



## Enhancement of Polysulfone Ultrafiltration Membrane Performance for Produced Water Treatment by Incorporation of Graphene oxide/Chitosan/Silicon dioxide Nanocomposite

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### Abstract

Oil and gas production is accompanied by generation of large amounts of produced water as usually three barrels of produced water is generated for each barrel of oil. Membrane-based water reclamation technologies have been applied to treat produced water. However, the presence of oil content in the produced water makes its separation very complicated due to the high affinity between oil droplets and the hydrophobic polymeric membrane. This, results in low permeate flux, low oil rejection and high irreversible fouling. In this study, graphene oxide (GO) was functionalized using chitosan (CH) to synthesize GO-CH that was further functionalized with SiO<sub>2</sub> to produce GO-CH-SiO<sub>2</sub> nanocomposite. Synthesized GO-CH-SiO<sub>2</sub> was embedded in the polysulfone membrane matrix to modify the pristine **Psf** membrane and impart super-oleophobic properties to the membrane. Produced nanocomposites properties were characterized using XRD, FTIR and TEM analyses, while synthesized membranes were characterized for their porosity, pore size, membrane resistance and hydrophilicity. Different ratios of GO:CH were applied with a fixed SiO<sub>2</sub> loading to produce modified membranes. Performance test for the membranes modified with 0.3wt % nanocomposite with a GO:CH ratio of (2:1) showed a 271% improvement in membrane flux compared to pristine membrane while a ratio of 1:2 (GO:CH) gave the lowest total fouling.

**Keywords:** Graphene oxide; Chitosan; SiO<sub>2</sub>; Produced water; Ultrafiltration

### 1 Introduction

The treatment of produced water generated by various industries, including the petrochemical, oil and gas sectors, has grown to be a major global concern. Untreated produced water discharge has a negative impact on the ecosystem in several ways by contaminating soil, surface water, and underground water. Methods of separation, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have shown considerable potential for membrane technology to treat produced

water (Shukla, Alam, Alhoshan, Dass & Muthumareeswaran, 2017; Yasir, Eljack & Kazi, 2020). A proper membrane must have a high pollution rejection rate and a stable, high-water flux at low operating pressure. The abundance of hydrophilic groups in graphene oxide (GO), including epoxy, hydroxyl, and carboxyl groups, gives GO good hydrophilicity and the potential for even further functionalization. Several chemical modification techniques have been proposed and verified to decrease the accumulation of GO on the membrane surface. One such method is creating multifunctional nanocomposites of GO (Mahmoudi, Ng, Ba-Abbad & Mohammad, 2015). To improve membrane hydrophilicity, anti-fouling properties and oil removal performance of the Psf membrane, chitosan (CH) and SiO<sub>2</sub> can be used to functionalize GO. Chitosan (CH) is a hydrophilic polymer, with hydroxyl groups and highly reactive amino groups, which has been used widely for functionalization of GO (Xue et al., 2018). On the other hand, SiO<sub>2</sub> is super oleophobic and has been used extensively to improve oil removal efficiency of the polymeric membranes (Mehta & Zydney, 2005). In our previous study, addition of GO-CH nanocomposite in the membrane matrix has shown improved membrane flux due to enhanced pore radius. In this study, to improve the oil rejection of the membrane while maintaining high membrane flux, GO has been functionalized with CH and SiO<sub>2</sub>. The synthesized nanocomposites were tested using FTIR and zeta analysis. With a constant SiO<sub>2</sub> loading, various GO:CH ratios were used to create customized membranes. The porosity, hydrophilicity, membrane flux, anti-fouling properties and oil removal efficiency were studied for the synthesized membranes and reported in this paper.

## 2 Methodology

### 2.1 Materials

Extra pure, fine graphite powder (99%), sodium nitrate (NaNO<sub>3</sub>, 99.9%), potassium permanganate (KMNO<sub>4</sub>, 99%), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), polysulfone pellets (99%, Mw 35,000), N-Methyl Pyrrolidone (NMP, 99.9%), Chitosan (95% deacetylation), Tetraethyl orthosilicate (TEOS, 95%) and bovine serum albumin (BSA, 99%) were all purchased from Sigma Aldrich. The oil emulsion was prepared using QALCO performance oil #64, purchased from Qatar Lubricant Company. The properties of the oil is given in Table 1.

**Table 1:** Properties of the oil used for preparing the water-in-oil emulsion

Flash Point	220°C
Appearance	Clear Amber Yellow
Physical State	Liquid
Vapor Density (air=1)	>1
Boiling Point	>260°C
Solubility in Water	Negligible
Specific Gravity	0.875
Viscosity	42-50 cSt
Conductivity	0 µS/cm

### 2.2 Synthesis of GO

The graphene oxide (GO) was synthesized following the modified Hummer's methods that has been previously used by Mahmoudi et al. (2015) (Mahmoudi et al., 2015). Initially, 115 mL sulphuric acid was taken in a round bottomed flask where 2.5g NaNO<sub>3</sub> and 5 gm graphite powder was added. The mixture was then stirred for 30 min in an ice bath until the temperature of the mixture reached 10 °C. While maintaining this temperature for 2 hours, 15 g KMNO<sub>4</sub> was added slowly. Then the temperature was increased to 35°C and maintained for 1 hour. Then, 230 mL distilled water was

added to the round bottomed flask slowly while maintaining the internal temperature of the mixture below 100°C. The solution was then stirred for 1 hour followed by addition of 300 mL distilled water. The process was completed by adding 10 mL 30% H<sub>2</sub>O<sub>2</sub> that changed the color of the mixture to brilliant yellow and reduced the residual KMNO<sub>4</sub>. The mixture was then cleaned by centrifugation and washed with HCl before GO powders were obtained by freeze-drying.

### 2.3 Preparation of GO-CH Multifunctional Composite

A suitable quantity of GO was mixed with an aqueous solution of 2% acetic acid. To finish the functionalization process, the mixture was then given the proper amount of CH and mixed for 5 hours. Prior to vacuum drying at 60°C, the mixture was centrifuged and then rinsed with ethanol. Three distinct ratios of the multifunctional GO-CH composite (2:1, 1:1, and 1:2) have been created in this study.

### 2.3 Preparation of GO-CH-SiO<sub>2</sub> Multifunctional Composite

To prepare GO-CH-SiO<sub>2</sub>, a mixture of ethanol and water was prepared where the ratio of ethanol to water was 5:1. The pH of this solution was increased to 9 using 25% ammonia. Then GO-CH nanocomposite and appropriate amount of TEOS was added to the solution. The obtained solution was sonicated for 15 mins and stirred at room temperature for 24 hours. The solution was then centrifuged and rinsed with water before they were vacuum dried at 60°C to obtain the GO-CH-SiO<sub>2</sub> nanocomposite.

### 2.4 Membrane Fabrication

The phase inversion method was used to prepare the GO-CH-SiO<sub>2</sub> doped polysulfone membranes. The correct amount of polysulfone was added to 25 mL of the NMP solution and stirred continuously for two hours at 300 rpm and 80°C to create the casting solution. To avoid the production of gas bubbles in the casting solution, this low stirring speed was found suitable. A suitable quantity of the GO-CH-SiO<sub>2</sub> multifunctional composite was dissolved in 5 mL of NMP solution in a separate beaker, and the mixture was ultrasonically agitated for 30 minutes. Then the two NMP mixtures were added together and stirred for 12 hours at room temperature. Filmography doctor blade was used to evenly spread a small amount of the prepared casting solution onto a glass plate to create the membrane film. The distance between the blade and the glass plate, which was maintained at 0.3 mm, was used to adjust the membrane thickness. After the casting solution had been evenly distributed across the glass plate, the phase inversion procedure was carried out by moving the glass plate into a bath of distilled water. The obtained membrane was removed from the glass plate and given a 30-minute rinse in distilled water. This process was used to cast 4 different membranes. Table 2 provides a summary of the elements and content of the various produced membranes.

**Table 2:** The membrane casting solution compositions

Membranes	NMP (wt%)	Psf (g)	GO:CH (ratio)	(GO:CH):SiO <sub>2</sub> (ratio)
M-0	30	6.144	-	
M-1	30	6.144	2:1	21:1
M-2	30	6.144	1:1	21:1
M-3	30	6.144	1:2	21:1

### 2.5 Characterization of prepared GO-CH –SiO<sub>2</sub> Multifunctional Composite

Using a Nicolet 6700 FTIR spectrometer, the functional groups present on the multifunctional nanocomposite were examined (Thermo Fisher Scientific Inc., MA). Additionally, utilizing XRD (Bruker D8 Advance, Germany) with CuK $\alpha$  radiation (1.5406 Å) in the 2 h scan range of 20–80°,

the nanocomposite's crystal phase composition was also examined.

## 2.6 Characterization of the Fabricated Membrane and Performance Analysis

### 2.6.1 Membrane Permeate Flux, Porosity, Pore Size and Resistance Analysis

The permeation tests were done by using a stirred dead-end cell, with a pressure of 4 bars. Before all studies, the membranes were compressed for 30 minutes at the same pressure. Equation 1 shows the calculations of the pure water permeate flux ( $J$ , LMH):

$$J = \frac{w_t - w_o}{A \times d_w \times \Delta t} \quad (1)$$

Where,  $w_o$  is the initial mass of the permeate water (gm),  $w_t$  is the mass of the permeate water at time  $t$  (gm),  $\Delta t$  is filtration time (sec),  $A$  is the surface area of the membrane ( $\text{cm}^2$ ) and  $d_w$  is density of water ( $0.998 \text{ gm/cm}^3$ ). The porosity ( $\epsilon$ ) of the membrane was determined using the gravimetric method and calculated as:

$$\epsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \quad (2)$$

Here,  $\omega_1$ ,  $\omega_2$ ,  $l$  and  $d_w$  corresponds to weight of the wet membrane (gm), weight of the dry membrane (gm) and thickness of the membrane (cm), respectively. The pore radius ( $r_m$ ) of the membranes were calculated using the porosity and Guerout–Elford–Ferry equation:

$$r_m = \sqrt{\frac{(2.9 - 1.75\epsilon)8\eta l Q}{\epsilon \times A \times \Delta P}} \quad (3)$$

Here,  $\eta$ ,  $Q$  and  $\Delta P$  corresponds to viscosity of water ( $8.9 \times 10^{-4} \text{ Pa.s}$ ), volume of the permeated pure water per unit time ( $\text{m}^3/\text{s}$ ) and the operating pressure (Pa), respectively. The membrane resistance ( $R_m, \text{m}^{-1}$ ) was calculated as:

$$R_m = \frac{\Delta P}{\mu J} \quad (4)$$

Here,  $\mu$  corresponds to the dynamic viscosity of water ( $0.000891 \text{ Pa.s}$  at  $25^\circ \text{C}$ ).

### 2.6.2 Membrane Fouling analysis

The fouling study was conducted using a solution of 1000 ppm BSA as model foulant. For each membrane, three dynamic cycles were conducted in the dead-end setup. Initially, the pure water steady state flux ( $J_{w0}$ ) was measured at 4 bars, then the feed was changed to the BSA solution where filtration was carried out for 1 hour 30 min and the permeate flux was ( $J_{wf}$ ) measured at the end. After the BSA filtration stage, the membrane was washed twice with distilled water and the pure water steady state permeate flux ( $J_{w1}$ ) was measured again at 4 bars. Using the data obtained at this stage, the total fouling ratio ( $R_t$ ), flux recovery ratio ( $FRR$ ), the reversible fouling ratio ( $R_r$ ) and the irreversible fouling ratio ( $R_{ir}$ ) were calculated as:

$$R_t = \frac{J_{w0} - J_{wf}}{J_{w0}} \times 100\% \quad (5)$$

$$FRR = \frac{J_{w1}}{J_{w0}} \times 100\% \quad (6)$$

$$R_r = \frac{J_{w1} - J_{wf}}{J_{w0}} \times 100\% \quad (7)$$

$$R_{ir} = \frac{J_{w0} - J_{w1}}{J_{w0}} \times 100\% \quad (8)$$

The second and third cycles were repeated following the above discussed methodology. The BSA rejection performance of the synthesized membranes were evaluated by using a UV-VIS spectrophotometer (UV-2700, Shimadzu) at 278 nm.

### 2.6.3 Industrial Wastewater Treatment

The industrial wastewater from Shell was treated using the dead-end cell setup. The UF process was carried out at 4 bars. The  $TOC$  concentration of the industrial wastewater before filtration, ( $TOC_i$ ), and after filtration, ( $TOC_f$ ), was measured using AQUAfast  $TOC$  Colorimeter (Orion AQ2040, Thermo Scientific, US). The  $TOC$  rejection ( $R_{TOC}$ ) was calculated as:

$$R_{TOC} = \frac{TOC_i - TOC_f}{TOC_i} \times 100\% \quad (9)$$

For each membrane, all testes were repeated three times and their average was considered in this work while the standard deviation is indicated by the error bars.

## 3 Results and Discussion of the Nanoparticles

### 3.1.1 Surface Zeta Potential Analysis

Zeta potential measurement, as shown in Figure 3, can further confirm the surface functionalization of GO, GO-CH, GO-CH-SiO<sub>2</sub>. The GO particles displayed negative zeta potential between the investigated pH ranges of 3 and 11.5 in the test. The functionalized GO-CH nanocomposites have a greater zeta potential than the GO nanoparticles within the studied range. As GO nanoparticles has many oxygens containing sites on its surface; whereas adding CH causes the GO surface to acquire nitrogen-containing groups, increasing the zeta potential. Moreover, for the nanoparticle with SiO<sub>2</sub>, the zeta potential over the tested range is lower than the zeta potential of GO-CH nanocomposite due to the presence of hydroxyl group on the surface of the GO-CH-SiO<sub>2</sub> nanocomposite.

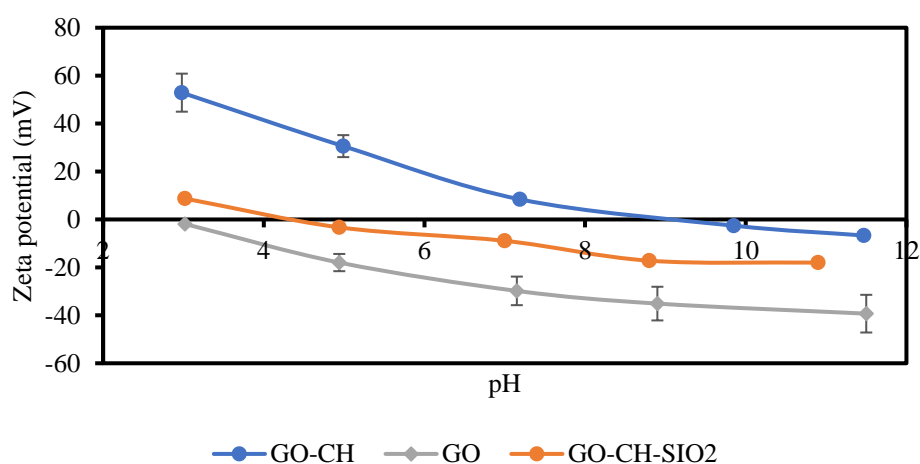


Fig. 1: Zeta potential measurement of GO, GP-CH and GO-CH-SiO<sub>2</sub> at various pH

### 3.1.2 FTIR spectra of GO, CH, GO-CH and GO-CH-SiO<sub>2</sub>

In this experiment GO, CH, GO-CH and GO-CH-SiO<sub>2</sub> were analyzed using fourier transform infrared (FTIR) technique that is shown below in figure.4. Due to C=C stretching vibration, there is an absorption

band at  $1600\text{ cm}^{-1}$  as shown in figure 4. Other bands at  $3400\text{ cm}^{-1}$  are stretching vibrations of oxygen carrying hydroxyl functional groups (OH). The absorbance bands seen along the CH curve at  $1100\text{ cm}^{-1}$  represents the C-O-C vibration,  $1600\text{ cm}^{-1}$  the N-H bending vibration,  $2900\text{ cm}^{-1}$  the C-H stretching vibration, and  $3450\text{ cm}^{-1}$  the O-H and N-H stretching vibration. Moreover, the absorbance band for the GO-CH nanocomposite demonstrates the presence of all the bands that were detected in the individual CH and GO curves. Finally, regarding GO-CH-SiO<sub>2</sub> nanocomposite, due to the SiO<sub>2</sub> it is stated that bands between  $900$  and  $1050\text{ cm}^{-1}$  represent composite characteristics of Si-OH species. Therefore, the strong band at around  $950\text{ cm}^{-1}$  is attributed to the stretching vibration of Si-OH.

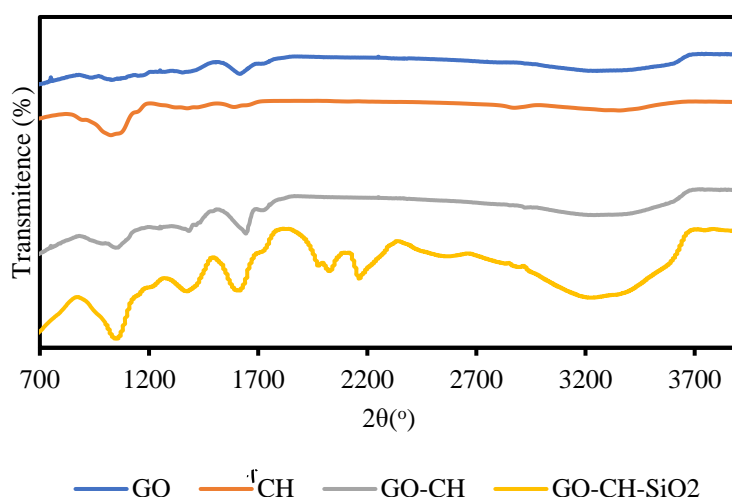


Fig. 2: FTIR spectra of GO, CH, GO-CH and GO-CH-SiO<sub>2</sub>

## 3.2 Characterization of the Membranes

### 3.2.1 Porosity and Resistance Study

Porosity was conducted to obtain the pore size of nanocomposites at synthesized membranes. Table 3 provides the values of porosity, pore radius, membrane resistance and contact angle. As shown in Table 3, the porosity, membrane resistance pore radius and contact angle for the pristine membrane (M0) were 57.3%, 17.9, 4.2 and  $87.4^\circ$ , respectively. Doping the membranes with GO-CH-SiO<sub>2</sub> nanocomposite improves the porosity and pore radius and decreases the membrane resistance and contact angle. The presence of hydrophilic functional groups, improved affinity between polysulfone membrane and the prepared nanocomposite and increased viscosity resulted in these improvements.

Table 3: Porosity, pore radius, resistance and contact angle of the synthesized membranes

Membrane	Porosity (%)	Membrane resistance	Pore radius (nm)	Contact angle ( $^\circ$ )
M0	57.3	17.9	4.2	87.4
M1	85.0	7.3	8.7	61.5
M2	93.3	8.1	7.5	55.8
M3	88.1	11.2	6.8	50.8

### 3.2.2 Pure Water Permeation Flux

Water permeation flux was determined to study the effect of CH on different concentration of GO-CH-SiO<sub>2</sub> nanocomposites. Figure 6 provides the flux values for each membrane. Comparing to the pristine membrane M0, M1 shows the highest flux of 23.13 LMH/bar, where porosity increased by 27.7%, pores expanded by 207%, membrane resistance decreased by 41% and contact angle reduced by 25.9°. Whereas M3 showed the lowest flux enhancement due to lower pore enlargement and the higher membrane resistance.

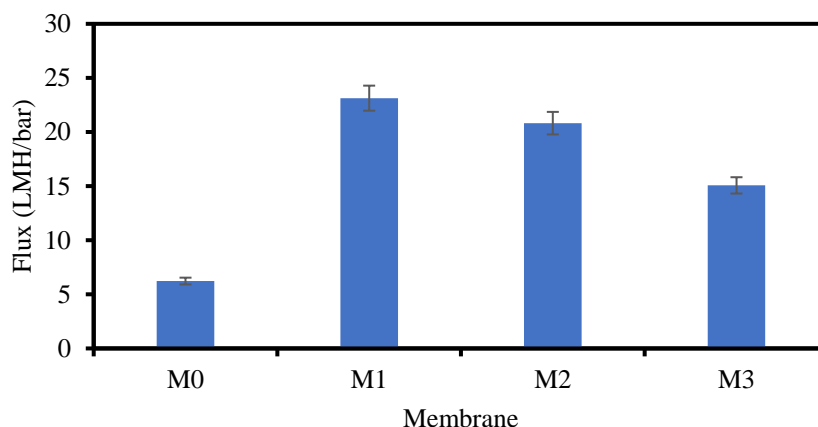


Fig. 3: Flux of GO-CH-SiO<sub>2</sub> membranes

### 3.2.3 Fouling Study

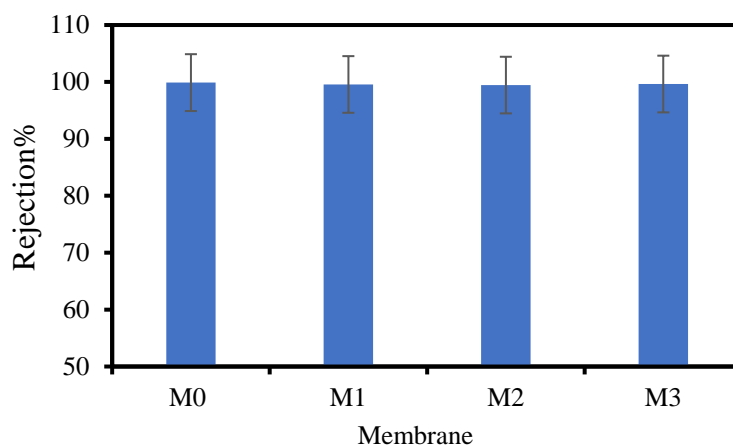
The fouling study in terms of total fouling ratio ( $R_t$ ), flux recovery ratio ( $FRR$ ), reversible fouling ratio ( $R_r$ ) and the irreversible fouling ratio ( $R_{ir}$ ) was conducted according to the method discussed in section 2.6.2, where 1000 ppm of BSA solution was used as the model foulant. The results of fouling flux shown in table 4. Out of four membranes, M3 showed the lowest total fouling (%) due to its lowest contact angle. Due to improved hydrophilicity, M1, M2 and M3 showed better anti-fouling properties than the pristine M0 membrane.

Table 4: Fouling properties for GO-CH-SiO<sub>2</sub> membranes

Membrane	$R_t$ (%)	FRR(%)	$F_r$ (%)	$F_{ir}$ (%)
M0	85.4	21.2	6.6	78.8
M1	90.7	69.3	59.9	30.7
M2	84.3	77.6	61.9	22.4
M3	47.9	74.2	22.0	25.8

### 3.2.4 Membrane Performance for Industrial Wastewater Treatment

Figure 8 shows the oil rejection performance of the synthesized membranes. As seen from Figure 8, all the synthesized membranes have shown greater than 99% oil rejection even at increased permeation flux. The increased pore size, as indicated by Table 3, did not affect the oil rejection performance due to the presence of super-oleophobic SiO<sub>2</sub> in the nanocomposite.



**Fig. 4:** Rejection percentage of GO-CH-SiO<sub>2</sub> membranes

#### 4 Conclusion

This study effectively synthesized the multifunctional nanocomposite GO-CH-SiO<sub>2</sub> and applied it to enhance polysulfone membrane. The hydrophilic functional groups, such as hydroxyl and carboxylic acid, which were present in the produced nanoparticles, were abundant. The composition of the produced GO-CH-SiO<sub>2</sub> nanocomposite was verified using FTIR studies. The ratios of GO and CH were changed during the nanocomposite synthesis between 1:2, 1:1, and 2:1, while the ratio of SiO<sub>2</sub> remained fixed at 21:1. Results showed an increase in the flux while adding GO-CH-SiO<sub>2</sub> nanocomposite, which resulted in increased porosity and pore radius and reduced membrane resistance and contact angle. Additionally, the improved hydrophilicity resulted in lower fouling rate. Finally, the presence of SiO<sub>2</sub> aided in high oil rejection at elevated membrane flux.

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