



## Research article

## Development of superhydrophilic tannic acid-crosslinked graphene oxide membranes for efficient treatment of oil contaminated water with enhanced stability

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## ABSTRACT

In the present age of industrialization, oil contamination in the waste water has become a huge global concern due to its several negative impacts on human health and aquatic ecosystem. In order to address this problem, a novel oleophobic and super-hydrophilic graphene-based membrane has been developed using simple and cost-effective vacuum filtration methodology. Prior developing the membranes, the graphene oxide (GO) sheets were cross-linked with tannic acid (TA) molecules in order to improve their mechanical and surface properties. To obtain the structural and morphological information of the membranes and their constituents, Field Emission Scanning Electron (FE-SEM) microscopy, X-Ray Diffraction (XRD), FTIR spectroscopy and Raman spectroscopy was used. When tested with simulated oilfield effluent samples, these membranes exhibited significant reduction in the values of chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS) and turbidity demonstrating low-oil adhesion and preferable oil rejection rates. Moreover, such crosslinked membranes are highly stable which can withstand the pressure of water filtration. In such a way, TA crosslinked GO membranes present a robust and efficient way to treat oil contaminated water released from various industries which can be reused for numerous further applications.

## 1. Introduction

Globally, one of the prominent challenges of the current era is the treatment of oily industrial effluents before releasing it into the environment or to use it for some other applications. A large amount of waste water, mixed with oil, is generated daily from different industries, such as metallurgical, pharmaceutical, petrochemical as well as petroleum refineries, posing a serious threat to the environment [1, 2, 3]. The issue of water pollution is considered as a significant problem in today's world, which can lead to the destruction of the ecosystem [4,5]. Moreover, the separation of emulsified oil from effluents is very challenging due to the small size of oil droplets. However, wide range of technologies, namely gravity settling, floatation, coagulation, adsorption, biological treatment and advanced oxidation processes, are being used for the treatment of the oily emulsion-based waste water [6, 7, 8, 9, 10]. In comparison, membrane filtration technique emerges as more powerful and possible future

technology for efficient oil/water separation, as the process is based on the mechanism of "size-sieving" which promotes the permeation of small water molecules from the membrane rejecting the bigger pollutants behind [11,12].

Graphene oxide (GO) is an emerging two-dimensional nanomaterial with unique physical and chemical properties which is being used for the oil/water separation applications in oil-based industries [13, 14, 15]. Recently, Diraki et al has conducted a study to remove diesel from oil/water emulsion in highly saline water using graphene oxide [16]. In particular, GO holds great potential in oil/water separation as compared to pristine graphene because of several oxygen functional moieties present over the surface rendering the developed membrane superhydrophilic [17]. In addition, GO nanosheets get self-assembled during vacuum filtration, on the microporous substrate generating nano-channels in between the sheets, which allows only water molecules to pass through [18, 19, 20]. Moreover, the deposition of GO onto

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polymeric microporous membranes exhibit antifouling properties because of its hydrophilicity and antibacterial properties [21,22]. In general, fouling of membrane takes place due to the accumulation of oil, micro-organisms and the inorganic particles which suppress the water permeability through the membrane. To prevent this, a layer of hydrophilic entities is recommended to deposit onto the polymeric membranes which forms a hydration layer and hinders the attachment of foulants [22].

However, the pure GO membranes suffer from the drawback of swelling during the filtration process due to which the interlayer spacing between the GO sheets is enhanced and the oil contaminants can easily pass through the membrane [23]. Therefore, it is desirable to chemically modify the graphene oxide nanosheets before their deposition to increase the stability [24,25].

In the present study, tannic acid crosslinked GO membranes have been developed for the first time to be deployed for efficient treatment of oil contaminated water. Tannic acid, a naturally extracted compound contains a large number of terminal phenolic hydroxyl groups which can interact with the functional groups of graphene oxide via electrostatic interactions [26,27]. Even, tannic acid molecules interact with the PVDF membrane via non-covalent interactions and make the coating stable. Unlike other hydrophilic coatings, such as polydopamine which clogs the pores of the membrane and reduces the flux drastically, TA coatings improve the water flux significantly during filtration [28]. One of the major advantages of crosslinking of GO is that the density of free functional groups is reduced and the mechanical properties of graphene sheets are enhanced. This study was done by Sun et al., using molecular dynamics simulations [29]. Therefore, the membranes developed from these cross-linked GO are highly robust. Also, tannic acid provides abundant hydroxyl groups over the surface of membrane making it hydrophilic and facilitates the efficient rejection of oil during filtration and subsequently prevents fouling of the membrane [30]. However, such membranes may not be suitable for waste water filtration where different

types of other pollutants are also present in water along with oil [25]. In such cases, tannic acid crosslinked membrane is advantageous since it only allows water molecules to pass through providing the clean water. In addition, such optimised technology will reduce the cost of the treatment process and increase the overall performance by overcoming the aforementioned limitations.

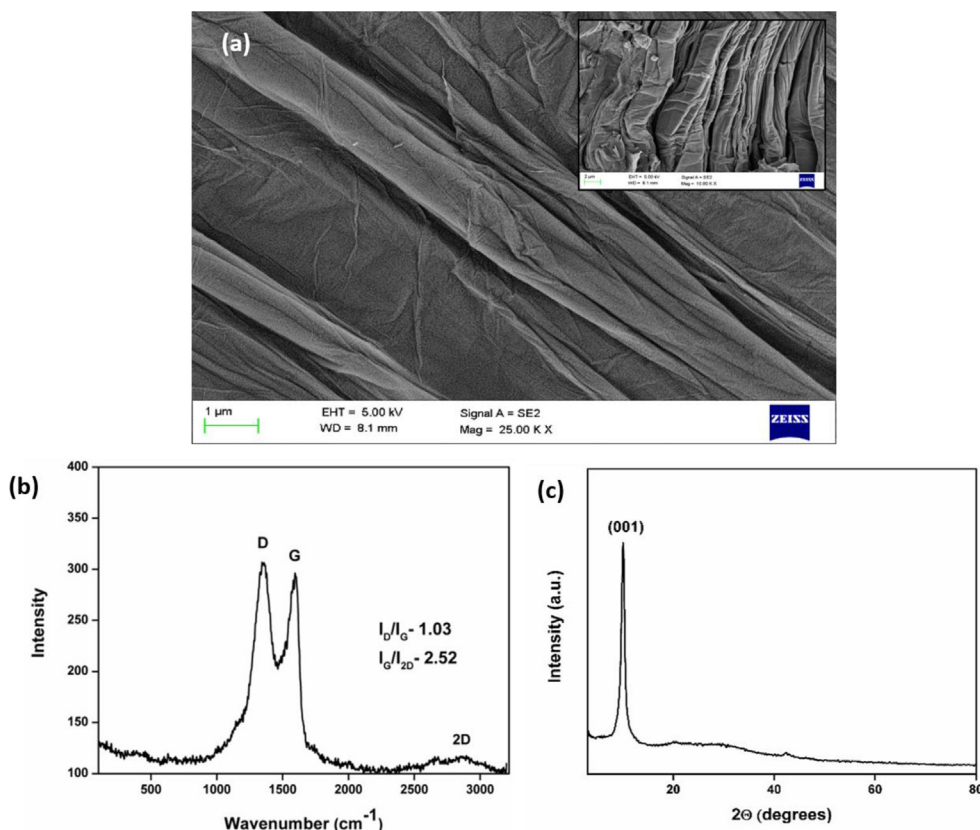
## 2. Experimental section

### 2.1. Materials

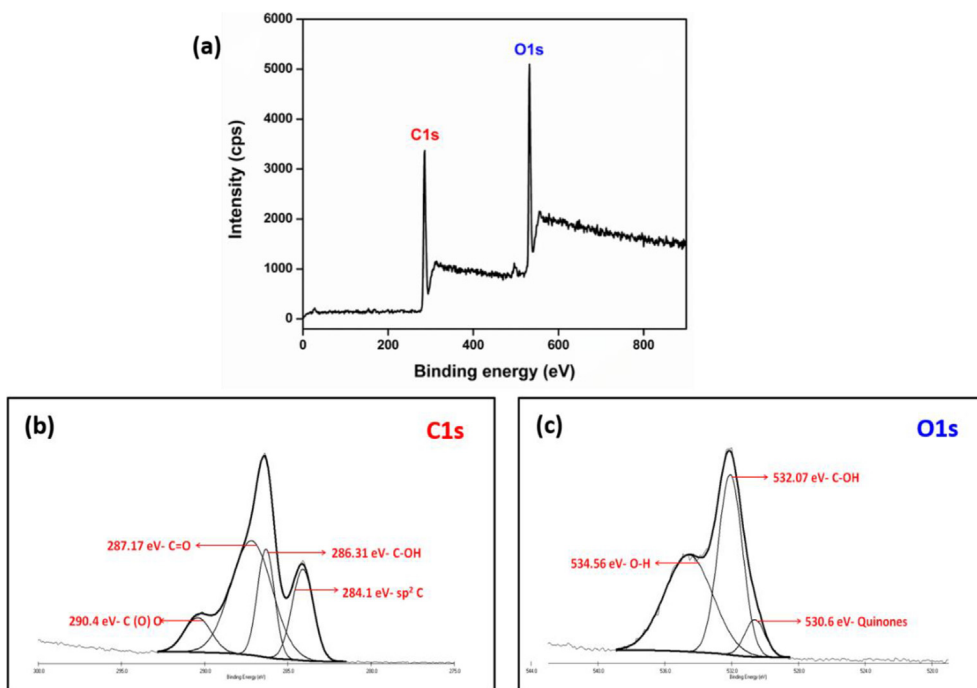
Graphite flakes were obtained from SRL chemicals, India.  $\text{H}_2\text{SO}_4$  (98%),  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$  (35% W/V), HCl (38% mol. wt.- 36.46) and tannic acid were purchased from SDFCL (S.D Fine Chemistry Limited) India.  $\text{KMnO}_4$  (mol. wt.-158.04) and Sodium Dodecyl Sulfate (SDS) were obtained from RFCL Pvt. Ltd. (India) and Sigma Aldrich, (India), respectively. Sodium Hydroxide (NaOH mol. wt.- 40) and Barium salt was procured from Himedia Lab Pvt. Ltd. (India). Polyvinylidene fluoride (PVDF) membranes and Zinc salt were purchased from Merck Life Science Pvt. Ltd., India. Hexane was obtained from Petrochem Private Ltd. All the reagents used were of analytical grade (AR). De-ionized water (18 m $\Omega$ ) was used in all aqueous preparations.

### 2.2. Methods

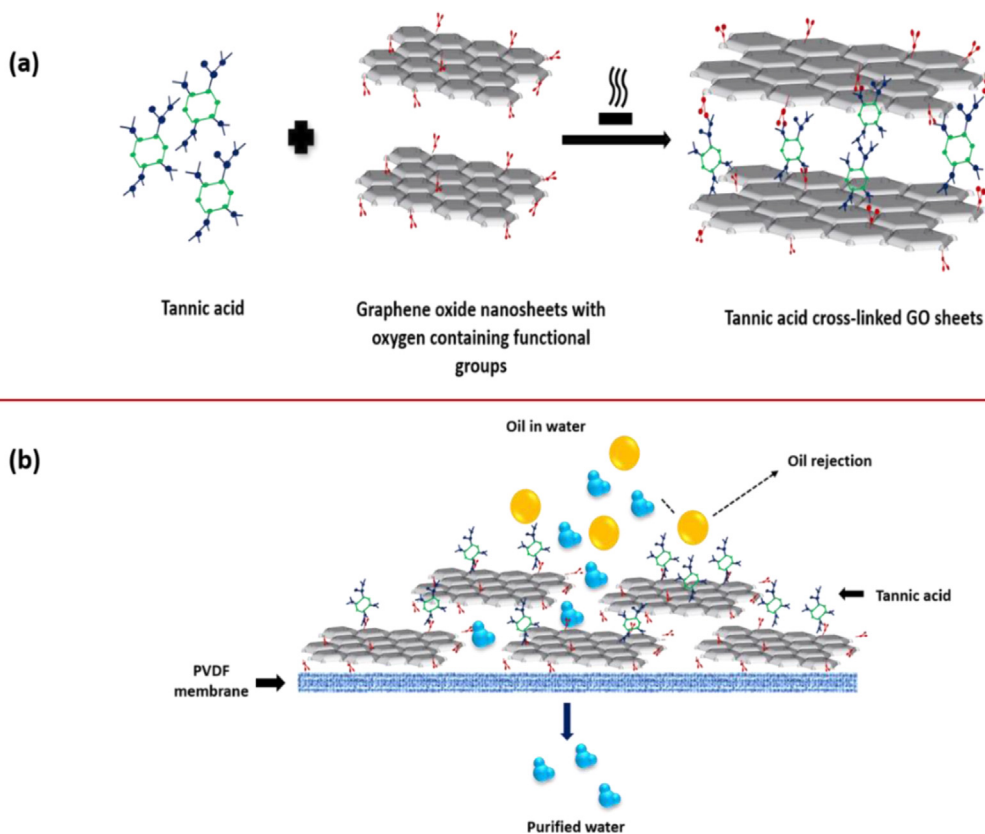
- (a) *Preparation of GO*: Graphene oxide sheets were synthesized by modified Hummer's Method. Briefly, a solution was made by adding concentrated  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  in the ratio 9:1. Graphite flakes (3g) were added to this solution. After stirring the acid-graphite solution for 5 min at room temperature, 18g of  $\text{KMnO}_4$  was added slowly so as to control the temperature of the reaction. The resulting solution was then stirred for 12 h at 50 °C before being cooled down to room temperature. 400ml of icy water was



**Figure 1.** (a) FE-SEM images of GO sheets (inset shows the lower magnification of GO) (b) Raman spectra of GO and (c) XRD pattern of GO.



**Figure 2.** (a) Wide scan XPS spectra for GO nanosheets, (b) deconvoluted regions for C1s and (c) deconvoluted regions for O1s showing the signature binding energies of different bonds present in GO.



**Figure 3.** (a) Schematic representation of cross-linking between tannic acid molecules and GO sheets and (b) Scheme representing the mechanism of oil rejection from crosslinked GO deposited membrane.

added to cooled solution containing 3ml of  $H_2O_2$ .  $H_2O_2$  was added dropwise till the color became yellowish brown (12ml). It was then allowed to be stirred for some time. After this, washing was performed with the help of centrifuge machine at 4000 rpm for 2

h. Washing was done multiple times with water, HCl and ethanol to bring the pH down to 6. Supernatant was discarded and the precipitate was taken out in a petri dish which was then dried overnight in an oven at  $60^\circ C$  [31].

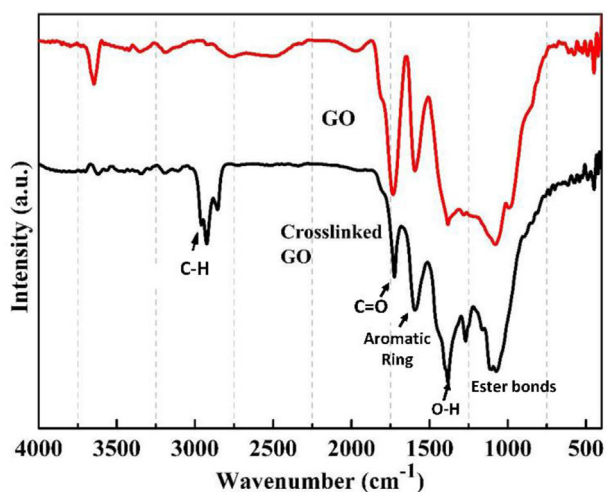


Figure 4. FTIR spectra for pure GO and TA crosslinked GO.

- (b) *Cross-linked membranes*: For the development of GO membranes, vacuum filtration method was used. In the typical procedure, GO was dispersed in deionized water using ultrasonication to make a homogenous dispersion with a final concentration of 0.5 mg/mL. In this, tannic acid was mixed under continuous magnetic stirring for overnight at 80 °C. The as-prepared black colored solution was then poured in the vacuum filtration set up and the crosslinked GO was deposited onto the microporous PVDF membrane. After the complete deposition, the membrane was removed from the setup and dried at 60 °C in vacuum.

### 2.3. Characterization

The surface morphology and elemental composition analysis of the GO and its crosslinked membranes was performed in Field Emission Electron Microscope (Carl Zeiss AG Ultra 55) equipped with Energy Dispersive X-Ray (EDX) Spectroscopy, operating at a voltage of 15kV. X-Ray diffraction (XRD) was done on a Rigaku Smartlab X-Ray diffractometer with Cu-K $\alpha$  radiation of  $\lambda = 1.5406\text{\AA}$  in the range of 20–90°. Raman Spectroscopy was carried out on LabRam Instrument equipped with Synapse CC Detector in the range of 50–3000 cm $^{-1}$ . FTIR spectroscopy was performed in the range from 4000–400 cm $^{-1}$  using KBr pellets.

### 2.4. Development of cross-linked GO membrane

For the deposition of cross-linked GO dispersion onto the microporous PVDF substrate, GO solution was poured in the vacuum filtration setup equipped with vacuum pump. After the complete deposition, the membrane was taken off and dried at 60 °C in vacuum oven.

### 2.5. Preparation of oil/water emulsion for testing

The simulated oil/water emulsion samples were prepared with hexane and DI water for the filtration tests. The oil-based emulsion was obtained by homogenizing 4 ml of oil in 400 ml of hexane: water mixture along with 3 mg of SDS as emulsifying agent, homogenized at 1500 rpm for 24 h. The inorganic metal salts were then added at required ratios maintaining the pH above 8–9. The prepared oil/water emulsion samples were very stable and no phase separation was observed during the entire filtration experiments.

### 2.6. In-house testing for oil/water separation

The real-time performance of the cross-linked graphene membranes for oil/water separation was investigated using vacuum filtration setup

against a surfactant-stabilized emulsion, prepared in the laboratory as mentioned above. To understand the efficiency of the membrane, oil concentrations were determined by Chemical Oxygen Demand (COD) following the method IS:3025 (part 58) -2006 Reaff.2017. The tests to evaluate total dissolved solids (TDS) in the feed and permeate were done as per IS:3025 (part 16) -1984 Reaff.2017. Similarly, the values for total suspended solids (TSS) and turbidity were evaluated as per protocol IS:3025 (part 17) -1984 Reaff.2017 and IS:3025 (part 10) -1984 Reaff.2017, respectively.

To check the efficiency of the membrane towards removal of heavy metals, inductively coupled plasma – optical emission spectroscopy (ICP-OES) was used for the feed and permeate. Zinc and barium were added as model heavy metals in the feed.

### 2.7. Membrane integrity tests

The cross-linked GO membranes were further tested for their integrity and stability in dynamic conditions by immersing a small portion of the membranes in water and agitating them for 360 h using an orbital shaker.

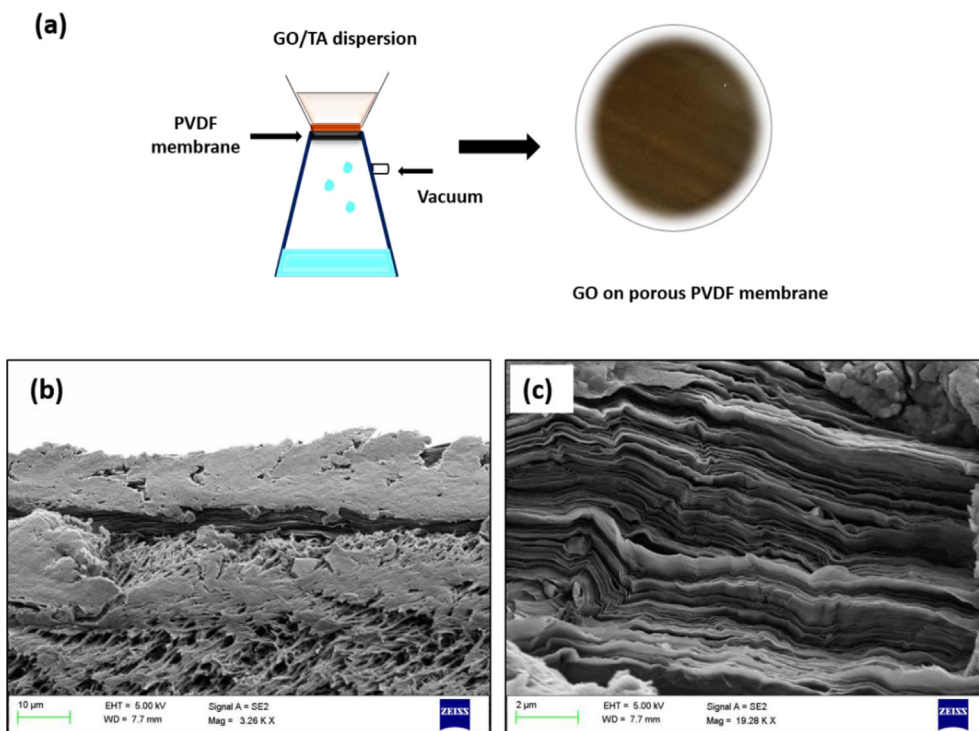
## 3. Results and discussion

In the present study, graphene oxide nanosheets have been prepared using one pot modified Hummer's method [31]. Figure 1(a) represents the FE-SEM images of GO which confirms the formation of sheet like structure. In Raman spectra of GO as shown in Figure 1(b), the characteristic D and G bands were observed at 1351 and 1588 cm $^{-1}$ , respectively corresponding to the defects and disorders in the graphene and bond extension of the sp $^2$  carbon atom pair, respectively. Moreover, the intensity ratio for D and G band ( $I_D/I_G$ ) was calculated as 1.03 to confirm the presence of defect sites in graphene oxide i.e. the introduction of sp $^3$  hybridized carbon atoms into sp $^2$  hybridized graphene layers [32]. Further, XRD was also performed to confirm formation of graphene oxide during the synthesis process. Figure 1(c) represents the typical XRD pattern of GO nanosheets where the intense peak at  $2\theta = 10.1^\circ$  is attributed to hexagonal (001) plane as per JCPDS No 41–1487, which occurs due to the oxidation and increased interlayer spacing between the GO sheets [31].

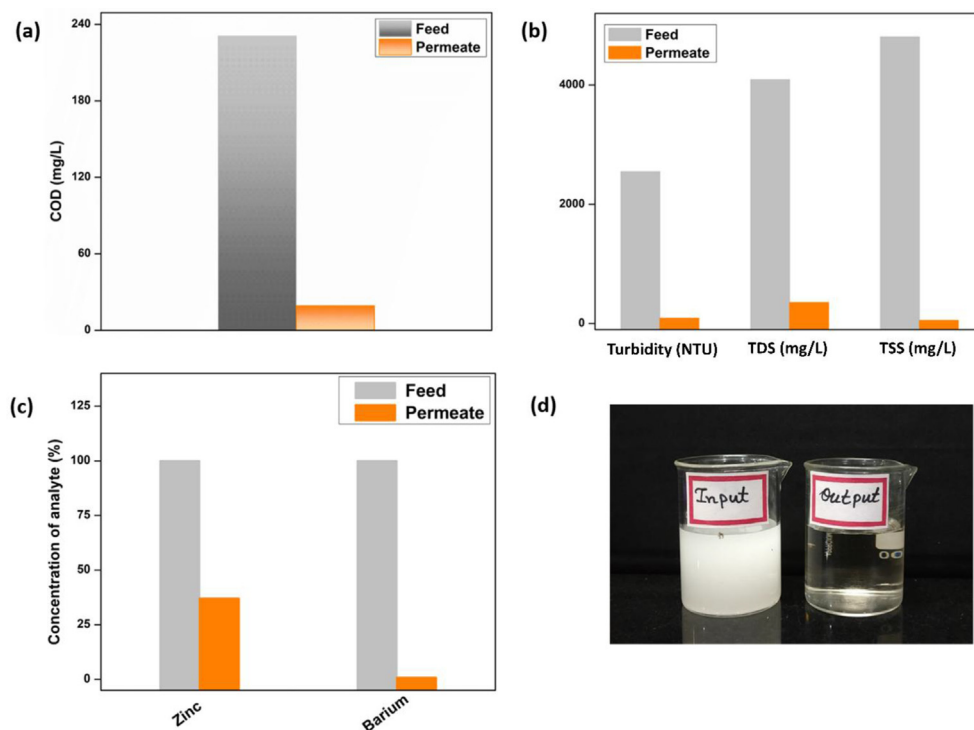
Further detailed information for GO and its functional groups was obtained from XPS analysis. The carbon and oxygen content of GO was also confirmed using XPS which has been shown in Figure 2. Figure 2(a) represents the wide scan XPS spectra for the graphene oxide nanosheets which clearly indicates the presence of carbon and oxygen in the sample. Further, the peaks for C1s and O1s were deconvoluted using software XPSPEAK 4.1, as shown in Figures 2(b) and 2(c), respectively. In Figure 2(b), the binding energy at 284.1 eV is assigned to sp $^2$  hybridized carbon atoms. Three more peaks are observed in C1s spectra at binding energy 286.31, 284.1 and 287.17 eV which are attributed to C–OH, C=O and O=C–O species, respectively. The deconvoluted XPS spectra for O1s is present in Figure 2(c). The binding energies at 532.07, 530.6 and 534.56 eV have been assigned to C=O, quinones and C–OH groups, respectively [33,34]. In addition, the total percentage of carbon and oxygen in graphene oxide sample was evaluated as 36.35 and 41.24%, respectively. So, all the data confirms the proper formation of graphene oxide.

In order to stabilize and improve the efficiency of the membranes, GO nanosheets were crosslinked with Tannic Acid (TA) molecules as schematically illustrated in Figure 3. TA molecules contain plentiful catechol and pyrogallol units which endow them mild reducing characteristics rendering GO sheets to be partially reduced. With the removal of oxygen functional groups, such membranes facilitate to increase the graphitic regions as compared to pristine GO, which further allows the frictionless flow of water molecules through the membrane. TA molecules also help in the assembly of the GO sheets to form stable membranes via strong  $\pi$ - $\pi$  attractions between graphitic regions of GO and strong covalent bonding between functional groups of GO and TA [35]. When deposited over a





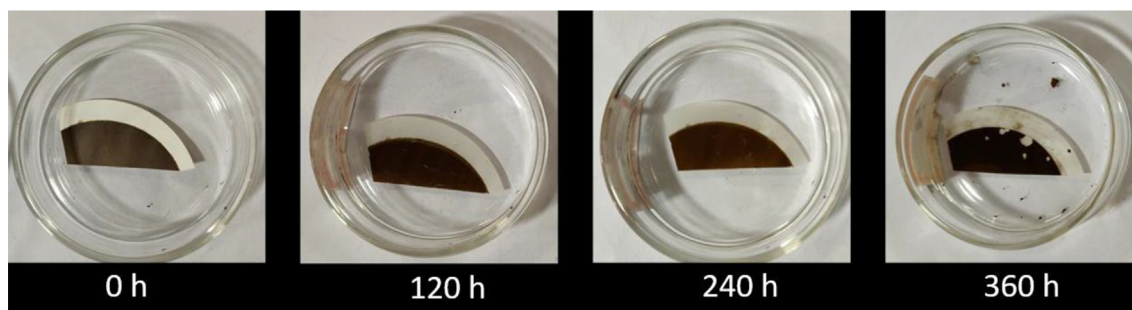
**Figure 5.** (a) Schematic representation of deposition of crosslinked GO-TA onto microporous PVDF membrane using vacuum filtration method (b) cross-sectional FE-SEM image of GO-TA deposited PVDF membrane and (c) High magnification FE-SEM image of self-assembled layers of GO nanosheets with interlayer nanochannels.



**Figure 6.** (a) COD testing plot for the feed and permeate obtained through direct filtration from crosslinked GO membrane; (b) Plot depicting the changes in turbidity, TDS and TSS from feed to permeate; (c) Plot depicting the percentage concentration of zinc and barium in feed and permeate (d) Digital photographs showing the visible difference between simulated oil feed and permeate obtained after filtration.

porous substrate, TA crosslinked GO membranes act as molecular sieves blocking all the solutes with hydrodynamic radii greater than the size of nanochannel behind, allowing only water molecules to pass through. In addition, the abundant hydroxyl groups on tannic acid makes the

membrane superhydrophilic due to which water preferentially passes through the membrane rejecting the oil from the surface. The process of oil rejection and water permeation through lamellar structure of GO-TA membrane has been schematically illustrated in Figure 3 (b).



**Figure 7.** Test depicting the stability of cross-linked membranes in water at different time intervals from 0 to 360 h.

The cross-linking of GO sheets with TA molecules was confirmed using FTIR spectroscopy, as shown in Figure 4. When compared to pristine GO, additional sharp peaks at  $2925$  and  $2860\text{ cm}^{-1}$  were observed, which are associated with the symmetric and antisymmetric -C-H-stretching vibrations of  $\text{CH}_2$  and  $\text{CH}_3$  groups, respectively, in tannic acid. More characteristic peaks of TA such as -OH bending vibration ( $1310\text{ cm}^{-1}$ ) and aromatic ring breathing vibration ( $1525\text{ cm}^{-1}$ ) can also be observed in crosslinked GO, which are blue-shifted at wavenumber  $1384$  and  $1598\text{ cm}^{-1}$ , respectively [36]. In addition, two strong peaks have been observed near  $1067$  and  $1731\text{ cm}^{-1}$  which corresponds to the -C-O-C- and -C=O- moieties of ester groups. It indicates that carboxylic groups of partially reduced GO have covalently bonded to hydroxyl groups of TA to form ester groups [37].

Further, the cross-linked graphene oxide was deposited onto micro-porous PVDF membranes using vacuum filtration method, as shown schematically in Figure 5(a). The PVDF membrane has emerged as the most widely used material in plenty of filtration applications due to its several outstanding properties. However, plain PVDF membrane suffers from the drawback of fouling and does not help in oil/water separation due to its inherent hydrophobic property. Therefore, hydrophilic entities (such as graphene oxide and tannic acid) are deposited on the PVDF surface so as to make it super-hydrophilic and hence prevent its fouling [38]. During the deposition process under vacuum, the cross-linked GO sheets self-assemble to make a layer-by-layer structure. Figures 5(b) and 5(c) shows the cross-sectional FE-SEM images of GO-TA membrane which confirms the formation of uniform lamellar structure with nanochannels between the GO sheets. In addition, average thickness of GO-TA membrane was found to be  $5.5\text{ }\mu\text{m}$  which can be tailored by changing the volume of GO dispersion.

Once the membrane was prepared, it was tested for the removal of suspended solids and organic matter (oil) from simulated oilfield effluent sample in terms of TDS and TSS and COD, respectively [39]. In general, COD is an indicative measure of amount of oxygen present over a volume of solution which is directly used to quantify oxidizable pollutants present in water. Figure 6(a) represents the COD values for the feed and permeate as  $230.7\text{ mg/L}$  and  $19.2\text{ mg/L}$ , respectively, achieving  $91.67\%$  rejection rate. This high efficiency of oil rejection may be due to the fact that there are abundant phenolic hydroxyl groups of tannic acid present over the GO nanosheets making the membrane superoleophobic and superhydrophilic. Similarly, a huge reduction was observed in the values of TDS and TSS from  $4092\text{ mg/L}$  to  $356\text{ mg/L}$  and from  $4810\text{ mg/L}$  to  $55\text{ mg/L}$ , with rejection rate of  $91.3\%$  and  $98.85\%$ , respectively as shown in Figure 6(b). It indicates that the lamellar structure of the membrane possesses nanochannels which only allows the water molecules to permeate through the membrane leaving behind all other contaminants [40,41]. In addition, the colour and turbidity of water are very important aspects in purification process as they determine the clarity and potability of water. It can be observed in Figure 6(b), the turbidity of feed was  $2550$  Nephelometric Turbidity Unit (NTU) which was reduced to  $55\text{ NTU}$  after direct filtration achieving  $96.45\%$  rejection rate. Moreover, the colour of the sample was also changed from milky white to colourless after passing the feed through the membrane as shown in Figure 6(d). All these values

were further compared with the conventionally used nanofiltration membranes which are being used to treat oil/water separation. Salahi et al., prepared PAN based nanofiltration membranes for the treatment of oily wastewater streams of desalter plant and observed  $80.3\%$  reduction in COD value where  $44.5\%$  reduction in the values of turbidity [42]. Similarly, Sarfaraz et al., developed the NPM-PAC (Nano porous membrane-powdered activated carbon) membranes to treat oily waste waters. It was noticed that alone NPM membranes were not efficient in process but the composite (NPM-PAC) membranes were capable to remove COD and TOC with an efficiency of  $78.1\%$  and  $90.3\%$ , respectively [43]. Even  $90.6\%$  removal efficiency of COD was achieved using commercial ultrafiltration membranes made up of polyethersulfone hollow fibers [44]. Thus, it indicates that TA crosslinked membranes are much more efficient in the removal of COD and total dissolved solids as compared to the membranes reported in the literature establishing its potential significance in oil waste water treatment.

In oilfield effluents, several heavy metals are also present which need to be considered during filtration. Therefore, the membrane has also been tested for removal of barium and zinc, from the simulated sample. These are very commonly found heavy metals in the effluent streams of oil refineries. Figure 6(c) represents the percentage reduction in the concentrations of barium and zinc present in feed and permeate, as measured in ICP-OES. In particular, a reduction of  $62.14\%$  and  $99.13\%$  in Zinc and Barium, respectively, was observed indicating excellent efficiency of the membrane. In such a way, GO based membrane with unique layered structure is a promising way to purify oil contaminated water.

### 3.1. Membrane integrity test

The crosslinked GO membranes were then tested for their structural integrity which is an important parameter for their practical application. The membrane integrity also defines the cyclability of the membrane and the cost of the overall filtration process. Figure 7 represents that the membranes are highly stable in water even up to  $360\text{ h}$  under constant agitation which indicates good life cycle of the membrane as compared to pristine GO membranes which disintegrate in even less than  $120\text{ h}$  [45]. The reason behind the high stability of crosslinked membrane is the combined effect of (i) strong  $\pi$ - $\pi$  interaction between the aromatic regions of graphene sheets and (ii) covalent interaction between the functional groups of GO and TA molecules which lowers down the density of free functional groups over the graphene surface and hence provides the structural stability and mechanical strength to the membrane [46]. Moreover, it has been studied that cracks in the graphene oxide sheets are always initiated and propagated along the path where the hydroxyl and epoxy groups are distributed. Therefore, crosslinking helps to fix these groups and prevents the rupturing of the sheets [29]. Besides, such membranes are much more stable as compared to cation modified GO membranes. Yu et al., conducted a study on the stability of cation modified GO membranes and found that Ca-GO membranes were not stable even at high concentration of Calcium while Al-GO membranes were stable for upto  $14$  days with the high concentration of Aluminium [47]. In another study, a complex membrane of PVDF/RGO/SiO<sub>2</sub>/PDA

composite was prepared by Peng et al., for oil water separation applications. However, the graphene started leaching from in the water the very first day of agitation [48]. Therefore, TA crosslinked membranes are advantageous and stable in aqueous solutions and can be used for multiple cycles when employed in the practical water filtration applications.

#### 4. Conclusion

In summary, Tannic acid crosslinked GO membranes were successfully prepared on a microporous substrate using simple and cost-effective vacuum filtration technique for efficient treatment of oil-contaminated water. All the characterization data confirmed the synthesis of GO and its membrane. When these membranes were investigated for the treatment of simulated oilfield effluent, 91.67% reduction was observed in the values of COD, along with significant reductions in the values of TDS, TSS and turbidity. In addition, the membranes demonstrated excellent ability to remove heavy metals from water along with significant stability. In such a way, the present study shows tannic acid cross-linked graphene oxide membranes to have a promising way towards futuristic water treatment applications.

#### Declarations

##### Author contribution statement

Akshay V. Singhal: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Robin George, Anshul Kumar Sharma: Performed the experiments.

Deepika Malwal: Analyzed and interpreted the data; Wrote the paper.

Indranil Lahir: Conceived and designed the experiments; Wrote the paper.

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##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

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