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Graphene Oxide Incorporated Polyethersulphone Membrane For Heavy Metal Ion Removal

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Abstract: The polymer based Mixed Matrix Membranes were prepared with different ratios of Graphene oxide (GO) and polyvinylpyrrolidone (PVP) via phase inversion technique. Graphene oxide (GO) was synthesized by Hummer's method and Characterized by FTIR, XRD, FESEM and HRTEM analysis. Polyethersulfone (PES) ultrafiltration (UF) membranes with and without GO were prepared for the removal of heavy metal ion. The prepared membranes were characterized by pure water flux (PWF), porosity, water content, membrane hydraulic resistance, contact angle, mean pore size, SEM (Scanning Electron Microscope), TGA (Thermo Gravimetric Analysis) and UTM (Universal Testing Machine) analysis. Studies were carried out to find out the rejection of proteins such as Trypsin, Pepsin, Egg Albumin (EA) and Bovine Serum Albumin (BSA). The extent of protein separation is directly proportional to molecular weight of protein. PES/GO membranes have better hydrophilic property compared to pristine PES membrane confirmed by contact angle and flux studies. Filtration results exhibited that the fouling resistance parameters were declined due to its higher hydrophilicity of hybrid membranes. After bovine serum albumin (BSA) solution inner fouling process, PES/GO membranes indicated higher water flux recovery ratio (FRR) value than pristine PES membrane. Meanwhile tensile strength of PES/GO membranes were decreased with increasing concentration of GO compared with those of pristine PES membrane.

Keywords: Hybrid Membranes, Graphene Oxide, Ultrafiltration, Antifouling performance.

I. INTRODUCTION

Membrane separations can be considered as promising technology for water treatment processes due to its several advantageous [1,2], but membrane fouling is the major problem. Polyethersulfone(PES) is one of the most used polymersin the preparation of commercial and laboratory ultra filtration and nano filtration membranes [3, 4]. In order to improve membrane permeability and anti fouling property, many efforts have been done to enhance membrane hydrophilicity, including material modification, polymer blend and surface modification [5, 6]. Adding inorganic nano particles to membrane matrix can enhance the membrane hydrophilicity, strength, permeability and antifouling characteristics [7, 8].Oxidation of graphite through chemical modification is widely used due to its low cast, easy access, ability to convert graphene and scalability [9-11]. Graphene Oxide (GO), a two dimensional carbon material, has covalently attached oxygen containing group on the surface including hydroxyl, epoxy, carbonyl and carboxyl group [12]. This functional group makes GO possess good hydrophilicity, easy to modify, good dispersion in water, and GO could damage the restrain the growth of E-coli [13]. Compatibility with polymer matrices can be improved due to the polar group presence on the surface of graphene material, but its inherent thermal and electrical conductivity reduced [14-16].

In this work GO sheets prepared by Hummer's method then characterized by FTIR, XRD, FESEM and HRTEM. Poly ether sulfone mixed matrix membranes were prepared with different concentration of graphene oxide with improved antifouling property. These membranes are characterized by contact angle, SEM, TGA and UTM, and then subjected to rejection of proteins and metal ions.

II. EXPERIMENTAL

2.1 Materials

Commercial grade Poly ether sulfone was purchased from Sigma Aldrich. Analar grades of N-methyl 2-pyrrolidone (NMP) from SRL chemicals was procured, sieved through molecular sieves for removing moisture and stored in dried condition. Graphite powder, sodium nitrate, con.H_2SO_4, potassium permanganate, hydrogen peroxide, and H_3PO_4 were purchased from sigma aldrich.. Analar grades of zinc (II) sulphate and Cadmium (II) sulphate were purchased from M/s. Sisco Research laboratories Private Limited, India. Analar grades of acetone and sodium lauryl sulfate (SLS) are purchased from Sigma Aldrich. Distilled water was employed for ultrafiltration experiments and also for the preparation of gelation bath. All chemicals were used without further purification.

2.2 **Synthesis of GO by Hummer's method**

Graphite powder (2g), sodium nitrate (1g) are added in concentrated H_2SO_4 (46 ml) taken in a round bottom flask (500ml) and allowed for continuous stirring in a magnetic stirrer for 2 hour. The mixture is kept under at ice bath (0-5^{o}C) and potassium permanganate is added pinch by pinch to the reaction mixture. Each pinch is added at a time interval of 60 seconds along with continuous stirring. The temperature should not exceed above 15°C and the mixture turn into dark green color which indicates that oxidation reaction is proceeding in the reaction mixture. This mixture is shifted to an oil bath, temperature kept at 35°C and stirred for further 1 hour. Once the temperature is attained 98°C, then distilled water (96 ml) is added drop by drop to the reaction mixture. This mixture is turned into golden yellow color and care should be taken while adding water.

The reaction mixture is kept in the oil bath along with stirring for half an hour. Further distilled water (280 ml) is added and continued constant stirring. Hydrogen peroxide (2 ml) is added to the reaction mixture and continued constant stirring for further half an hour. The reaction mixture is cooled down to room temperature and brown color solution is obtained. The final mixture is centrifuged and washed with distilled water for several times. Small amount of acetone is mixed with purified product and transferred into petri dish and kept in the hot air oven at 60°C for 8 hours [9].

2.3**Fabrication of PES/GO incorporated MMMs**

Membranes were prepared by phase inversion technique using a pneumatically flat sheet membrane casting system. PES with different concentration of GO (0, .25, .5, .75,1) wt % and 1 wt % of PVP as a pore forming agent in N- Methyl 2-Pyrrolidone (NMP) solvent were dissolved by constant mechanical stirring for 4 h at room temperature. The homogeneous solution was tightly closed and kept for 6 h to get rid of air bubbles. The blend solution was casted on through membrane casting system, then immersed into a gelation bath having solvent, non-solvent, and surfactant. After 2 h of gelation the membrane was removed, washed thoroughly with distilled water to remove adhering surfactant and solvent. These membranes were stored in water with 0.1% formalin solution in order to remove the bacteria and fungi reactions.

Table 1. Casting solution compositions of ultrafiltration membranes

Membrane code	PES (wt %)	Solvent (wt %)	GO (wt %)	PVP (wt %)
M 0	15	84	0	1
M.25	15	83.75	0.25	1
M.50	15	83.50	0.5	1
M.75	15	83.25	0.75	1
M 1	15	83	1	1

2.4 characterization of GO

The synthesized GO was characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) to confirm the presence of functional groups and the morphology of GO was observed by Field emission scanning electron microscope (FESEM) and High resolution transmission electron microscope (HRTEM) analysis.

2.5 Characterization of membranes

The prepared mixed matrix membranes morphology was observed by SEM (scanning electron microscope), thermal stability of the membranes were analyzed by (Thermo Gravimetric Analysis). Contact angle of membranes were tested by goniometer (Dataphysics, Germany)to determine the hydrophilicity of the membranes.

III. RESULTS AND DISCUSSION

FT-IR spectrum of the Graphene oxide was shown in Fig 1, the broad peak around 3435 cm^{-1} corresponds to O-H stretching vibration, peak at 1727 cm^{-1} was due to the strong carbonyl stretching respectively [18]. The peaks at 1390 cm^{-1} and 1224 cm^{-1} corresponds to C-OH and C-O-C stretching vibrations. The peak around 1091 cm^{-1} is due to the C-O stretching vibrations indicating the presence of the epoxides group in the graphene oxide layers and peak 1627 cm^{-1} is attributed to vibration of the adsorbed water molecules and contributions from aromatic C=C. [19,20]. From the results, it can be identified that GO formed effectively. Other researchers also attain the similar results [21, 22]

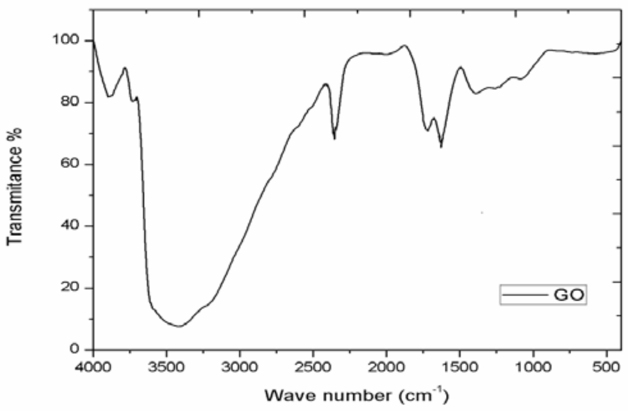
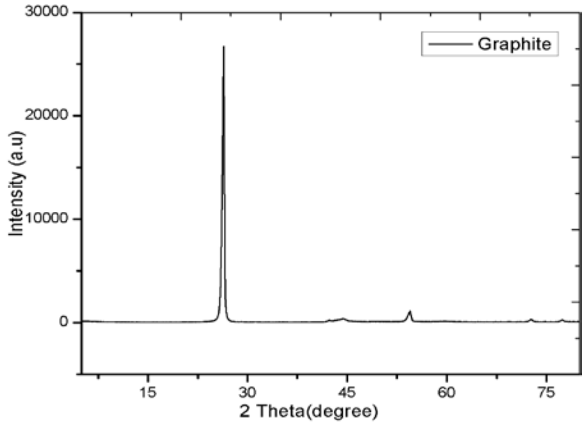


Fig 1. FTIR spectrum of Graphene Oxide (GO)



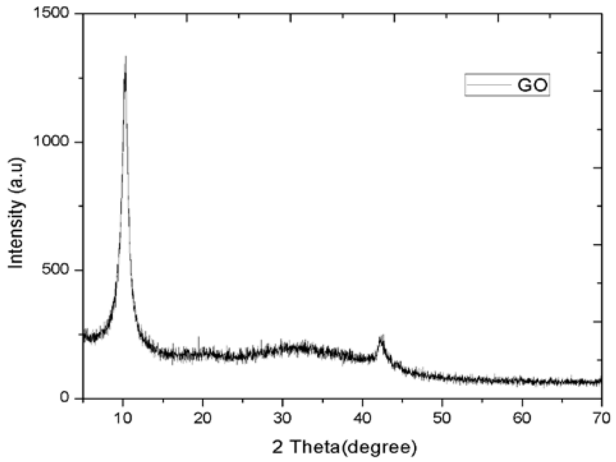
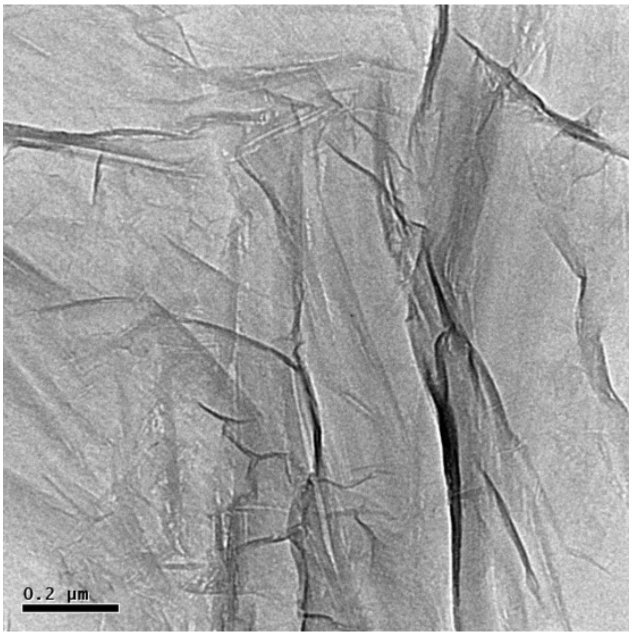


Fig.2 XRD images of graphite and graphene oxide

Fig.2 shows XRD spectrum of graphite and graphene oxide. Pristine graphite shows a very intense and sharp peak at 2θ= 26.42°.Graphene oxide shows a sharp peak at 2θ=10.35° with layer-to-layer distance (d-spacing) of 0.853 nm. This value is larger than that of graphite (0.336), which clearly confirms the presence of the highly oxidized graphene oxide, which is mainly due to the chemical oxidation that disrupts the ordering of graphite layers, and introduces various oxygen functional groups in the graphite [23].

HRTEM images of prepared GOat different magnification were shown in fig 3. GO nano sheets tends to congrete together to form a multi layer agglomerates. The individual nano sheets have sizes extending from tens to hundreds of square nanometer [24]. SEM image of GO was shown in fig 4. It shows large flakes of GO with a few layer thick was prepared successfully



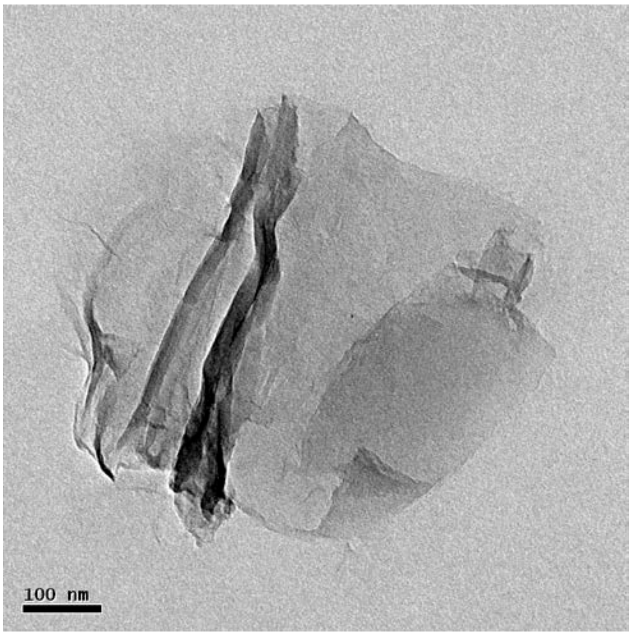


Fig.3 HRTEM images of graphene oxide at different magnification.

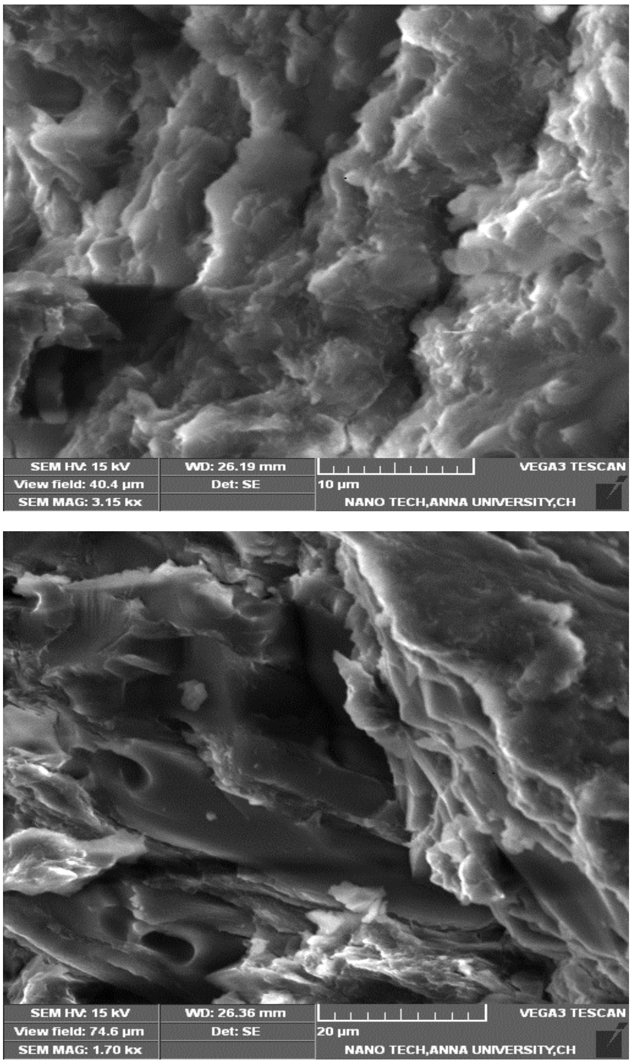
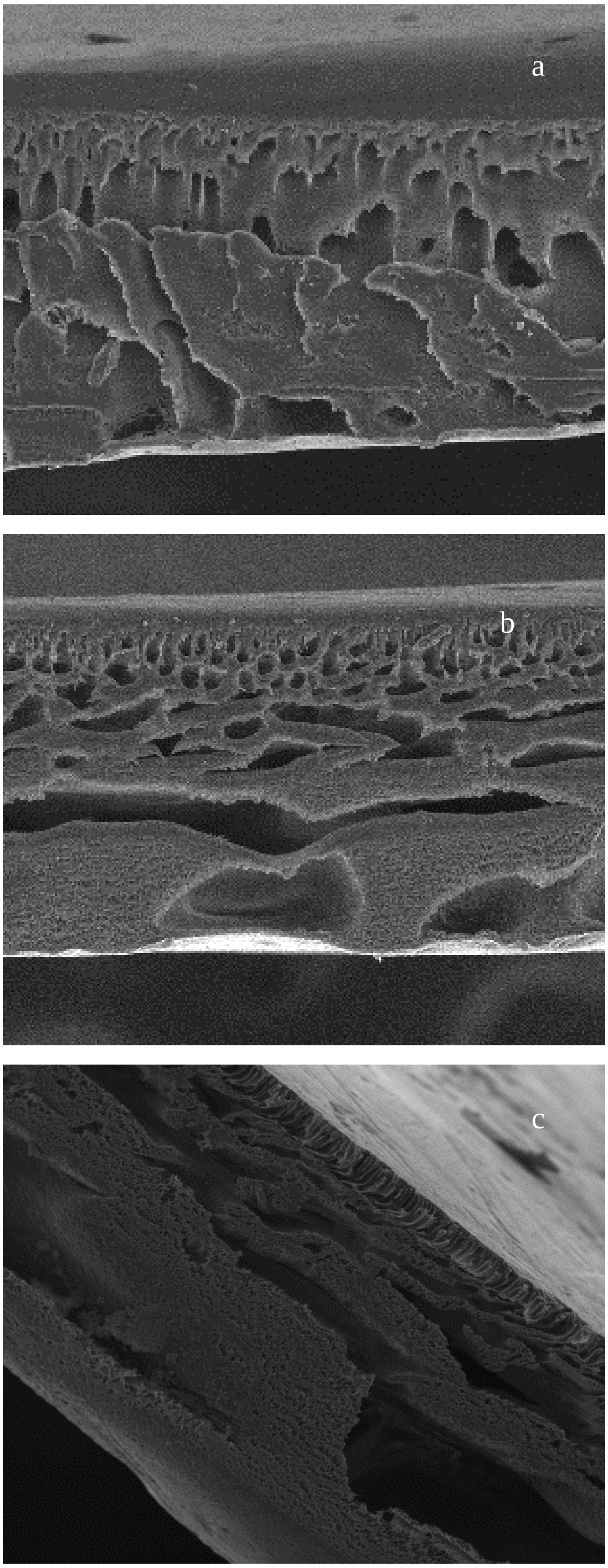


Fig.4 FESEM images of graphene oxide

Cross sectional SEM micrographs of the prepared membrane were presented in fig 5. Pure PES membrane has sponge like structure and very few small separated pores were shown in fig 5a). In general, asymmetric membrane consists of a top skin layer and a porous sub layer at the bottom. Fig 5b) represents membrane with .25% GO has top skin layer, small pores in middle and followed by large pores. From fig 5c) represents membranes with 0.5 and .75% GO shows, finger like top layer was formed and small pores are enlarged in bottom layer region. But the sponge parts still exist as a significant part of the membrane. Further increase in concentration of GO in membrane matrix shows, sponge like pores are replaced by a finger like bottom layer. In general these structures have low resistance to water permeation [25]. This issue was confirmed by other similar studies [26, 27]. The rate of pore formation is directly related to the rate of exchange of solvent and non solvent in the coagulation bath of phase inversion process. In coagulation process, the exchange rate of solvent and non solvent is faster, larger pores, finger like pores and more channels were formed. If the exchange rate of solvent and non solvent is lower, then small pores, drop like pores, sponge and non void structure was formed. Addition of GO into the membrane matrix modified the bottom layer effectively due to



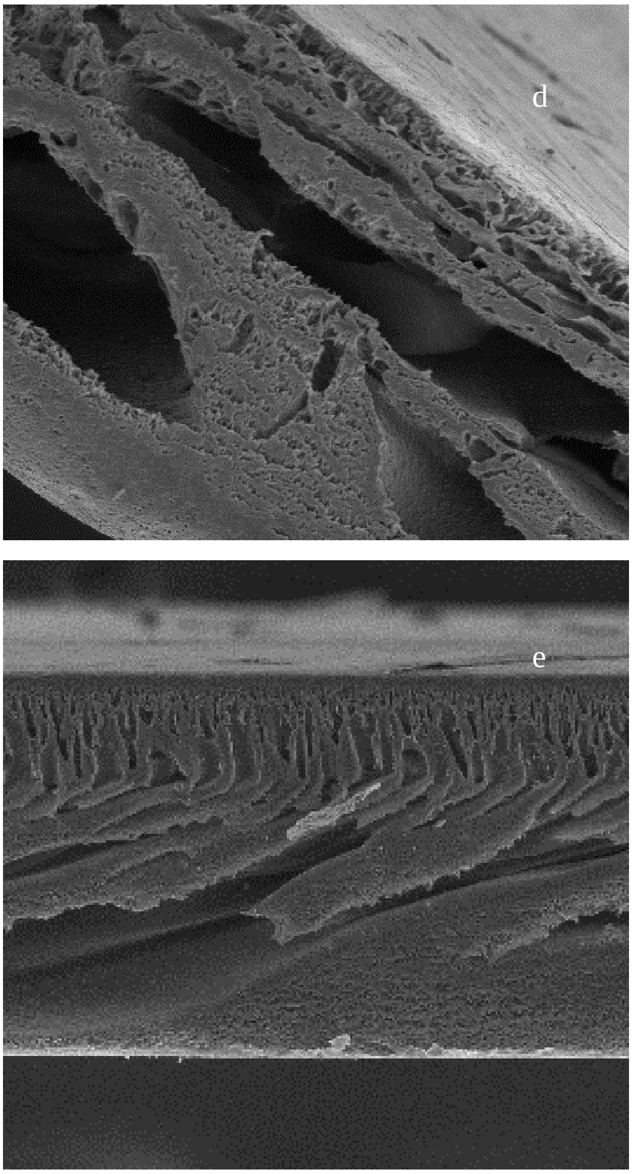


Fig 5. SEM images of a) M0, b) M.25 c) M.50 d) M.75 and e) M1

thermodynamic instability in casting solution. As a result, large pores on the bottom layer were formed.

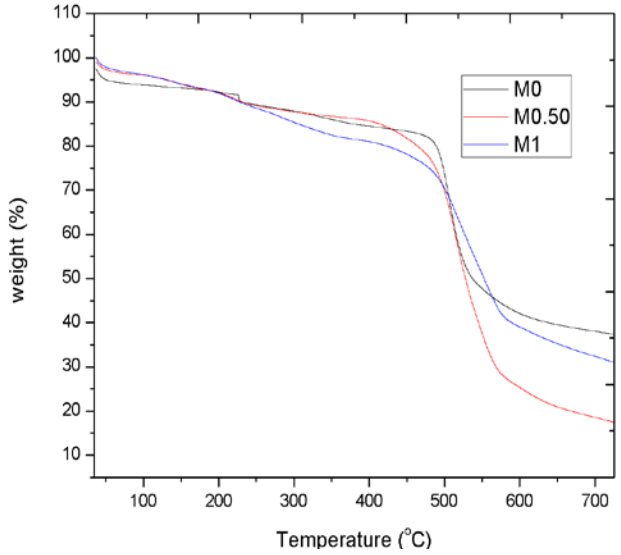


Fig 6. TGA analysis of M0, M0.50 and M1

The thermal stability of the pure PES, PES with 0.5% and 1% GO was examined as shown in fig 5. All membranes have similar thermo-gram. Pristine PES membrane has major weight loss region in the range of 490 ^{0}C whereas M0.5 membrane has major weight loss region in 420^{0}C and M1 membranes has 410 ^{0}C. There is no much difference in thermal stability of the mixed matrix membranes.

Hydrophilicity of the membrane was determined from contact angle and pure water flux. Pristine PES membrane has contact angle of 69.6 which gradually reduced as 58.4, 50.2, 46.5 and 44.6. The increase in concentration of GO in polymer matrix, reduces the contact angle of the membrane in decreasing trend due to the presence oxygen functional groups on the surface of the membrane. Hydrophilicity inversely related to contact angle. This determined that, GO improves the hydrophilicity of the membrane. Further confirmed by, the pure water fluxes of all membranes as shown in fig 8. But for M1 membrane the pure water flux was decreased from 97 to 92 $lm^{-2}h^{-1}$ due to the agglomeration of GO nano particle on the membrane surface. Similar results were obtained in other study [28].

The porosity of all membranes was calculated by using eqn 7. Fig 8 shows porosity of the membrane increases with increase in concentration of GO in polymer matrix already seen from SEM. Simultaneously, pore uptake volume of the membrane increases, so water content of the membrane also increases gradually as shown in fig 8. For M1 membrane, aggregation of GO nano particles may block the pores, thus reduces the porosity.$R_m$value for pristine PES membrane was 3.31 m^{-1} and decreased to 2.84 m^{-1} for M.25 membrane. Similarly corresponding decrease in the resistance of M.50, M.75 and M1 membranes were observed. An increase in composition of GO enhances the size of pores where observed from SEM, which results in lower R_m value [21]. The mean pore radius of all membranes were calculated and tabulated in table 2. Increase in concentration of GO content enlarged the mean pore radius of the membranes upto 0.75% and the decreased. This behavior is similar to the pure water flux of the membrane [21].

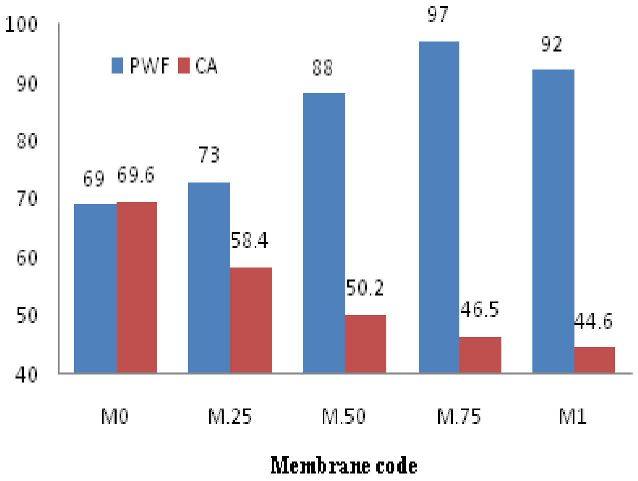


Fig 7. Pure water flux and static contact of prepared membranes

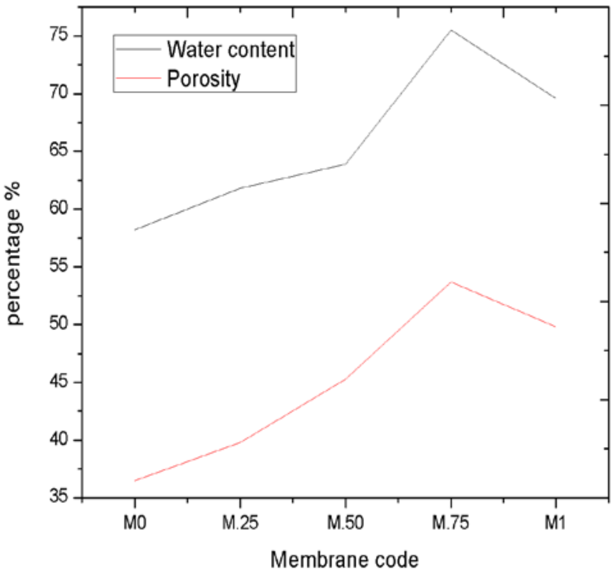


Fig 8. Water content and Porosity angle of prepared membranes

Table 2.Pure water flux, R_M, porosity, water content, Mean pore radius and contact angle of pure PES and PES/GO membranes

Membrane code	**PWF ($lm^{-2}h^{-1}$)**	**R_M (m^{-1})**	**Porosity %**	**Water content %**	**Mean pore radius (nm)**	**Contact angle**
M0	69	3.31	36.5	58.2	29.65	69.6
M.25	73	2.84	39.8	61.8	32.94	58.4
M.50	88	2.77	45.3	63.9	35.19	50.2
M.75	97	2.07	53.7	75.5	42.18	46.5
M1	92	2.56	49.8	69.6	38.57	44.6

3.2 Rejection of metal ions

The polyethyleneimine and metal ion containing solutions were filled in the feed reservoir. For each run, the first few ml of permeate was collected and analyzed with AAS. The percentage rejection of each metal ion was calculated.The percentage rejection of each metal ion was shown in fig 9. The increase in concentration of GO content decreases the rejection of both metal ions. Pristine graphite has 92% rejection of $Cu^{2+}$and 87% rejection of Zn^{2+}, which further reduces gradually with increase in concentration of GO embedded in polymer matrix.

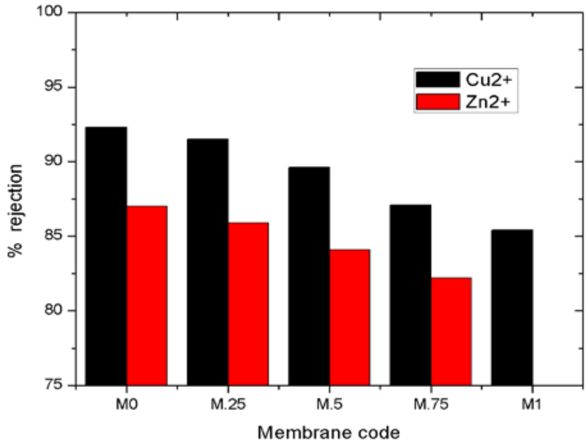


Fig 9. Percentage rejection of metal ion for prepared membranes

IV. CONCLUSION

GO sheets were successfully prepared by Hummer's method. The characteristic peaks in FTIR and XRD analysis confirm the presence of oxygen containing groups in prepared GO.TEM analysis further determined the exfoliation of GO through its microscopic morphology. Mixed matrix membranes consisting of various concentration of GO were fabricated, those membranes are characterized with SEM and TGA. Ultrafiltration experiments were done for the prepared membranes. We conclude that the incorporation of GO in membranes improve the hydrophilicity, which was confirmed from flux and contact angle of the membrane. Antifouling property of the membranes increased with embedded GO in polymer matrix and the rejection of metal ion was studied.

V. ACKNOWLEDGMENT

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