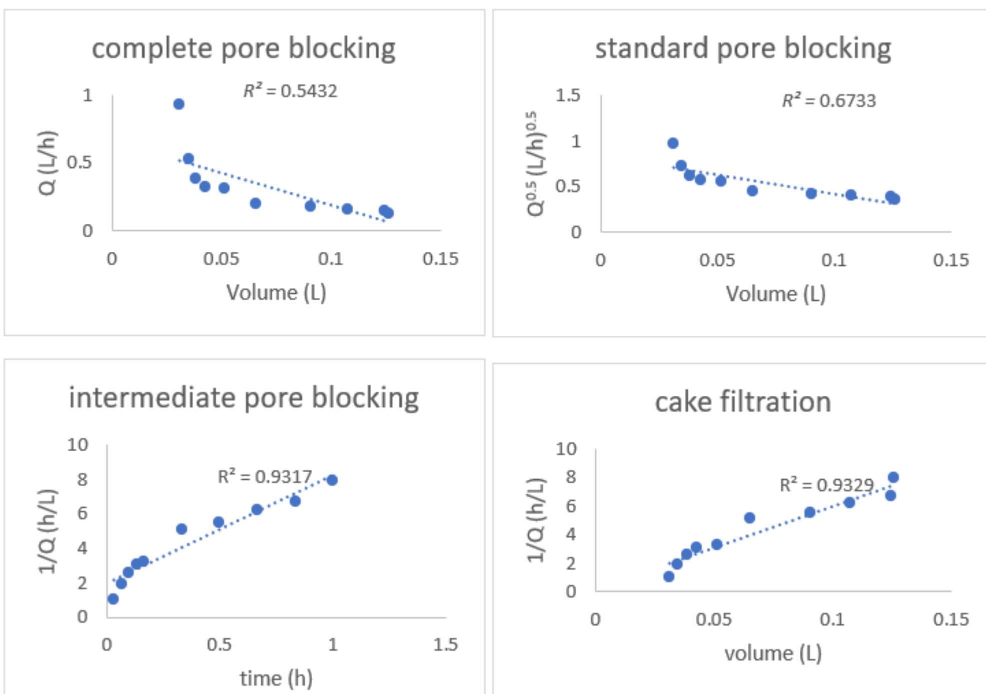

FIGURE 7: Pore blocking models plot for GPN membrane at 3 bar.

According to the model values, filtration stability at 2 bar was found to be relatively close to that at 3 bar, particularly in the case of cake filtration and intermediate blocking models (Table 2). However, the best fitting condition (2 bar) was chosen on the basis of the highest R^2 values in order to keep the fouling and flux of the filtration process in balance. Despite having a higher TMP results in greater permeate flux before a critical or limiting flux is established, such TMPs will invariably result in increased energy consumption.

TABLE 2: Linear regression values for pore blocking models of GPN membrane

TMP	R^2 of filtration models			
	Complete blocking	Standard blocking	Intermediate blocking	Cake filtration
2 bar	0.6081	0.736	0.9473	0.9609
2.5 bar	0.4738	0.5927	0.8776	0.8816
3 bar	0.5432	0.6733	0.9317	0.9329

It is evident from the Table 2 that cake filtration dominated all other filtration mechanisms with the highest R^2 at all the applied TMPs. Before the cake filtration prevailed, other blocking mechanisms (complete, standard, and intermediate blocking models) played a minor role in pore blocking. This phenomenon indicates that the process may be able to accommodate longer filtration times because the residual foulants will not completely block the membrane pores but instead, will form cake layers that will act as a secondary filter for the filtration process.

Multi-metal ions rejection

To validate the applicability of GPN membrane on the multi metal ions rejection, the filtration was conducted using simulated wastewater. Generally, metal ions removal from aqueous solutions is attributed to two types of interactions which are electrostatic and Van der Waals. The electrostatic interaction is related to the surface charges formed on the absorbent surface, whereas the Van der Waals interaction is related to the coordination of functional groups with metal ions [26]. In the formation of GO, the graphite carbon network with sp2 hybridization is severely disrupted, and then the carboxyl groups are positioned at the edges. Therefore, metal ions can be coordinated due to the presence of OH and COOH groups in GO. Metal ions compete each other for these interactions when dealing with nanocomposites. Metal ions are eventually eliminated through a three-step method that involving external diffusion, diffusion into the nanocomposite, and adsorption in the nanocomposite [16]. The results of the multi metal ions rejection showed in the order of Pb > Al > Cu > Fe as illustrated in Figure 8. The highest and lowest removal percentage is related to Pb and Fe, respectively.

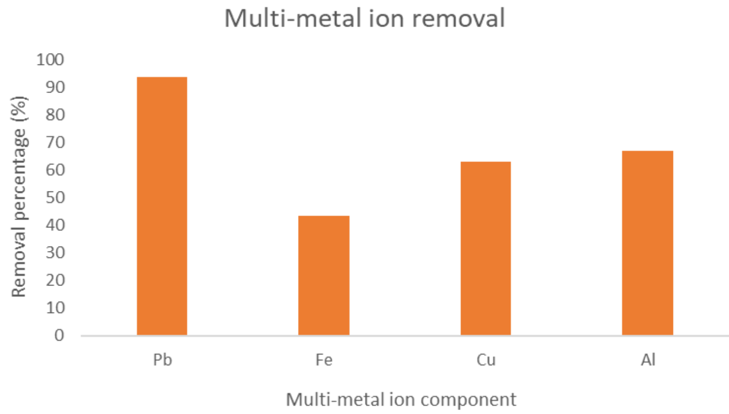

FIGURE 8: Heavy metals rejection using GPN membrane

CONCLUSION

In conclusion, the new fabricated GPN membraned demonstrated enhanced performance pertaining to its permeation flux and Pb ions removal. Linear fitting of single membrane fouling models to experimental data showed good linearity ($R^2 > 0.96$) of cake filtration model. The cake layer model mechanism indicating that the process may be able to accommodate longer filtration times. This study also employed simulated wastewater containing multi-elements of heavy metals ion to validate the applicability of the GPN membrane in real wastewater treatment. The removal percentage of heavy metals rejection in descending order of Pb, Al, Cu and Fe were 94, 67,63 and 43%, respectively. Therefore, the utilization of GPN membrane will ultimately help reduce metal and preserve our diminishing freshwater worldwide so that the treated wastewater to become a significant source of clean water.

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