Synthesis of Two-Dimensional Nanomaterial Based Hybrid Membrane for Antibiotic Removal from Wastewater

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Abstract. The presence of high concentrations of antibiotics in wastewater has paved the way for the development and spread of pathogens with antimicrobial resistance (AMR). Coupled with the global water stress, this leads to adverse effects on both the environment and human health. Conventional wastewater treatment plants lack antibiotic removal efficiency, hence untreated wastewater eventually finds its way into groundwater or surface water. Nanomaterial-based membrane technology has shown outstanding characteristics, particularly two-dimensional (2D) nanomaterials. In this study, graphene oxide (GO), MXene ($Ti_3C_2T_x$), and GO)/MXene composite (50% GO/$Ti_3C_2T_x$) membranes were fabricated by vacuum-assisted filtration for antibiotic removal from wastewater. The membranes' rejection and permeability were tested. Membrane hydrophilicity and surface morphology were evaluated through water contact angle and Scanning Electron Microscopy (SEM) respectively. When compared to pristine GO and $Ti_3C_2T_x$ membranes, the composite GO/$Ti_3C_2T_x$ membrane possessed a lamellar structure with a higher interlayer spacing and higher stability. Additionally, the fabricated membranes resulted in more effective tetracycline removal from water.

Keywords: Antibiotic, Graphene oxide, MXene, Tetracycline, Two-dimensional materials, Membranes.

1. Introduction

Water scarcity is a global challenge, and it is projected to become a more critical issue by 2050 (Singh & Pradhan, 2016). Moreover, it is estimated that by 2030, 1.6 billion people will lack safely managed drinking water (Water and Sanitation - United Nations Sustainable Development). Along with the on-going water crisis, the development of antimicrobial-resistant pathogens due to the existence of antibiotics in wastewater pose another serious threat. The world uses between 100,000 and 200,000 tons of antibiotics every year, and the majority of these antibiotics are released into the environment as either their parent chemicals or their active metabolite (Hou et al., 2019). Therefore, they have been regularly found in surface water, groundwater, and soil (M. K. Liu et al., 2017). One of the most popular antibiotics for maintaining human health is tetracycline, and it has been extensively detected in wastewater treatment effluent (Li et al., 2016). Accordingly, it is highly crucial to develop sustainable and efficient treatment methods to remove antibiotics from wastewater, hence tackling water scarcity and the growth of antimicrobial resistance. Membrane processes are highly effective advanced treatment technologies, specifically at removing organic pollutants (Ankush et al., 2019). Nanocomposite-based membrane technology has attracted the attention of researchers due to the outstanding features of nanomaterials, particularly two-dimensional (2D) nanomaterials such as MXene and graphene oxide (GO). Recently, nanochannel membranes created using novel nanomaterials and microporous materials by layer-by-layer assembly techniques, in situ growth, and surface coating, etc., have emerged as promising candidates for achieving high permeance and good selectivity in water treatment, particularly biomedical separation application (Wang et al., 2021). In this work, 2D nanomaterials, MXene ($Ti_3C_2T_x$), and GO, were utilized to develop composite membranes of 1:1 ratio to improve pristine membranes' properties. The fabricated membrane was proven to have high antibiotic removal efficiency.

2. Materials and methods

GO was synthesized using the improved method (Marcano et al., 2010). 1.0 g of graphite flakes was added to a mixture of 9:1 of H_2SO_4/H_3PO_4 (120:13.3 mL) while stirring. Then 6.0 g $KMnO_4$ was added to the resulting mixture, producing an exotherm. The mixture was heated at 50 °C, and kept stirring overnight. The reaction was terminated by adding 150 mL of cold DI water containing 3 mL H_2O_2. After that, GO was washed using DI water. To synthesize $Ti_3C_2T_x$, aluminum was etched from the MAX phase (Ti_3AlC_2) to get 2D layers. This was done using in situ HF. $Ti_3C_2T_x$ was then washed using DI water to increase its pH. Both GO and $Ti_3C_2T_x$ were freeze-dried to get their powder form.

To prepare three membranes: GO, MXene, and 50%GO/$Ti_3C_2T_x$, a known mass of the dried forms of GO and MXene was dispersed and sonicated in water to form a solution. Two equal quantities of both solutions were mixed and sonicated for 1 h. Using vacuum-assisted filtration, GO solution, MXene solution, and 1:1 MXene GO solutions were filtered forming thin layers of membranes.

Membranes' surface wettability was evaluated through a goniometer (Krüss GmbH' Drop Shape Analyzer). Membranes were characterized using a Scanning Electron Microscope (Quanta 250 ESEM). Surface images were taken to analyze the structural morphologies of the membranes. To test the membrane performance, 50 mL of DI water was filtered multiple times at 1 bar, and the water permeability (P_m) was calculated as follows:

$$P_m = \frac{V}{A \times \Delta t \times P}$$

where V represents pure water permeate volume (L), A is the membrane effective area (m^2), P is the pressure, and Δt is the permeation time (hr). To find the antibiotic rejection, a 10 ppm tetracycline solution was prepared and filtered using the three fabricated membranes. The membrane solute rejection (R%) was calculated as follows:

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100$$

Where C_f is the feed concentration and C_p is the permeate concentration (ppm).

3. Results and Discussion

$Ti_3C_2T_x$ has a water contact angle of 62.2 ± 1.40° making it hydrophilic. This is attributed to the surface functional groups (F, O and OH). However, GO showed a contact angle of 32.3 ± 1.21° indicating a higher hydrophilic nature due to the presence of oxygen-containing functional groups on its surface. This test proved the synthesis of composite membrane, as the contact angle decreased upon adding GO to $Ti_3C_2T_x$, showing an increase in the wettability in comparison with pristine $Ti_3C_2T_x$ membrane as illustrated in Table 1 and Figure 1.

Figure 1. Contact angle images of (a) GO, (b)50%GO/ $Ti_3C_2T_x$, and (c) $Ti_3C_2T_x$.

Table 1. Contact angle of pristine GO, $Ti_3C_2T_x$, and composite membrane.

Membrane	**Contact angle (°)**
GO	32.3 ± 1.21°
50%GO/$Ti_3C_2T_x$	52.2 ± 3.18°
$Ti_3C_2T_x$	62.2 ± 1.40°

Figure 2 shows the SEM images taken for the GO, $Ti_3C_2T_x$, and 50%GO/MXene composite membranes before and after antibiotic filtration. On the surface of the $Ti_3C_2T_x$ membrane (Figure 2 (a)), large amounts of multilayer $Ti_3C_2T_x$ nanosheets were observed, resulting in wrinkles/rough surface to the membrane. The surface image of the pristine GO membrane, Figure 2 (b), also demonstrates a certain degree of wrinkling, which is the usual structure of the GO membrane surface. In the GO/MXene composite membrane, Figure 2 (c), wrinkles are still observed. These wrinkles can enhance the strength and flexibility of the membrane while providing a high specific surface area for the membrane (T. Liu et al., 2020). In Figure 2 (d) the post-treatment composite membrane is still retaining the same morphology but with small particles on the surface explaining the presence of tetracycline rejected upon filtration.

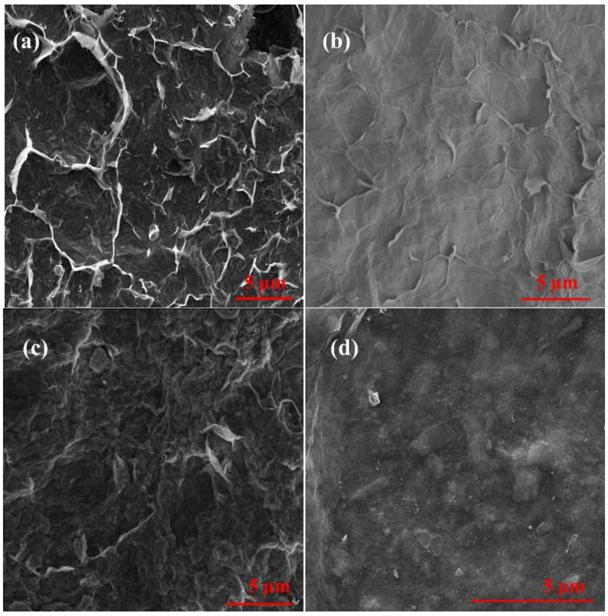

Figure 2. SEM images of fabricated membranes. (a) $Ti_3C_2T_x$ (b) GO, and (c) 50%GO/$Ti_3C_2T_x$ membranes prefiltration and (d) 50%GO/$Ti_3C_2T_x$ membrane post-antibiotic filtration

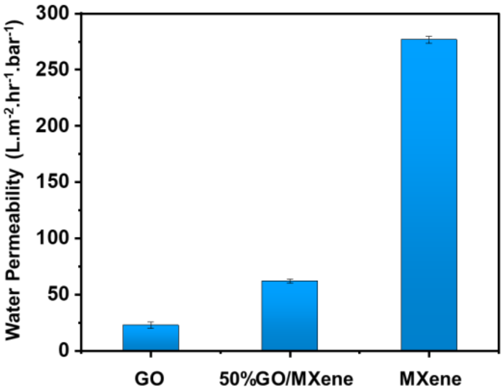

Figure 3. Pure water permeability of GO, 50%GO/$Ti_3C_2T_x$, and $Ti_3C_2T_x$ membranes.

Figure 3 demonstrates the results of P_m of the three fabricated membranes. GO membrane has a relatively low P_m of around 25 L.m^2.hr^{-1}.bar^{-1}. Introducing $Ti_3C_2T_x$ to the GO membrane resulted in a clear increase in the water flux. This is due to the increase in the interlayer spacing of the composite membrane. $Ti_3C_2T_x$ has a very high P_m, reaching around 275 L.m^2.hr^{-1}.bar^{-1} which is 11 times greater than that of the pure GO membrane. This shows a trend of increased P_m moving from pristine GO membrane to pristine $Ti_3C_2T_x$ membrane.

The trend of antibiotic rejection is opposite to the flux, in which the rejection decreases moving from pristine GO membrane to pristine $Ti_3C_2T_x$ membrane. GO membrane showed the highest rejection of around 99.9%. Pristine $Ti_3C_2T_x$ membrane has a relatively low rejection of about 43% due to its elevated spacing between the nanosheets. However, its addition to the GO membrane did not affect the rejection of antibiotic. As shown in Figure 4, GO/$Ti_3C_2T_x$ composite membrane was still able to reject 99.7% of the antibiotic.

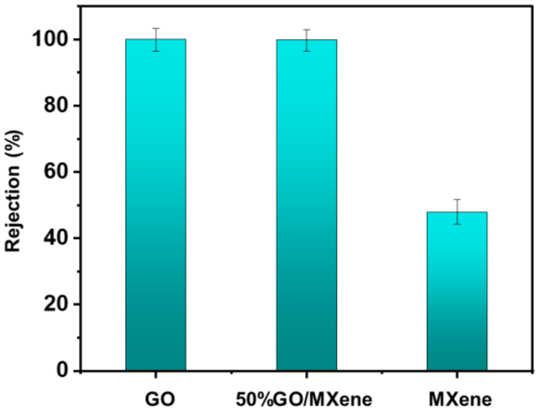

Figure 4. Rejection (%) of tetracycline using the GO, 50%GO/$Ti_3C_2T_x$, and $Ti_3C_2T_x$ membranes.

4. Conclusions

The presence of antibiotics in wastewater poses a threat to both the environment and human health, especially with the development of antimicrobial resistance. The impact of antibiotics extends to reach treatment processes, in which they deteriorate separation efficiency. Therefore, it is highly important to develop and implement technologies supporting the wastewater treatment process and effectively removing antibiotics. Among the various processes, membrane technology has distinguished aspects that are enhanced by implementing two-dimensional nanomaterials. Two-dimensional nanomaterials are a class of nanomaterials, which contain one or a few atomic thicknesses. They are considered among the most promising materials for various applications owing to their unique structure and distinctive characteristics (Bhimanapati et al., 2015). This study explained the potential of GO/MXene composite membranes in the removal of antibiotics from water. The composite membrane was successfully fabricated using layer-by-layer assembly in which it had a typical lamellar structure with higher interlayer spacing compared to the pure GO membrane and superior hydrophilicity compared to the pure $Ti_3C_2T_x$ membrane. The resultant hybrid membrane exhibited an improved P_m in comparison with pristine GO without compromising the rejection of tetracycline antibiotics, which exceeded 99% removal. Hence, it is anticipated that GO/ $Ti_3C_2T_x$ membranes will significantly increase the potential of the emerging 2D membranes for practical applications like wastewater treatment (Wei et al., 2019).

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