

Incorporation of negatively charged MWCNT-fGO self-assembled nanomaterials into PLA polymeric membranes for wastewater treatment

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Abstract The incorporation of nanomaterials in membrane's matrix aims mainly to improve the properties of the membranes such as hydrophilicity, mechanical strength, thermal stability, water flux. Multi-walled carbon nanotubes (MWCNT) and functionalized graphene oxide (fGO) have recently attracted attention, as they have proved to have potential in various applications. In this study, self-assembled MWCNT-fGO nanocomposite was synthesized and used as a filler in environmentally-friendly polylactic acid (PLA) membranes. The membranes were fabricated following the phase inversion method with different concentrations of MWCNT-fGO (2, 4, 6 and 8 wt.%). In addition, the membranes were tested for the removal of heavy metal ions from wastewater. The results showed that a considerable removal can be achieved using the composite membranes. For instance, the highest Cu²⁺, Ni²⁺ and Zn²⁺ removal (e.g., 89%, 35%, and 39%, respectively) was observed in the 8 wt.% MWCNT-fGO PLA membrane. This was achieved at water flux of 850 L·m⁻²·h⁻¹ (LMH). On the other hand, the pristine PLA membrane water flux was around 450 LMH and was capable of achieving 82, 25, and 30% rejections for Cu²⁺, Ni²⁺ and Zn²⁺, respectively. These results showed the potential of the MWCNT-fGO PLA membranes application in treating heavy-metal containing wastewater.

Keywords: Membrane filtration; wastewater treatment; carbon nanotubes; graphene oxide; self-assembly.

1. Introduction

Water security is a crucial challenge facing most of the Middle East countries including the United Arab Emirates (UAE). The country was categorized as one of the world's most water-scarce nations. Therefore, the development in the wastewater treatment technologies has become an attractive area of research nowadays. Membrane technologies considered as simpler and more efficient than other conventional separation technologies. Therefore, they have increasingly been considered as promising technology in various applications including wastewater treatment [1]. Utilizing membrane processes in wastewater treatment have proven as a viable method to purify water, in which they provide attractive solutions for low

separation efficiency, high-cost removal of contaminants, and weak structural properties. Furthermore, the search for renewable/biodegradable materials in the field of polymeric membranes has received a great deal of attention due to concerns about the environment and sustainability of dwindling petroleum materials [2]. Biodegradable polymeric membranes can be easily disposed at the end of their life without having any negative impacts on the environment. Polylactic acid (PLA) is a biodegradable polymer that has the potential of replacing conventional fossil-based materials used in membrane fabrication. However, pristine PLA membranes have some limitations in the removal of contaminants from wastewater such as heavy metal ions. Therefore, researchers often use nanomaterials as a filler in these membranes to enhance their properties and removal efficiencies. From those nanomaterials, carbon-based material such as MWCNT and GO are widely used due to their unique structures, chemical, and physical properties [3]. Therefore, in this study, novel MWCNT-fGO was synthesized and used as a filler in the PLA membrane. These membranes were tested for the treatment of heavy metals-containing wastewater and characterized using various techniques.

2. Materials and methods

2.1. Materials

PLA pellets were obtained from Good Fellow Co., UK. N, N-Dimethylacetamide (DMAc) (Mw = 87.12 g/mol, purity of ≥99%), polyvinylpyrrolidone (PVP, Mw: 40 kDa), copper nitrate (Cu(NO₃)₂), nickel chloride (NiCl₂) and zinc chloride (ZnCl₂) were all purchased from Sigma-Aldrich. HACH detection cuvettes were used to measure the concentration of heavy metals in wastewater and treated filtrate using HACH DR3900 UV/Vis spectrophotometer.

2.2. Synthesis of oxidized MWCNT (MWCNT-COOH)

In order to produce the functionalized MWCNT with COOH [1], 2 g of MWCNT was mixed with sulphuric acid

and nitric acid in a 3:1 volume ratio. The solution was kept for 30 mins at room temperature until the reaction was completed and no more heat produced. After that, the solution was heated to 70°C and kept stirring for 3.5 h. Following that, the solution was allowed to cool down to room temperature. Lastly, to stop the reaction, the solution was poured to an iced water beaker and washed 3-4 times using deionized water.

2.3. Synthesis of fGO

GO will be prepared using simplified Hummer's method [4]. Initially, Around 1.3 g of natural graphite flakes were added to a mixture of sulfuric acid and phosphoric acid at a volume ratio of (4:1 ratio). After that the solution is stirred for 3 minutes. Following that, 18 grams of potassium permanganate (KMnO₄) is then added slowly into the solution. The solution is kept stirring for 3 days at room temperature until the graphite is fully oxidized. Due to oxidation the color of the mixture will change from dark purplish green to dark brown. The oxidation process is stopped by adding hydrogen peroxide (H₂O₂). The bright yellow color of the solution indicates the high oxidation of graphite. Deionized (DI) water (DIW) and 1 M aqueous solution of hydrochloric acid (HCl) are used in washing GO for 3-4 times until a pH of 5-6 is achieved. The collected thick solution of GO is put in dialysis tubes made from cellulose, which allows the escape of substances with molecular weights less than the molecular weight of GO particles so the impurities can escape under osmotic pressure. The dialysis tubes are placed in a beaker of deionized DI water with a stirrer for 2 to 3 days. The GO is then collected in a beaker and deionized DI water is added to make the solution of 900 ml. 515 ml of the 900 ml collected GO sample solution is taken to prepare the FGO (positively charged) and the remaining solution is dried to convert it into powder. The preparation of fFGO is done prepared according to the literature [5]. Initially, 1.75 g of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) are added to the solution at room temperature and left to stir for 3 to 4 hours. EDC/NHS act as intermediate materials to accelerate the reaction rate and the final coupling efficiency by creating a bulky group for the (ED) to easily replace it. Then, around 2.5 g of ED is added to the GO solution drop wise by drop under continuous stirring, while it is stirring. The solution is alkaline, however the reaction favors acidic condition therefore HCl is added to ensure that the solution is became acidic since this reaction favors acidic conditions. Lastly, fGO was collected through After that the solution is centrifuged centrifugation.

2.4. Preparation of self-assembled negatively charged MWCNT-fGO nanomaterials

The positively charged fGO was mixed with the negatively charged MWCNT-COOH with different ratios of (e.g., 20:80, 30:70 and 40:60). The negatively charged materials overweight the positively charged materials and therefore the nanocomposite is negatively charged. Self-assembly of the positively charged fGO and the negatively

charged MWCNT is due to the electrostatic attraction as they have opposite charges. MWCNT-fGO composite improve the hydrophilicity in the membrane, because the presence of MWCNT-COOH between GO sheets provides micro channels for the penetration of water. By using zeta potential analysis, 20:80 MWCNT-fGO gave the highest negative charge of -36.5 mV compared to -27.5 mV for 40:60 and -32.6 mV for 30:70. Therefore, the PLA membranes were fabricated using different concentrations of 20:80 MWCNT-fGO ratio.

2.5. Fabrication and characterization of mixed matrix nanocomposite membrane

Phase inversion method was used to prepare all the composite membranes. In addition, pristine PLA membrane was prepared using the same method and used for comparison. Table 1 below illustrate the concentrations used in this process.

Table 1: concentration of materials used to fabricate the membranes

PLA (wt. %)	PVP (wt. %)	MWCNT-fGO (wt.%)	DMAC (wt. %)
15%	2%	0%	83
15%	2%	2%	83
15%	2%	4%	83
15%	2%	6%	83
15%	2%	8%	83

2.5.1. Porosity and Mechanical strength

The porosity of the membranes was determined using the dry-wet method. Initially, membrane samples with a total area of 5 cm² are dried in a vacuum oven at 60°C for 2 h, and their weight was recorded (W_d). Then, the samples are dipped in Galwick™ wetting liquid and their weight was measured after removing all excess liquid (W_w). The porosity ε (%) was calculated using Eq.1:

$$\varepsilon (\%) = (W_w - W_d) / (A \times \rho_w \times \delta) \times 100 \quad (1)$$

Furthermore, the Membranes water flux were calculated using Eq.2 $Pure\ Water\ Flux = \frac{V}{A \times t}$ (2)

Where V is the collected water volume in L, A is the membrane's effective surface area in m², t is the time needed to collect water in hours.

3. Results and discussion

The porosity and mechanical strength of the membranes were analyzed and the results are shown in Fig.1. The porosity of the composite membranes increased considerable after the incorporation of the nanomaterial. For instance, the porosity increased from 30% in the pristine PLA membrane to as high as 45% in the 8wt.% composite PLA membrane. This improvement in the porosity can be related to the hydrophilic nature of the

nanomaterial. During the phase inversion process, hydrophilic fillers can adsorb water, and this creates more site for water penetration. Eventually, this will lead to a more porous structure.

The mechanical strength of the membranes was also improved upon the incorporation of the nanocomposite. For example, the mechanical strength increased from

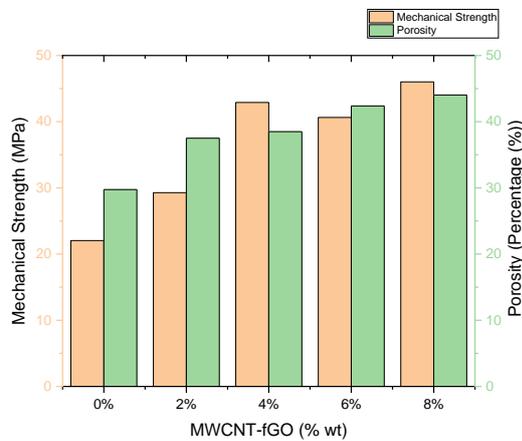


Fig 1: Membranes porosity and mechanical strength of the pristine PLA and composite membranes

The DI water flux and contact angle were evaluated, and the results are displayed in Fig. 2. It can be clearly seen that the DI contact angle decreases with the increase in the MWCNT-fGO nanocomposite concentration. For instance, the contact angle decreased from 60° in the 2 wt.% MWCNT-fGO PLA membrane to 50° in the 8 wt.% MWCNT-fGO PLA membrane. On the other hand, the pristine PLA membrane contact angle was as high as 80°. The reduction in the DI water contact angle and the increase in the hydrophilicity is mainly related to the hydrophilic nature of the nanomaterial added.

The improvement in the hydrophilicity and porosity had a direct impact on the water flux of the membranes. For instance, the composite membranes water flux increased considerably to as high as 850 LMH in the 8 wt.% membrane. This is compared to as low as 450 LMH in the pristine PLA membrane. This concludes that the improvement in the porosity and hydrophilicity contributed significantly to the improvement in the DI water flux of the membranes.

Lastly, to further evaluate the potential of the newly fabricated membranes, they were tested for the removal of heavy metal ions from wastewater. The results shown in Fig. 3 revealed decent improvement in the rejection of Cu²⁺, Zn²⁺, and Ni²⁺. The highest removal of these three heavy metal ions was observed in the 8 wt.% PLA

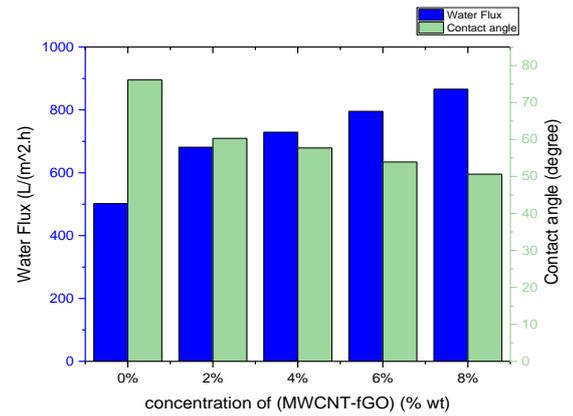


Fig 2: Water flux and contact angle

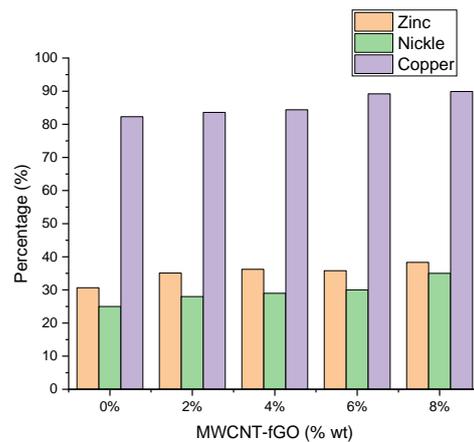


Fig 3: Heavy metals removal

4. Conclusion

In this study, self-assembled MWCNT-fGO was integrated into PLA membranes with different concentrations. The membranes were fabricated using phase inversion method. Then they were characterized and tested to remove heavy metals. The addition of nanomaterials increased the water flux, hydrophilicity, and heavy metal ions rejections. This showed the potential of these membranes in treating heavy metal-containing wastewater.

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