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

Hiyam Khalil[1], Lobna Nassar[1], Vijay S. Wadi[1], Vincenzo Naddeo[2], Fawzi Banat[1], Shadi W. Hasan[1]

[1]Center for Membranes and Advanced Water Technology (CMAT), Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates

[2]Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno - Via Giovanni Paolo II #132, 84084 Fisciano (SA), Italy

*Corresponding author: Email: shadi.hasan@ku.ac.ae; Phone: +971-2-810-92371

Abstract The integration of nanomaterials in membrane's matrix aims to improve the membrane's hydrophilicity, mechanical strength, thermal stability and water flux, which are vital membrane properties needed to active efficient removal of contaminants. Multi-walled carbon nanotubes (MWCNT) and functionalized Graphene oxide (fGO) have recently attracted attention, as they have proved to have potential in various applications. The main objective of this work was to fabricate polylactic acid (PLA) membranes incorporated with negatively charged, self-assembled MWCNT-fGO using phase inversion method. Different concentrations of MWCNT-fGO 2,4,6 and 8 wt% of the polymer were fabricated.

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 courtiers including 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 for 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 varies applications [1]. Utilizing membrane processes in water/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 mechanical, thermal and chemical stability. The search for renewable biodegradable materials in the field of polymer science 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 in the environment. PLA is a biodegradable polymer that has a great attention to replace conventional fossil-based materials used in membrane fabrication. Nanoparticles are integrated into polymeric membranes to enhance the desired properties for wastewater treatment process. Carbon-based nanoparticles such as MWCNT and GO are considered as the most studied nanomaterials due to their unique structures and their ability to enhance the thermal, mechanical and antifouling ability of the polymeric membranes [3].

2. Preparation of nanomaterials

2.1. Synthesis of oxidized MWCNT (MWCNT-COOH)

In order to produce MWCNT-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 min at room temperature until the reaction was done and no more heart produced. After that, the solution was heated to temperature of 70°C and kept stir-ring for 3.5 h. Then, the solution was cooled down to room temperature. In order to stop the reaction, the solution was poured to an iced water beaker and washed 3-4 times using deionized water.

2.2. Synthesis of fGO

GO will be prepared using simplified Hummer's method [4]. Around 1.3 g of natural graphite flakes are added to a mixture of sulfuric acid and phosphoric acid at a volume ratio of 4:1. After that the solution is stirred for 3 minutes.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 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 water with a stirrer for 2 to 3 days. The GO is collected in a beaker and deionized water is added to make a 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 FGO is done according to the literature [5]. 1.75 g of 1-ethyl-3-(3-dimethylaminopropy) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) are added to the solution at room temperature and leave 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. Around 2.5 g of ED is added to the GO solution drop by drop, while it is stirring. The solution is alkaline, however the reaction favors acidic condition therefore HCl is added to ensure that the solution is acidic. After that the solution is centrifuged for 3-4 times with DIW.

2.3. 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 20:80, 30:70 and 40:60. The negatively charged materials overweight the positively charged materials therefore the composite is negatively charged. Self-assembly of the positive 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.

3. Fabrication and characterization of mixed matrix nanocomposite membrane

In mixed matrix nanocomposite PLA membranes, nanomaterials are dispersed in the polymer dope solution. This incorporation of nanomaterials into the polymers enhance the hydrophilicity, charge density, thermal and mechanical stability of the membrane. The technique used in fabricating the membrane can vary based on the type of polymer used to fabricate the membrane and the desired membrane's structure. Phase inversion is the most commonly used method to fabricate membranes with different structure due to the rapid film formation and lower cost of this technique. The synthesized membranes were vary in the nanomaterials concentrations to study the effect of nanomaterials on the membrane performance. Membrane characterization were carried out in order to understand the structure and performance of the fabricated membrane.

3.1. 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 is recorded (Wd). Then, the samples are dipped in Galwick™ wetting liquid and their weight is measured after removing all excess liquid (Ww). The porosity ε (%) was calculated using Eq.1:

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

The porosity and mechanical strength of the membrane increase with increasing the concentration as shown in **Fig 1**.

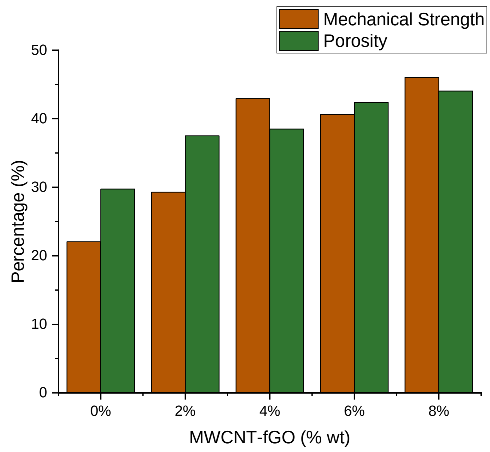

Fig 1: Membranes porosity and mechanical strength

3.2. Water flux and contract angle

Membranes water flux were calculated using Eq.2:

$$Pure\ Water\ Flux = \frac{V}{A \times t} \qquad (2)$$

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. Adding nanomaterials to the membrane matrix increases its water flux and membrane's hydrophilicity by decreasing its contact angle.

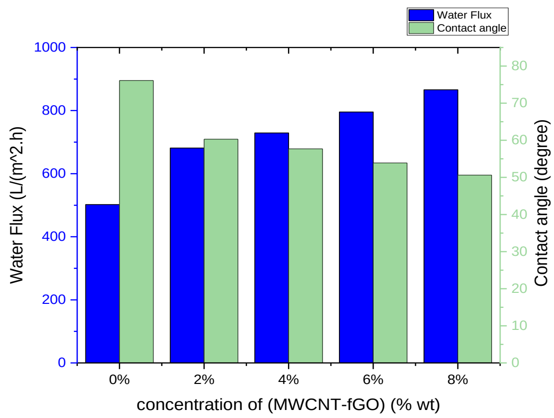

Fig 2: Water flux and contact angle

The main objective of this study was to fabricate and enhance the performance of PLA membranes incorporated with MWCNT-fGO nanomaterials. Further membrane characterization and filtration analyses were carried out to achieve optimal concentration of MWCNT-fGO.

3.3. Heavy metals removal

The removal of heavy metals is considered as one of the major concern in wastewater treatment. The results were obtained at a pH of 7 as shown in **Fig 3**. The results show high rejection of copper with a percentage around 85% for all the membranes. However, the removal of zinc and nickel is not very low compared to copper due to the least hydration and first hydrolysis constant of Cu^{2+}.

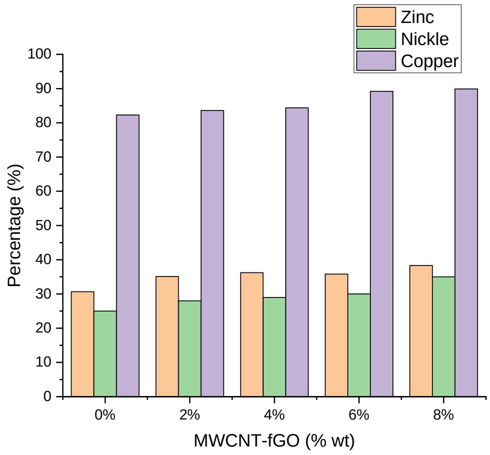

Fig 3: Heavy metals removal

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 increases the water flux and hydrophilicity of the membranes. However, it didn't improve the removal of heavy metals. Thus, further research work should be done in enhance the rejection of heavy metals.

References

[1] S. N. Kane, A. Mishra, and A. K. Dutta, "Preface: International Conference on Recent Trends in Physics (ICRTP 2016)," *J. Phys. Conf. Ser.*, vol. 755, no. 1, 2016, doi: 10.1088/1742-6596/755/1/011001.

[2] T. Gurunathan, S. Mohanty, and S. K. Nayak, "A review of the recent developments in biocomposites based on natural fibres and their application perspectives," *Compos. Part A Appl. Sci. Manuf.*, vol. 77, pp. 1–25, 2015, doi: 10.1016/j.compositesa.2015.06.007.

[3] D. Cheah, "Proposed Electromigration in Graphene Oxide / Reduced Graphene Oxide Systems Proposed Electromigration in Graphene Oxide / Reduced Graphene Oxide Systems," no. November, pp. 0–32, 2015.

[4] M.Y. Ashfaq, M. A. Al-Ghouti, and N. Zouari, "Functionalization of reverse osmosis membrane with graphene oxide and polyacrylic acid to control biofouling and mineral scaling," Sci. Total Environ., vol. 736, p. 139500, 2020, doi: 10.1016/j.scitotenv.2020.139500.

[5] S. V. Kumar, N. M. Huang, H. N. Lim, M. Zainy, I. Harrison, and C. H. Chia, "Author ' s personal copy Sensors and Actuators B : Chemical Preparation of highly water dispersible functional graphene / silver nanocomposite for the detection of melamine."