Fabrication of Ultrathin Graphene Oxide Membrane for water purification using Ink-jet printing

Fayaz Hussain*, Muhammad Sohail , Moiz Ullah Baig, Saad Arif, M. Daniyal Ahmed

***Abstract*-Low-cost, fast, and scalable method to produce Graphene Oxide (GO) membrane for water purification was studied. GO was synthesized using Tour's Method. Results of XRD, FTIR and SEM confirmed the formation of GO. The synthesized GO was dissolved in deionized water to form a dispersed ink. The viscosity of ink was increased by adding ethylene glycol and glycerin. The particle sizes of GO were in the range of ~200-350 nm. The ink was printed on commercially available PVDF membrane using ink-jet printer. The membrane was first attached over transparent film for support. The ink-jet printer successfully printed on the membrane, giving a yellowish-brown color to the membrane. A coating thickness of 11.5 µm was obtained. Membrane was used, after drying at 50°C for 2 hours, for water filtration using gravimetric method. The GO membrane fabricated using printing technique offered high rejection of salts, making it cost and energy efficient. The membrane rejected 90% of calcium carbonate, 98% of sulfate, and 71% of nitrate. The TDS of the sample was decreased by 78.6% of its value. The printing of GO using ink-jet printing can be a promising route to low cost fabrication of GO membrane.**

***Key words:* Filtration, Graphene oxide, Ink-jet-printing, Tour's Method**

I. INTRODUCTION

Water scarcity is on the most challenging goal to address for sustainable development of modern world. Approximately 1.6 billion people reside in countries where water scarcity is an alarming problem and it is expected to double in the next 20 years. Urbanization and population growth will collectively aggravate the situation in these countries [1]. The use of seawater and underground water is not unlimited due to the presence of contaminants and the high cost associated with its removal [2, 3]. Therefore, there comes the need for employing cost-effective techniques to purify contaminated water and desalinate seawater, as 97% of earth's water is seawater. Out of the many techniques available there, reverse osmosis, distillation, and ion exchange, are the most common ones. But these techniques are not economically feasible, which minimizes their utility [3].

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Graphene, an allotrope of carbon, was synthesized for the first time by Giems et al. in 2004, using graphite and scotch tape [7]. Although, the term 'graphene' was first used by Boehm et al. in 1986, for a single layer of carbon [8]. It is a two-dimensional single layer of sp2 bonded carbon atoms organized in a hexagonal lattice, having a carbon-carbon bond length of 0.142 nm [9]. Graphene exhibits some exceptional chemical and mechanical properties such as; Young's modulus 1 TPa [10], thermal conductivity (5300 W m-1 K-1) [11], and surface area (2630 m2 g-1) [12]. Because of these excellent properties, it is used in a lot of applications such as solar cells, super capacitors, batteries, and water purification [13].

Being a member of the carbon family, it is bound to show some excellent mechanical properties. Lee et al. found out the tensile strength of graphene membrane to be 130 GPa, breaking strength 200 times than steel, and Young's Modulus of 1 TPa [10]. Sharma et al. showed that single layer graphene is ten times more reactive than multi-layer graphene, by using Raman Spectroscopy. They also had one more finding, that

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the reactivity of the bulk is two times lesser than the reactivity of the edges of the graphene sheet [14].

Graphene oxide, an analogous to graphene is a compound of carbon, oxygen and hydrogen; yield by strong oxidation of graphite which introduces oxygenated functionalities in the graphite structure. GO turns out to be a favorable material for particular applications such as membranes, thin films, optoelectronics, biodevices or as a drug-delivery material. [13]. The graphene oxide possesses the following properties. The presence of oxygen functionalities, graphene oxide is easily dispersible in water and other organic solvents. For electrical properties, graphene oxide is often considered as electric insulator by reason of disruption in its sp2 bonding network. Graphene oxide become more adaptable for a lot of applications because it has the potential to be functionalized with respect to desired applications. [15, 16]

In 2004, Giems et al. produced graphene for the first time via Scotch tape method. They placed highly oriented pyrolytic graphite between the scotch tape and continuously peeled off the surface and then dissolved it in acetone. Deposition of flakes took place when oxidized silicon wafer was dipped in acetone. The properties of graphene were then studied using those flakes [7, 17]. Li et al. employed Chemical Vapor Deposition (CVD) technique to produce graphene on copper substrates using a mixture of hydrogen and methane [18]. Choucair et al. produced graphene by solvothermal analysis followed by sonication. They formed an intermediate solid by reacting ethanol and sodium, which was then pyrolyzed. After pyrolysis, the fused array of graphene sheets was dispersed by sonication [19]. These were some of the methods to produce graphene. But it is still a challenge to produce graphene on a large scale and that too of high quality, which hinders its large scale industrial application despite its excellent properties [17]. Therefore, Graphene Oxide (GO) turns out to be a favorable material for our particular application i.e. water purification [20], due to its mass production, excellent dispersion in water, and atomically thin thickness. GO finds applications in energy storage, electronics, biosensors etc., but with a little compromise on properties as compared to when pure graphene is used [21, 22].

Membrane is the barrier which separates two different phases. Membrane technology can be classified as microfiltration, nanofiltration, ultrafiltration, reverse osmosis etc. [23]. A membrane used for water purification should have: large water permeation, excellent mechanical stability, high salt rejection, and excellent fouling resistance [24]. In 2012, Nair et al., discovered that GO membrane blocked everything in the vapor form and allowed the permeation of water. It was the first time when GO was used as a filtration membrane. They employed Hummer's Method to produce 1 micrometer GO sheets. They used two methods to obtain a GO membrane. First one was spray coating a solid surface with GO solution followed by etching. Second one was vacuum filtering the GO solution on alumina [25]. Other than spray coating and vacuum filtration, several methods such as evaporation, drop-casting, and spin coating are also used to deposit GO on substrates for water purification [22]. Han et al. deposited GO membrane of 22-53 nm thickness by vacuum filtration. It showed a rejection of >99% of methyl blue (organic dye) and 20-60% salt rejection of different salts. The water permeability obtained was 21.8 L/(m2.h.bar) [26].

Huang et al. used vacuum filtration to study the salt concentration, effects of feed pressure, and pH on water filtration performance by depositing 500 nm GO membrane [27]. Akbari et al. used casting method on a polymeric support to deposit GO membrane. But the main problem associated with this method was a thick deposition of GO membrane that results in less stability over a long time. Other problem was to uniformly cast the GO membrane on the polymer [28]. Thus, for the deposition of GO membrane, a speedy, scalable, simple, and uniform thickness, method still remains a question.

Present study aims to focus on graphene and membrane technology to produce a cost-effective and scalable method for water purification Printing technique is used to deposit an ultrathin GO membrane on a Polyvinylidene fluoride (PVDF) support for water purification. The reason for choosing PVDF was its high purity, thermal stability, and chemical resistance [29]. A stable graphene-based thin film was printed through ink-jet printer on membrane for water filtration, whereas the water containing different kinds of molecules, ions or particles.

II. METHODOLOGY

Water purification using RO is an expensive technique, so we have put our efforts to originate another technique which uses lesser energy and yields more water at a high permeation rate than RO. The experimental work that we have done for this purpose is as follows:

A. *Materials and Chemicals Required*

Graphite flakes, Sulphuric acid, Sodium nitrate, Phosphoric acid, Hydrogen peroxide, Deionized water, Potassium permanganate, Hydrochloric acid, Ethylene glycol, Glycerin, Polyvinylidene Fluoride membrane, etc. were used during different stages of synthesis of GO and subsequent printing of PVDF membrane.

B. *Production of Graphene Oxide*

Synthesis of graphene oxide can be done by various methods. Wet chemical synthesis is the most common method for production of GO in which graphite is oxidized as well as exfoliated during the reaction. Hummer’s method is the most commonly used method for the production of graphene oxide. In this method, concentrated sulfuric acid (H_2SO_4) is added to the mixture of sodium nitrate ($NaNO_3$) and graphite and it is then cooled. Potassium permanganate ($KMnO_4$) is then added and after subsequent heating, stirring, cooling, and drying, GO is obtained. But the problems generally faced are; generation of toxic gases, less controllability of temperature, and low yield. Therefore, Marcano et al. improved this method to counter all the problems by excluding $NaNO_3$, including phosphoric acid (H_3PO_4), and increasing $KMnO_4$. This method known as Improved Hummer’s Method or Tour’s method [30]. In the present study Tour’s Method is used, steps of Tours method were as follows, 120 ml of H_2SO_4 was poured into the beaker. 1 gm graphite powder was added and stirred for around 15 minutes for homogenization. 13.3 ml of phosphoric acid was added and stirred for 30 minutes. 6 gm of potassium permanganate was added very slowly to avoid the rise in temperature, which turned the color of solution to green shown in *Fig. 1* (a), followed by stirring for 8 hours. With the passage of time, green color turned to brownish shade. 50 ml of DI water was added during stirring, the temperature of the reaction then increased rapidly to 98°C with effervescence leading to a color change to brown represented in *Fig. 1*(b). This temperature was maintained by heating. Furthermore, dilution was done by adding 100 ml of DI water while stirring for around 30 minutes. The reaction was then stopped with 3 ml H_2O_2, the appearance of yellow color indicated the termination of reaction shown in *Fig. 1*(c).

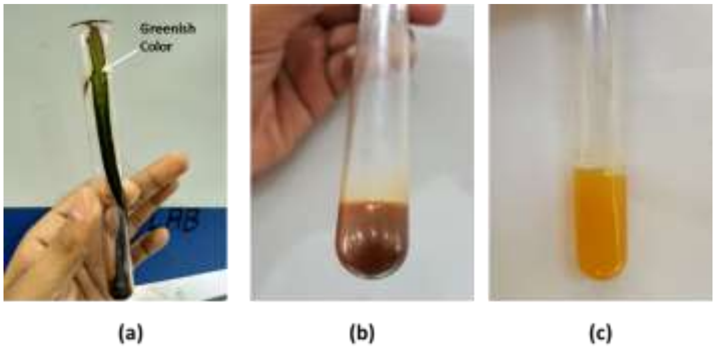

Fig. 1. Stages of Graphene Synthesis (a) $KMNO_4$ addition, (b) DI water and (b) H_2O_2 addition

a) *Cleaning and Drying*

Following the above-mentioned methods, GO was extracted from the produced mix by ensuring the washing and drying procedures as follows: The mix was washed with 1M solution of hydrochloric acid. This solution was added to the mix and then centrifuged at 3000 rpm for 1 hour. The supernatant was decanted away, and the remnant washed again. This cycle was repeated 3-4 times, then the remnant was washed with DI water DI water washing was done repeatedly to obtain a pH of 7. Afterwards, the remnant was collected and dried at 60oC for 12 hours, drying all the liquid present in the mix. Finally, a flaky GO was obtained and then ground to acquire GO powder shown in *Fig. 2*.

B.

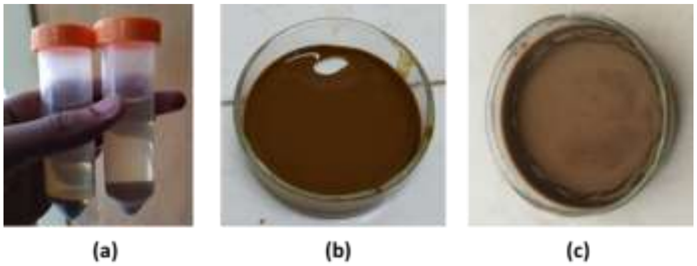

Fig. 2. GO synthesis by (a) Centrifuging, (b) collection and (c) drying

C. Preparation of Ink

As a matter of fact, we took up the printing technique, so for its achievement, the prerequisite was ink preparation. The ink concentration varies with the amount of GO dissolved in the solvent and generally ranges between 0.5-9 mg/ml. The steps taken in the preparation of ink were as follows: 200 mg of GO powder was added in 100 ml of DI water. The mix was ultrasonicated for 2 hours to disperse all GO particles in DI water in order to split any remaining agglomerates in GO powder. As for getting ink, the sonicated dispersion was then centrifuged at 10000 rpm for 1 hour to remove any larger particles in it. Lastly, the supernatant (dispersed ink) was collected and the residue was discarded. There was a need to increase ink's viscosity as only water-based ink created a glitch by dripping from the cartridge. Therefore, ethylene glycol and glycerin were added for viscosity increment. Correspondingly, 200 mg was added in 50 ml of water along with 45 ml of ethylene glycol and 5 ml glycerin. The obtained ink in Fig. *3* was then ready for printing.

Fig. 3. Representation of GO ink prepared at concentration of 2mg/ml

D. Printing the Membrane

We used an HP desk-jet printer for this purpose and took the following steps: At first, the cartridge was filled with the prepared GO ink. Some trials were performed on raw papers to ensure that the ink was printing properly or not. Then, the membrane was attached over an OHP film for support. Otherwise, it would have been torn apart by the printer. The printing took place, giving a yellowish-brown color to the membrane. Then, the membrane was dried at 50°C for 2 hours. Finally, a GO based membrane in Fig. *4* was obtained to be used in the water purification process.

Fig. 4. The picture of printed GO membrane on PVDF support

A. Filtration Mechanism

A gravimetric filtration mechanism was used, Fig. *5*, on which different results were obtained by testing the printed membrane's performance.

Fig. 5. Gravimetric filtration mechanism used

B. Hardness Test

Hardness of water basically refers to the presence of dissolved calcium and magnesium ions in water. In order to evaluate the hardness (presence of calcium) of our filtered and tap water, titration method was favored. EDTA (ethylene diamine tetra-acetic acid) solution was used as a titrant, capturing the calcium ions present in the sample. A buffer solution was added to water sample having a constant pH of 10 because this high pH is essential for the reaction between EDTA and calcium ions, also Eriochrome black T (metal ion indicator) was required to indicate the end point during titration. During titration, sample water was taken in a conical flask and then buffer solution was added while shaking it gently, which was followed by adding an indicator to it, resulting in the color change of water to red wine color. Then titration was performed until the color changed from red to blue. The reading of burette and the sample water used was then noted, repeating the procedure 3-4 times to get an accurate average value. Once these values were obtained, the presence of calcium ions were calculated by multiplying the fraction of EDTA solution (ml) used to water sample (ml) by 1000 ppm.

C. Spectrophotometry

Spectrophotometer is a rapid and efficient method for water quality analysis. It works on the principle of Beer-Lambert Law in which the intensity of light is measured. In spectrophotometry, two glass cuvettes of either 10 or 25 ml each, sample water, powder pillows (prepackaged chemicals by company), and graduated measuring cylinder are required. First, the sample water was measured through measuring cylinder accurately and poured it into those two cuvettes, then in one of those cuvettes, specific powder pillows were added in accordance with the test being performed. After adding it, the sample was shaken gently for 1 min and then left for about 5 mins for thorough mixing, and finally those samples were analyzed in a spectrophotometer. This method was used to determine the presence of nitrate, phosphate, and sulfate in our filtered water.

III. RESULTS AND DISCUSSIONS

A. Characterization

The X-Ray diffraction pattern of Graphite shown in *Fig. 6* has been recorded using X-Ray diffractometer with monochromatic Cu-Ka radiation (0.1540 nm) operated at 40 kV and 30 mA, with angle of diffraction (2ϴ) ranging from 0° to 80°.

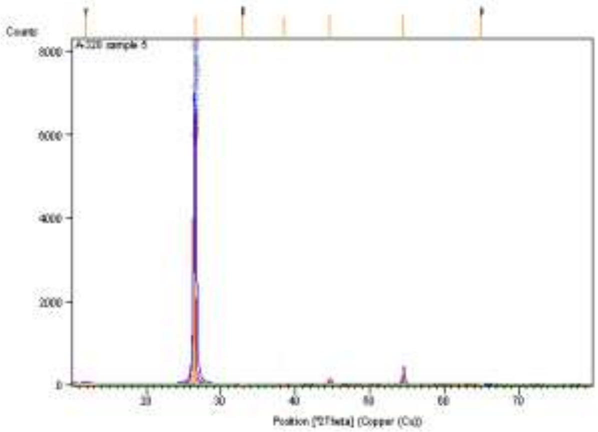

Fig. 6. XRD pattern of Graphite powder

The X-Ray diffraction pattern of Graphene Oxide shown in *Fig. 7* has been recorded using X-Ray diffractometer with monochromatic Cu-Ka radiation (0.1540 nm) operated at 40 kV and 30 mA, with angle of diffraction (2ϴ) ranging from 0° to 20°.

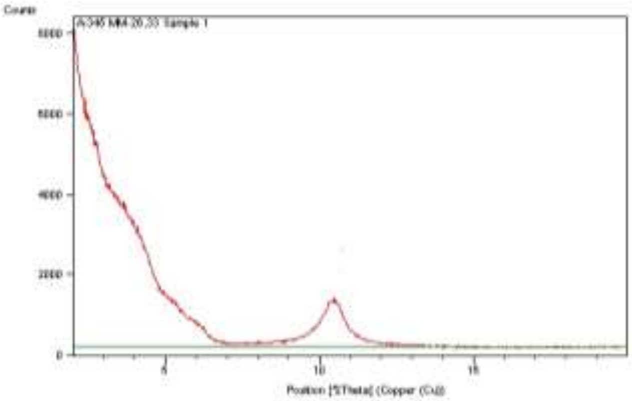

Fig. 7. XRD pattern of GO powder

TABLE 1

COMPARISON OF XRD PATTERNS OF GRAPHITE AND GRAPHENE OXIDE

Product Name	**2ϴ (Degrees)**	**d-spacing (Å)**
Graphite	26	3.3
Graphene Oxide	11	8.3

The XRD pattern in Fig. *7* shows the peak at 11° of GO prepared through Tour’s method with the d spacing of 8.3 Å which is representative for GO and become an evidence as in Fig. *6* the Graphite has a peak at 26° for with d spacing of 3.3 Å. The spacing for GO is about double of Graphite is due to the presence of functionalized groups in GO structure. This propose that the functionalized groups in GO inferred the stacking of GO sheets was not well-ordered results in peak broadening. [31]

SEM micrographs were taken in order to study the morphology and characteristics of microstructure of GO flakes and also for the GO particles dispersion in GO ink.

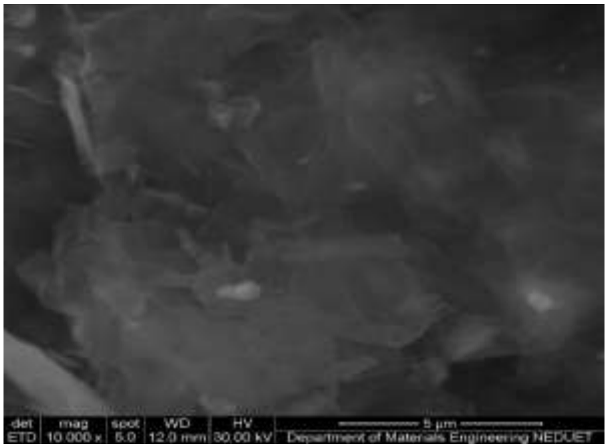

Fig. 8. SEM micrograph shows the layers of GO flakes

Fig. *8* shows the SEM micrograph of GO at 10,000x. It is evident that GO has layers in its structure. This SEM image of GO is in resemblance with the image reported by Shahriary et al. [32]

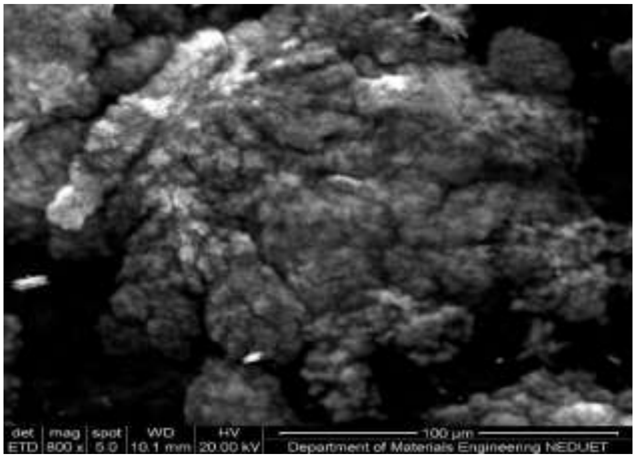

Fig. 9. SEM micrograph shows the agglomerated particles of GO in GO ink at 800x magnification

Fig. *9* shows the SEM micrograph of particles of GO in ink at 800x. The exfoliation of graphite is evident due to disturbance in its structure. It is in resemblance with the image reported by Paulchamy et al. [33]

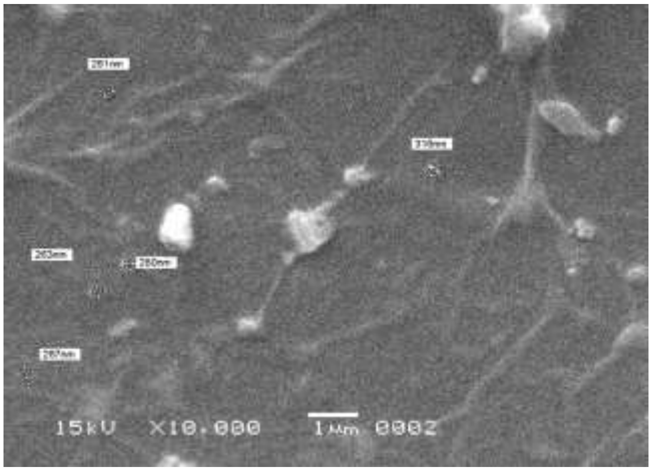

Fig. 10. SEM microograph shows the GO particle size in ink at 10,000x magnification.

Fig. *10* shows the SEM micrograph of particles of GO in ink at 10,000x. A wrinkled and folded morphology of GO is apparent. It is in resemblance with the image reported by Lilloja et al. [34]. The particle sizes are in the range of ~200-350 nm.

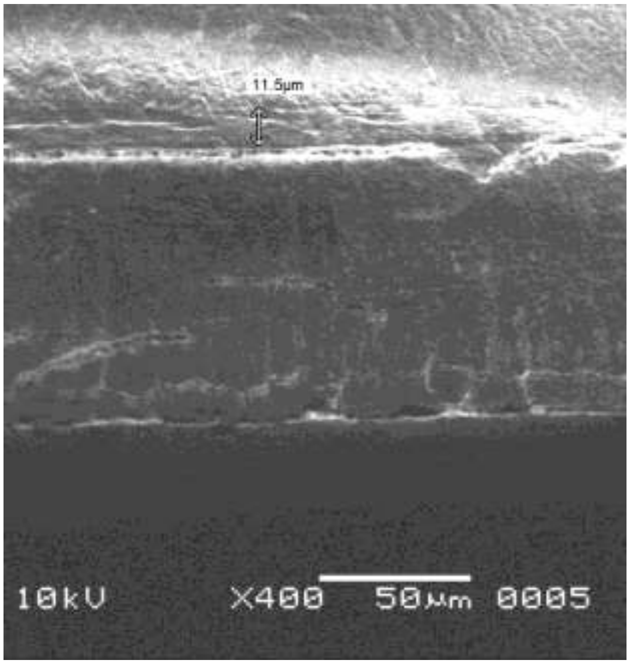

Fig. 11. The coating thickness of printed GO membrane over PVDF substrate examined by SEM micrograph

Fig. *11* shows a SEM micrograph of the cross-section of GO-coated-PVDF membrane. It can be clearly seen that there is a uniform 11.5 µm coating of GO on the PVDF substrate.

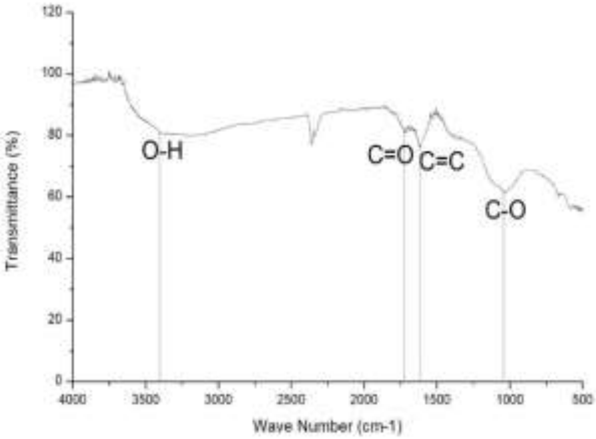

Fig. 12. Identification of functional groups in GO flakes obtained by using FTIR spectroscopy.

The spectrum in Fig. *12* obtained by FTIR confirms the existence of oxygen functionalities in GO where wide and broad peak at 3401 cm^{-1} attributed to O-H group. The peak at 1726 cm^{-1} ascribed the C=O group in carboxylic acid while peak at 1614 cm^{-1} attributed to benzene ring and the peak at 1042 cm^{-1} accredited for C-O (epoxy) group. All these functionalities are similar to that obtained by Somanathan et al. [35]

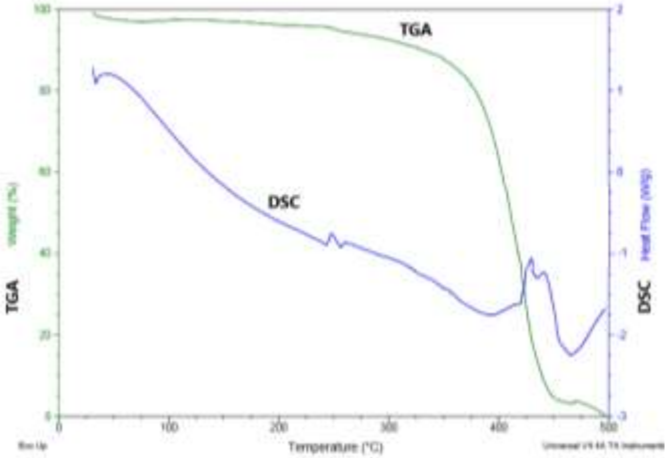

Fig. 13. Behavior of TGA curve of GO membrane on PVDF substrate observed over different temperatures

TGA in Fig. *13* was done in an inert environment at a rate of 3°C/min. TGA was performed to examine the nature of GO on PVDF membrane. The hybrid membrane has become the evidence for hydrophilicity of GO membrane that the TGA curve of GO/PVDF membrane in Fig. *13* showed 4% weight loss below 150°C because of water absorption which eventually evaporates, and then weight loss is observed. The obtained TGA curve is in resemblance with the curve reported by Ayyaru et al. [36].

A. Viscosity

The viscosity of GO ink having 2 mg/ml concentration was found to be 3.5 m Pa.s. It is similar to what obtained by Li et al. [37].

B. 3.3 Water Purification Performance

The water purification performance of GO membrane over PVDF support can be seen in charts at below in which the GO coated PVDF membrane successfully rejected 90% of $CaCO_3$, 98% of Sulfate, and 71% of Nitrate. TDS of the sample was decreased by 78.6% of its value.

TABLE 2

PURIFICATION PERFORMANCE OF GO MEMBRANE

Testing Name	Before Filtration (mg/L or ppm)	After Filtration (mg/L or ppm)
Hardness ($CaCO_3$)	2000	200
Sulfate	2000	40
Nitrate	10	2.9
TDS	12000	2560

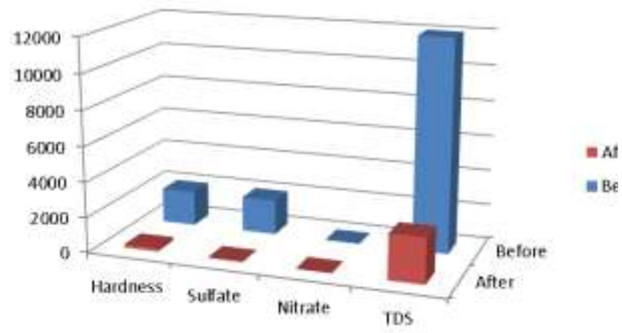

Fig. 14. Bars showing reduction in Hardness, Sulfate ions, Nitrate and TDS after treating with membrane

IV. CONCLUSIONS

GO was synthesized using Tour's Method. Results of XRD, FTIR and SEM confirmed the formation of GO. The synthesized GO was dissolved in deionized water to form a dispersed ink. Centrifuging up-to 10000 rpm was necessary to finely disperse the agglomerates. The dispersed ink was not viscous enough to be used as an ink for ink jet printer. There was a need to increase ink's viscosity as only water-based ink created a glitch by dripping from the cartridge. Ethylene glycol and glycerin was found to be a suitable agent to increase the viscosity of ink. The particle sizes of GO were in the range of ~200-350 nm. The ink was printed on commercially available PVDF membrane using ink-jet printer. The membrane was first attached over transparent film for support. The ink-jet printer successfully printed on the membrane, giving a yellowish-brown color to the membrane. A coating thickness of 11.5 µm was obtained. Membrane was used after drying at 50°C for 2 hours for water filtration as per the gravimetric method. The GO membrane offered high rejection of salts; where the membrane rejected 90% of calcium carbonate, 98% of sulfate, and 71% of nitrate. The TDS of the sample was decreased by 78.6% of its value. The printing of GO by ink-jet printing would be a promising route to low cost fabrication of GO membrane.

ACKNOWLEDGEMENT

The authors gladly acknowledge the Department of Materials Engineering, NED University of Engineering and Technology, for providing all the essential resources/facilities for this research.

REFERENCES

[1] Roson, R. and R. Damania, *The macroeconomic impact of future water scarcity*. Journal of Policy Modeling, 2017. 39(6): p. 1141-1162.

[2] Lapworth, D.J., et al., *Emerging organic contaminants in groundwater: A review of sources, fate and occurrence.* Environ Pollut, 2012. 163: p. 287-303.

[3] Wang, Z., et al., Effective desalination by capacitive deionization with functional graphene nanocomposite as novel electrode material. Desalination, 2012. 299: p. 96-102.

[4] Xu, P., et al., *Use of iron oxide nanomaterials in wastewater treatment: a review.* Sci Total Environ, 2012. 424: p. 1-10.

[5] Hu, Z., Y. Chen, and J. Jiang, *Zeolitic imidazolate framework-8 as reverse osmosis membrane for water desalination: insight from molecular simulation.* J Chem Phys, 2011. 134(13): p. 134705.

[6] Fornasiero, F., et al., *pH-tunable ion selectivity in carbon nanotube pores.* Langmuir, 2010. 26(18): p. 14848-53.

[7] K. S. Novoselov, A.K.G., S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Electric Field Effect in Atomically Thin Carbon Films.* Science, 2004. 306: p. 666 - 669.

[8] H. P. BOEHM, R.S., E. STUMPP, *Nomenclature and terminology of graphite intercalation compounds.* Carbon, 1986. 24(2): p. 241 - 245.

[9] Slonczewski, J.C. and P.R. Weiss, *Band Structure of Graphite.* Physical Review, 1958. 109(2): p. 272-279.

[10] Lee, C., et al., *Measurement of the elastic properties and intrinsic strength of monolayer graphene.* Science, 2008. 321(5887): p. 385-8.

[11] Alexander A. Balandin, S.G., Wenzhong Bao, Irene Calizo, DesalegneTeweldebrhan, Feng Miao, and Chun Ning Lau, *Superior Thermal Conductivity of Single-Layer Graphene.* Nano Lett, 2008. 8(3): p. 902 - 907.

[12] Zhu, Y., et al., *Graphene and graphene oxide: synthesis, properties, and applications.* Adv Mater, 2010. 22(35): p. 3906-24.

[13] Fuente, J.d.L., *Graphene applications & uses [Online].* Available:http://www.graphenea.com/pages/graphene-uses-applications, Accessed August 2018.

[14] Sharma, R., et al., *Anomalously large reactivity of single graphene layers and edges toward electron transfer chemistries.* Nano Lett, 2010. 10(2): p. 398-405.

[15] Kim, S., et al., *Non-swelling graphene oxide-polymer nanocomposite membrane for reverse osmosis desalination.* Journal of Membrane Science, 2018. 562: p. 47-55.

[16] Homaeigohar, S. and M. Elbahri, *Graphene membranes for water desalination.* NPG Asia Materials, 2017. 9(8): p. e427.

[17] Phiri, J., P. Gane, and T.C. Maloney, *General overview of graphene: Production, properties and application in polymer composites.* Materials Science and Engineering: B, 2017. 215: p. 9-28

[18] Li, X., et al., *Large-area synthesis of high-quality and uniform graphene films on copper foils.* Science, 2009. 324(5932): p. 1312-4

[19] Choucair, M., P. Thordarson, and J.A. Stride, *Gram-scale production of graphene based on solvothermal synthesis and sonication.* Nat Nanotechnol, 2009. 4(1): p. 30-3.

[20] Joshi, R.K., et al., *Graphene oxide: the new membrane material.* Applied Materials Today, 2015. 1(1): p. 1-12.

[21] Papageorgiou, D.G., I.A. Kinloch, and R.J. Young, *Mechanical properties of graphene and graphene-based nanocomposites.* Progress in Materials Science, 2017. 90: p. 75-127.

[22] Fathizadeh, M., et al., *Printing ultrathin graphene oxide nanofiltration membranes for water purification.* J. Mater. Chem. A, 2017. 5(39): p. 20860-20866.

[23] Mulder, M., *Basic principles of membrane technology, 2nd ed.* 1996.

[24] Li, D. and H. Wang, *Recent developments in reverse osmosis desalination membranes.* Journal of Materials Chemistry, 2010. 20(22): p. 4551.

[25] Nair, R.R., et al., *Unimpeded permeation of water through helium-leak-tight graphene-based membranes.* Science, 2012. 335(6067): p. 442-4.

[26] Han, Y., Z. Xu, and C. Gao, *Ultrathin Graphene Nanofiltration Membrane for Water Purification.* Advanced Functional Materials, 2013. 23(29): p. 3693-3700.

[27] H. B. Huang, Y.Y.M., Y. L. Ying, Y. Liu, L. W. Sun and X. S. Peng, *Chem Commun.* 2013. 49: p. 5963-5965.

[28] Akbari, A., et al., *Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide.* Nat Commun, 2016. 7: p. 10891.

[29] Liu, F., et al., *Progress in the production and modification of PVDF membranes.* Journal of Membrane Science, 2011. 375(1-2): p. 1-27.

[30] Daniela C. Marcano, D.V.K., Jacob M. Berlin, Alexander Sinitskii, Zhengzong Sun, Alexander Slesarev, Lawrence B. Alemany, Wei Lu, and James M. Tour, *Improved Synthesis of Graphene Oxide.* ACS NANO, 2010. 4(8): p. 4806 - 4814.

[31] Fatima Tuz Johra, J.-W.L., Woo-Gwang Jung, *Facile and safe graphene preparation on solution based platform.* Journal of Industrial and Engineering Chemistry, 2014.

[32] Leila Shahriary, A.A.A., *Graphene Oxide Synthesized by using Modified Hummers Approach.* International Journal of Renewable Energy and Environmental Engineering, 2014. 2(1).

[33] Arthi G, P.B. and L. Bd, *A Simple Approach to Stepwise Synthesis of Graphene Oxide Nanomaterial.* Journal of Nanomedicine & Nanotechnology, 2015. 06(01).

[34] Lilloja, J., et al., *An Oxygen Reduction Study of Graphene-Based Nanomaterials of Different Origin.* Catalysts, 2016. 6(7): p. 108.

[35] Thirunavukkarasu Somanathan, et al., *Graphene Oxide Synthesis from Agro Waste.* Nanomaterials, 2015.

[36] Sivasankaran Ayyaru, Y.-H.A., *Application of sulfonic acid group functionalized graphene oxide to improve hydrophilicity, permeability, and antifouling of PVDF nanocomposite ultrafiltration membranes.* Journal of Membrane Science, 2017.

[37] Li, P., et al., *Preparation of Graphene Oxide-Based Ink for Inkjet Printing.* J Nanosci Nanotechnol, 2018. 18(1): p. 713-718.