Dyes are one of the major toxic compounds originating from inadequately treated industrial effluents causing degradation of water bodies compounding to the global scarcity of freshwater resources. Wastewater and effluents containing dyes are difficult to treat since dyes are mostly resistant to light, oxidizing agents and aerobic digestion [1]. Dyes are capable of colouring water streams and reducing light penetration even at very low concentration levels hence presenting negative or toxic effects to human and aquatic life [2].

Direct disposal of dyes contaminated wastewater into water streams is increasingly regulated and harsh environmental laws are being implemented in most countries [3]. In order to comply with these strict regulations, effective means of separating, removing or degrading dye molecules from contaminated wastewater are being developed [4]. Due to the stability of most dye molecules to light, oxidizing agents and microbiological degradation and high energy required to break down the dye molecules, several separation processes including photocatalysis, adsorption, coagulation, flocculation, chemical oxidation, biodegradation and membrane processes have been implemented as a systemic approach for wastewater treatment [5].

1. Introduction

A series of polyethersulfone membranes containing Ag@HPEI@GO composite was fabricated using non-solvent induced phase separations (NIPS) to mitigate against biofilm causing bacteria and modulate solute rejection. All materials produced and used were fully characterised using a combination of appropriate physicochemical techniques including FTIR, XRD, BET, SEM, AFM. The GO-based fillers exhibited bactericidal activities. The bactericidal activities of GO, HPEI@GO against Escherichia Coli (E. coli) were observed at 8 mg mL$^{-1}$ whilst Ag@HPEI@GO composites exhibit bactericidal activities against E. coli at 4 mg mL$^{-1}$. Against Klebsiella pneumonia (K. pneumonia), GO bactericidal activities were observed at 8 mg mL$^{-1}$ whilst HPEI@GO and Ag@HPEI@GO bactericidal activities on K. pneumonia were observed at 4 mg mL$^{-1}$. Against Staphylococcus aureus (S. aureus), GO exhibit bactericidal activities at 8 mg mL$^{-1}$, HPEI@GO and Ag@HPEI@GO composites exhibit bactericidal activities on S. aureus at 4 mg mL$^{-1}$. The aforementioned microorganisms are among the microorganisms that cause biofilm formation on surfaces. The membrane performance was assessed by measuring pure water flux, solute rejections and fouling propensity with three different organic dye molecules and bovine serum albumin (BSA). All composite membranes (GO/PES, HPEI@GO/PES, and Ag@HPEI@GO/PES) exhibited increased hydrophilicity and higher pure water flux compared to the baseline PES membranes with concomitant increase in fouling resistance. The observed flux recovery ratios (FRR) were 80% (GO/PES), 70% (HPEI@GO/PES) and 69% (Ag@HPEI@GO/PES) respectively compared to the 45% FRR observed for the baseline PES membrane after BSA fouling. Congo red (CR) used as an indicator for molecular cut-off of UF membranes was rejected above 95% by all nanocomposite membranes. Furthermore, the nanocomposite membranes-maintained rejection for the positively charged methylene blue (MB) of above 90% whilst rejection observed for amaranth (AR) dye decreased from 80 to 58% with increasing filler content in the PES matrix. The results demonstrate the positive influence of GO, HPEI@GO and Ag@HPEI@GO nanofillers on flux, fouling and solute rejection performance of resultant PES nanocomposite membranes.
approach towards wastewater decolourisation [5, 6]. In order to overcome these limitations, conventional separation techniques such as adsorption, coagulation, flocculation and membrane processes have found favour for dye wastewater remediation [4,5,6,7]. However, among the aforementioned processes, membrane separation have been extensively used in wastewater treatment including for dye separation, water reclamation and ground water restoration to minimize the effect of the ever increasing water pollution [7,8,9] and to cope with the wide range of water quality problems to attain safe drinking water [10].

In wastewater separation, membranes techniques are seen as a more economical alternative [9]. Amongst membrane separation processes, ultrafiltration (UF) membranes are preferred in wastewater separation because of their relative advantages in selectivity, cost, and permeability compared to microfiltration (MF with higher flux but lower selectivity and cost), nanofiltration (NF with low flux but higher selectivity and cost), reverse osmosis (RO with low flux but highest selectivity and cost) [3]. As a result UF membranes offers a balanced performance criteria and justified efficiency in the separation of dyes and other large organic molecules [10]. However, the main limitation associated with UF membranes are the relative inefficiency of separating dissolved dyes of smaller molecular size due to their relatively larger pore sizes (0.01 μm compared to microfiltration) [11] and the general propensity of membrane fouling.

Membrane fouling is generally caused by the deposition or growth of foulants such as contaminating microorganisms, colloids, inorganic or organic compounds on membrane surfaces, which do not only increase maintenance and operational cost but also reduces membrane performance stability, life span and water flux [12,13,14]. Biofouling related with microorganism of microbial proteins are reportedly common and can result to biofilm formation on membrane surfaces, which can lead to membrane pores blockage, degradation and flux retardation [12,15,16]. Efforts in improving UF membranes molecular cut-off for smaller molecules include modulating their surface properties [22]. For instance, increasing the charge density on the membrane surface results in a larger hydration layer that results in smaller apparent pore sizes as well as conferring a secondary solute rejection mechanism in addition to size exclusion [17]. The inclusion of highly functionalised fillers or organic modifiers such as hyper branched polyethyleneimine (HPEI) and zwitterions. has demonstrated that these desired properties can also be attained through this approach [19, 20]. These type of membrane modifications are also known to influence other membrane surface properties such as roughness, hydrophilicity and charge which also improve the fouling performance of resultant membranes [9, 23]. Also, the inclusion of inorganic fillers such as AgNPs [16], graphene oxide (GO) [15], and HPEI [23] with renowned bactericidal activities within the polyethersulfone (PES) matrix minimises biofilm formation [12].

Graphene based nanomaterials such as single-layer graphene, multi-layer graphene, chemically converted graphene and graphene oxide (GO) are regarded as one of most sort nanomaterials due to their high surface area, tightly packed two dimensional honeycomb lattice, good thermal and mechanical stability, well organized carbon network building blocks, good optical properties, and prominent electron transport [24]. The active functional groups of GO such as the hydroxyl, epoxy, carbonyl and carboxyl groups, which arise from the oxidation of graphite, renders GO hydrophilic, increases their dispersion in water and minimize their aggregation in polymeric substrate, without compromising the polymer integrity [25]. Hence making GO excellent candidate for the modification of polymeric materials which have received great attention globally [25]. The GO based nanocomposite membrane can be used to tune transport pathways and polymeric microstructure towards permeation flux and antifouling properties and maximize the permeate flux of the pristine membrane [26], enabling their use in various membrane separation applications. For example, by modifying GO with HPEI and its deployment into PES matrix, Yu and co-worker [23] reported antibacterial properties against E. coli as well as improved antifouling properties of the nanocomposite membranes. By deploying GO into poly(phenyl)sulfone matrix, Shukla and co-worker [26] reported improved surface charge, antifouling and hydrophilic properties.

In this study, membrane fouling resistance and selectivity were enhanced by blending hydrophobic GO and HPEI@GO composites into PES matrix to improve hydrophilicity and the surface chemistry of the resultant membranes respectively. In order to further improve fouling resistance of the membranes specifically against biofilm forming bacteria, the Ag containing composites, Ag@HPEI@GO, were introduced into the formulation. Therefore, the synthesized Ag-based fillers were also phytochemically screened against some biofilms causing microorganisms such as E. coli, K pneumonia and S aureus with promising results. The results of these membrane formulations are reported herein and demonstrate that this approach offers promise for improving UF membrane applications in wastewater applications.

2. Experiment

2.1. Materials

Polyethersulfone (PES: mw 80,000 gmol−1) granules, N,N-dimethyacetamid (DMAC), synthetic graphite flakes (20 μm), sulphuric acid (98%), potassium permanganate (99%), orthophosphoric acid (85%), hydrochloric acid (32%), hydrogen peroxide (30% in H2O), absolute ethanol, diethyl ether, polyvinylpyrrolidone (PVP: mw 10,000 gmol−1), silver nitrate (99%), polyethyleneimine (MW 25 000), dimethyl sulfoxide (DMSO), amaranth dye (AM), methyl blue (MB), Congo red (CR), methyl orange (MO) and bovine serum albumin (BSA) were purchased from Sigma-Aldrich (South Africa) and used as received. GO [25], HPEI@GO [26] were prepared following literature methods.

2.2. Synthesis of GO and GO@HPEI

GO was synthesised from industrial graphite flakes using the improved method by Marcano et al. [25]. In short, graphite flakes (3.00 g) were gradually added to a mixture of concentrated H2SO4 sulphuric acid (360 mL) and H3PO4 orthophosphoric acid (40 mL in a ratio of (9:1) producing a slight exothermic reaction. KMnO4 (18.00 g) was slowly added to the stirred mixture to minimise rapid temperature increase due to the exothermic reaction, followed by heating at 50 °C for 12 h. The reaction was allowed to cool to room temperature and then transferred into a mixture of H2O2 (30%, 3 mL) and ice (400 mL). The solid material was washed twice with water (200 mL), HCl (200 mL) and twice with ethanol (200 mL), and finally with diethyl ether (200 mL). The brown solid (5.4 g) was vacuum dried overnight at room temperature. HPEI@GO was synthesized by a method adopted from Zhang et al. [26]. Briefly, GO powder (0.10 mg) was uniformly suspended in an ultrasonic bath in DMAC (50 mL) solvent for 30 min. Thereafter, HPEI (0.14 mg) was added to the homogenous mixture and sonicated for another 30 min and stirred for a further 12 h. The obtained product was recovered using a centrifuge and the obtained pellet dried in an oven at 80 °C.

2.3. Synthesis of Ag@HPEI@GO composites

A mixture of PVP (1.35 g) and AgNO3 (4.3 g) was sequentially added to a stirred mixture of HPEI@GO composite (100 mg) in 50 mL DMAC solution. The mixture was heated at 80 °C for 25 min. The resultant product was recovered using a centrifuge, washed and dried at 60 °C. Herein, DMAC was used as the reducing agent, PVP as a capping agent and AgNO3 as precursor for Ag NPs.

2.4. Fabrication of PES membranes

The membranes were fabricated using phase inversion technique. The casting solution was prepared by firstly dissolving PES granules and PVP powder in DMAC over 24 h at RT. This was followed by the addition of solids to the polymer solution and the resulting mixture stirred until a
homogeneous consistency was achieved. The casting solution was left under vacuum to dissipate air bubbles before use. Three casting solution formulation were made, i.e., the P₁ series with GO, the P₂ series with HPEI@GO and the P₃ series with Ag@HPEI@GO as contained in Table 1.

3. Characterization of the nano fillers and the PES membranes

All prepared materials were characterized by a combination of techniques, including Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Atomic force microscopy (AFM), transmission electron microscope (TEM), scanning electron microscope (SEM) and water contact angle (CA) measurements.

The FTIR spectral of the GO-based fillers were collected using a Bruker Vector-22 mid-IR spectroscopy (Bruker, Karlsruhe, Germany). The powder GO-based samples were grounded with KBr powder and pressed into pellet and analysed by passing the infrared radiation through the powder GO-based fillers were weighed into a cleaned sample holder and exposed to X-ray beam between 2θ = 50° and 70°. The shape and morphology of the prepared graphene-based fillers were obtained using a transmission electron microscopy (a Tecnai TEM JOEL, JEM 2010, Japan). A desired quantity of each sample was dispersed and sonicated in ethanol for 10 min to obtain a homogenous dispersion which was deposited on the surface of a carbon coated copper grid and analysed.

A VEGA3 TESCAN TC scanning electron microscopy (VEGA 3 TESCAN, Czech Republic) was used to evaluate the surface, cross section morphology as well as determine the elemental composition, the membranes and the graphene-based fillers. The membrane samples were frozen in liquid nitrogen for 10 min, fractured, mounted on the SEM stump and sputter coated with carbon before imaging. The graphene-based fillers were mounted on a carbon tape, pressed onto a brass plate and frozen in liquid nitrogen for 10 min, fractured, mounted on the SEM stump and exposed to X-ray beam between 2θ = 5° and 70°. The shape and morphology of the prepared graphene-based fillers were evaluated using a VEGA3 TESCAN TC scanning electron microscopy (VEGA 3 TESCAN, Czech Republic).

The thermal stability of the graphene-based fillers was evaluated using PerkinElmer thermogravimetric analyser (TGA) instrument, TG DTA, DT-40 (Shimadzu, Japan). The samples were heated from room temperature to 800 °C under flowing nitrogen at a heating rate of 10 °C min⁻¹. Changes in the weight profile of the graphene-based fillers as a function of temperature over time (C) was used as a factor in determining its thermal stability.

The crystallinity of the synthesised graphene-based fillers was determined using a D8 advance diffractometer (X Pert, Germany) equipped with PSD Vantec 1 detectors and Cu Kα radiation (λ = 1.5406). The dried graphene-based fillers were placed on a low background sample holder and exposed to X-ray beam between 2θ values of 0–80° at an applied voltage of 40 kV and 40 mA current. The effectiveness of the synthesised graphene-based fillers against biofilm causing microorganisms was evaluated using the minimum inhibitory concentrations (MICs) technique [27]. The bacterial strains used were E coli, K pneumonia and S aureus. Adopting the scheme well-defined by Andrew et al. [28], the MIC experiment was carried out using the 96-well microtitre plate and the bacteria strains in four repeated cycle and four different dosage to ascertain accuracy. The three bacteria strains were inoculated overnight in an incubator at 37 °C in Mueller Hinton (MH) broth solution prepared according to the manufacturer’s instruction and allowed to grow for 24–36 h. The growth rate of each bacterium was compared with a 0.5 McFarland’s standard. MH broth (5.5 mL) was dispensed in McCartney bottles previously autoclaved at 121 °C. In this experiment, streptomycin was used as the positive control (streptomycin was prepared by weighing 0.032 g in 1 mL of distilled water) while DMSO was used as a negative control. Each of the prepared graphene-oxide-based fillers was weighed into a cleaned autoclaved MacCourtney bottles. Dissolved in a minimum amount of DMSO and the remaining volume were made up to 5.5 mL using MH broth solution (the outer wells of the plate were filled with sterile distilled water). For each bacterium, serial dilution was carried out from 31.25 μg mL⁻¹ to 16 mg mL⁻¹ and bacterial culture of 10 μL were added to each well in both horizontal and vertical position and grown overnight. The plates were incubated again for another 2 h after the addition of 10 μL Resazurin sodium salt solution (0.02% (w/v)). The wells were visually inspected for colour changes (Figure 5).

The surface roughness parameters of the prepared PES membrane were captured using the atomic force microscopy (AFM nanoscale IV, Vecco, Santra Clara, California USA) with the spring constant of 0.12 N m⁻¹. The AFM images were made possible by capturing the top active surface area of the dried PES membrane (membranes were dried for 24 h at RT) at a scan scale of 10 μm by 10 μm, to define the membrane average roughness and the root mean square roughness (Rq and Rq) respectively.

The surface hydrophilicity of the membranes was studied using the CA measurement (G10, KRUS, Hamburg Germany). Using the sessile drop techniques at RT, deionised water was deposited on the top surface (active side) of each membrane. An average of five drops was reported to minimise error variations and increase accuracy.

The UF-PES membranes were prepared using a sheen automatic film applicator model number 1133N (CA, USA). The blended casting solutions at RT were poured onto the glass plate, left to settle for 90 s. The membranes were casted at a transverse speed of 50 mm/s.

3.1. Pure water flux and solute rejection

Pure water flux and solute rejection efficiency of the membranes were evaluated using N₂ pressurized Sterlitech HP4750 dead-end cell (Sterlitech, Kent, Ohio, USA) with 8.04 cm² effective surface area. For all rejection studies, the stirred cell was equipped with magnetic stirrer to mitigate the effects of concentration polarization on the membrane surface. Prior to pure water flux evaluation, each membrane was firstly pre-compacte at 300 kPa for 30 min and water flux was evaluated at 200 kPa using deionized water. Dye rejection was also carried out at 200 kPa using 100 ppm dye solution. The concentration of the dye molecule present in feed and permeate dye solutions were determined using the UV-Vis spectroscopy using UV-Vis Shimadzu model UV-2450, Japan).

The pure water and BSA containing water flux (Jw) was determined using Eq. (1) [29]:

\[ J_w = \frac{V}{A t} \]

where, V is the volume (m³) of the permeate water, t is permeation time (s), and A is membrane surface area (m²).

The rejection percentage of dye solutes was calculated using Eq. (2) [29]:

\[ R = \left[ 1 - \left( \frac{C_p}{C_i} \right) \right] \times 100\% \]
where, $C_p$ and $C_f$ are concentration of dissolved solutes in the permeate and feed water solutions, respectively.

### 3.2. Antifouling studies through BSA and organic dyes solutions

Fouling assessment of membranes was undertaken using two approaches. In the first, BSA was used as a foulant whilst in the second instance the organic dyes were used as foulants. The results obtained from these assessments are discussed separately. The membranes prior to BSA rejections were subjected to pure water flux, after which the water in the stirred cell was replaced with the BSA solution to obtain the BSA flux. The fouled membranes were immersed in water and shaken for 30 min. The water flux of the cleaned membrane ($J_{w2}$) was measured. Using the parameters obtained from the fouling study, the flux recovery ratio (FRR) and the fouling resistance of the membranes were determined using Eq. (3) [30].

\[
\text{FRR} \% = \left( \frac{J_{w}}{J_{w2}} \right) \times 100\% \tag{3}
\]

where $J_{w2}$ is the pure water flux of the cleaned membrane and $J_w$ is the initial pure water flux before the membrane was fouled.

The total fouling ($R_t$), reversible fouling ($R_r$), and irreversible fouling ($R_{ir}$) parameters of the prepared membranes were evaluated using Eqs. (4), (5), and (6) respectively [30].

\[
R_t = \left[ 1 - \left( \frac{J_{w}}{J_{w0}} \right) \right] \times 100\% \tag{4}
\]

\[
R_r = \left[ \frac{J_{w0} - J_{w}}{J_{w0}} \right] \times 100\% \tag{5}
\]

\[
R_{ir} = \left[ \frac{J_{w0} - J_{w}}{J_{w0}} \right] \times 100\% \tag{6}
\]

From the above equations, $R_t$ represents the degree of flux decline caused by total fouling, $R_r$ indicates the fouling caused by loose attachment of protein solution on membrane surfaces and pores which can be washed off by ordinary cleaning in water or back washing. $R_{ir}$ indicates the fouling resulted from the tight attachment of protein molecules on the membrane surface and membrane pores leading to total flux decline and membrane degradation which can only be washed off by chemicals.

### 4. Results

#### 4.1. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of GO and HPEI@GO were as expected (Figures 1A and 1A’) [30, 31]. In short, all the main functional groups were observed (Figure 1A-A’). For example, the characteristic bands for C=O (1721 cm$^{-1}$), C–O (1220 cm$^{-1}$) and OH (3465 cm$^{-1}$) functional groups on the

![FTIR spectra](image_url)

Figure 1. Structural analysis of GO, HPEI@GO and Ag@HPEI@GO composites A-A’): FTIR spectra indicating characteristic bands of appropriate functionalised groups, B): XRD spectra and C): TGA spectra.
GO nanosheets were observed [31]. The vibration pattern of HPEI@GO composite showed the disappearance of C=O and C=O functional groups and the appearance of –CN (1252 cm⁻¹) and –NH (1386 cm⁻¹) groups. This is attributed to chemical reaction between the NH₂ groups of the HPEI and the C=O and CO groups of the GO nanosheets resulting in the formation of amides (CN) together with a secondary amine (NH) and oxygen functional groups. The presence of functional oxygenated groups on the basal plane seen in all the synthesised GO-based fillers indicates that the carbon structure of the graphite material was not destroyed by the oxidation of graphite, the grafting of HPEI and the decoration with AgNPs [31, 32]. The peaks at 2970 cm⁻¹ and 2890 cm⁻¹ on the HPEI@GO molecular chain could be attributed to the vibration pattern of –CH₂–H (2820 cm⁻¹) groups. The presence of functional oxygenated groups on the basal plane and edges of GO nanosheet served as site for chemical modification of GO and greatly influence the direct application of GO in membrane performance [33, 34]. The obtained FTIR results indicate the successful synthesis and modification of GO sheets and its composite.

4.2. X-ray diffraction (XRD)

The XRD spectra of the synthesised GO-based fillers are presented in Figure 1B. GO exhibit a sharp crystalline peak at 2θ of 9.6° in line with literature [35, 36]. After the coordination of HPEI onto GO, this band slightly shifted to 2θ of 10.2° with concomitant decrease in its intensity. In addition to this, a broad band centred at 2θ (29) emerged indicative of the increased amorphous nature of HPEI@GO composite indicative of increased distance between graphene sheets. These sharp crystalline peaks observed in GO and HPEI@GO completely disappeared upon addition of AgNPs onto HPEI@GO composite, i.e., in Ag@HPEI@GO composite. The composite Ag@HPEI@GO thus only showed diffraction patterns attributed to the AgNPs at 38°, 44°, 65° and 78°. This confirms the successful grafting of HPEI and decoration of AgNPs onto GO platelets as observed in the FTIR characterisation earlier (Figure 1A-A’).

4.3. Thermogravimetric analysis (TGA)

The thermal stability of the synthesized graphene-based fillers was evaluated using the TGA analysis (Figure 1C). A gradual weight loss of approximately 13% observed between 98 and 158 °C for GO sheets was attributed to the loss of adsorb moisture held in the structural lattice of the GO sheets as well as the loss of liable oxygen functional groups such as carboxyl groups [3,16]. The sharp decomposition of approximately 75% weight loss observed between 164 and 223 °C was attributed to the loss of more stable oxygen functional groups (epoxy groups). The final decomposition of the carbon skeleton was observed between 273 and 670 °C [35, 37, 38, 39]. The initial weight loss between 98 and 137 °C in HPEI@GO and 98 and 135 °C for Ag/HPEI@GO composites a weight loss of approximately 5% and 4% was observed respectively. This was again attributed to the loss of adsorbed moisture on the graphene-based fillers. The second thermal events observed from 135 to 390 °C in HPEI@GO and 152–496 °C in Ag/HPEI@GO composites accounting to weight loss of 61 and 60% respectively was attributed to thermal decomposition of NH, CN, and oxygen functional groups held in the GO lattice [40]. The skeletal degradation of the GO composite was observed between 446 and 760 °C for HPEI@GO and 522 and 752 °C for Ag/HPEI@GO. The thermal stability of the synthesized graphene-based fillers indicates that GO is relatively thermally unstable to graphite [41,42,43,44] but less stable than its modified composites, HPEI@GO and Ag/HPEI@GO.

4.4. Assessment of the GO-based fillers against biofilm causing microorganisms

The effectiveness of the synthesized GO-based fillers against biofilm causing microorganisms is demonstrated in Figure 2A-C, evaluated using MICs showed improving performance. For instance, the GO nanosheets exhibited inhibitory activity against S aureus at 4 mg mL⁻¹ and at 8 mg mL⁻¹ for K pneumonia and E coli respectively as indicated by the observed colour changes (Fig. 2A-C). Zheng and co-worker reported previously that GO prepared by the chemical oxidation of graphite have improved antibacterial activities [45]. The HPEI@GO and Ag@HPEI@GO composites exhibit inhibitory effects against S aureus (4 mg mL⁻¹) and K pneumonia (8 mg mL⁻¹) and E coli (8 mg mL⁻¹) respectively. This demonstrates that grafting HPEI onto the surface of the GO sheets and its decoration with Ag NPs improved the antibacterial effect of GO against K pneumonia. This is envisaged to translate in the reduction of biofilm formation and longer life span of the membranes in practice. This is in line with previous reports showing good antimicrobial effects exhibited by introduction of AgNPs [8,18,56] and HPEI molecules in [48] filtration membranes.

4.5. Membrane morphology

The cross section, surface morphology and EDS analysis of the prepared UF membranes (0.1 wt.% GO) is shown in Figure 3P–P₃a for the rest, see Fig. S3A). A porous skin layer with finger-like and dense sub-layer structure was observed in all the prepared membranes, which is typical for asymmetric membrane [49, 50]. In all the modified PES membranes series, increased weight concentration of the fillers in the PES matrix resulted to increased membrane porosity. This effect is attributed to the incorporated hydrophilic functionalities (C=O, C=O, OH and Ag NPs) present on the surface of the GO-based fillers. Furthermore, as observed in Figure 3 and Fig. S3A, the pore sizes for the modified membrane also increased with increased filler concentration in the PES matrix. However, these effects were more pronounced in P₁ (GO/PES membrane) membrane series, which was attributed to the high content of oxygen functionalities found in GO, among the modified membranes indicative of increased hydrophilic character. Incorporation of hydrophilic and charge functionalities into a polymer matrices is reported to promote membrane’s hydrophilic properties [44, 51, 52, 53]. The surface morphology of the composite membranes exhibited uniformly distributed fillers with no signs of agglomeration on the membrane surface observed indicative of optimum loading conditions which is envisaged to contribute to the stability and integrity of the fabricated membranes [30]. The elemental composition (i.e., C, O, N and Ag) observed by the EDS analysis affirms the successful preparation of different composites of modified PES membranes.

4.6. Atomic force microscopy (AFM)

The effect of the GO-based fillers on the surface roughness parameters is captured in Table 2 (mean roughness (Rq) and the mean square of the Z data (Rq₂)) and Fig. S4A. The unmodified PES membrane displayed the highest roughness values of ca. 61.39 nm, which decreased with the incorporation of the fillers. This decreased to ca. 14.00 nm and 11.00 nm for the GO@PES membrane series and to ca. 11.00 nm and 9.00 nm for the HPEI@GO/PES membrane series, and finally to ca. 15.00 nm and 8.00 nm for the Ag@HPEI@GO/PES membrane series. In fact, it was observed that an increase in the concentration of the fillers in the membrane matrix led to a decrease in the roughness parameters of the corresponding PES membranes. This could be attributed to the preparation technique employed for the UF-PES membranes. The significant decrease in the surface roughness of the composite membranes is an indication that the membranes might possess less propensity to fouling [43, 44, 45].

4.7. Membrane surface hydrophilicity and pure water flux

The surface hydrophilicity of all the membranes was assessed using water contact angle (WCA) measurements [48]. In general, the WCA values (Figure 4A, Table 2) decreased with increasing concentration of
the fillers within individual series. For instance, the WCA of the unmodified membrane (76° ± 1.14) was decreased to the range of 63° ± 0.51 and 56° ± 0.65 as the GO@PES content increased in the membrane matrix. The WCA value was decreased to the range of 67° ± 0.72 and 58° ± 0.61 in the HPEI/GO@PES membrane series. The final WCA range in the Ag@HPEI@GO/PES membrane series was 69° ± 0.83 and 64° ± 0.76. These observations clearly indicated that GO imparted the highest influence on WCA than HPEI or the combination Ag@HPEI. This is in line with earlier reports correlating decreased WCA with increasing GO content [7]. The decrease in WCA is attributed to the presence of water-loving groups such as CO2H, C–O, OH, CN, and NH2 in the incorporated fillers, i.e. GO and HPEI [48, 56].

For example, Xiang et al. showed that decreasing WCA with increasing GO in PES membranes led to consequential increase in resultant flux [57].

4.8. Fouling assessment using BSA solution

In the first instance, membrane fouling was assessed using BSA (50 ppm) solution (Figure 5). Pure water flux of the membranes before fouling ($J_1$), the BSA solution flux during fouling ($J_2$) and the pure water flux of the cleaned membrane after fouling ($J_3$) were measured and used to establish fouling behavior. The observed decrease in water permeation through the membrane when BSA solution was passed was a consequence of BSA forming a cake layer on the membrane surface leading to blockage of pores and deterioration of membrane flux [58]. The baseline PES membrane had the lowest water flux recovery after washing of the BSA cake layer removal process, as indicated through the relatively higher irreversible fouling value (Figure 5B). The flux recovery ratio (FRR) of the baseline membranes was the lowest of the fabricated membranes (Figure 5B) at 45% ± 0.9. This was improved to between 80% ± 1.60–90% ± 1.8 for the GO@PES membrane series, between 72% ± 1.44–80% ± 1.62 for the HPEI@GO/PES membrane series and between 69% ± 1.38–70% ± 1.40 for the Ag@HPEI@GO/PES membrane series. The FRR ratio increased with increased concentration of the GO-based
Figure 3. Cross section and surface morphology (inset: EDS) of the fabricated membranes, P-P*: PES, P1a-P1a*: 0.1 wt.% of GO/PES, P2a-P2a*: 0.1 wt.% of HPEI@GO/PES, and P3a-P3a*: 0.1 wt.% of Ag@HPEI@GO/PES membranes.
Comparing the total fouling ($R_t$), reversible fouling ($R_r$) and the irreversible ($R_i$) parameters (Fig. S5-E), for the fabricated membranes further demonstrated the effectiveness of the fillers on membrane fouling performance. The total fouling of a membrane film is the sum of the reversible and irreversible fouling parameters of the membrane film ($R_t = R_r + R_i$). The $R_i$ indicates fouling caused by loose attachment of foulants on the membrane surface and pores which can be washed off by ordinary cleaning or backwashing (using water), $R_r$ indicates fouling caused by the strong attachment of the foulants on the membrane surface and micro-pores which can only be washed off by chemical cleaning [30].

The PES membrane is more prone to irreversible fouling compared to the composite membranes having the highest value of $R_i$ 71% ± 1.42 and $R_r$ 54% ± 1.08 with the lowest $R_i$ value of 17% ± 0.34. The $R_i$ of the series of GO@PES membranes were decreased to the range of 65% ± 1.30–60% ± 1.2 while the $R_r$ values improved to the range of 15% ± 0.30–10% ± 0.21 and the $R_r$ was also improved to the range of 50% ± 1.00. Similar trend of decreased $R_i$ and $R_r$ values and increasing $R_r$ values were observed for HPEI@GO/PES and Ag@HPEI@GO/PES composite membranes. This indicates that the composite PES membranes are less prone to irreversible fouling which would translate into longer lifecycle of the membrane, with the more hydrophilic GO resulting in the best performance for this parameter. These findings are in agreement with the findings of Lin et al. [61], Safarpour et al. [30], Ganesh et al. [62], and Yu et al. [48], that addition of hydrophilic groups into a polymer matrix promotes membranes antifouling properties.

### 4.9. Fouling assessment using organic dye solutions

Dyes are one of the major constituent of industrial wastewater and effluents [2]. More so, dyes are commonly found in various industrial processes such as paper and plastics manufacturing, dyeing of clothes, leather treatment and printing, resulting to ever increasing discharge of dye containing effluent in the ecosystem over the last few years. Highly coloured dye solution are not only reported to block the penetration of sunlight and oxygen essential for the survival of aquatic organism but in some cases, dye solution can undergo anaerobic degradation to form potentially carcinogenic compounds which may end up in food chain [2, 63, 64, 65]. Evaluating the antifouling propensities of the fabricated UF membranes against organic dyes was therefore deemed appropriate. This was achieved using 50 ppm simulated organic dyes (MB, MO, AM and CR) wastewater was achieved using 50 ppm simulated organic dyes (MB, MO, AM and CR) wastewater filtered through the membranes in the stir cell.

Each fouled membranes were immersed in deionised water after the filtration process for 24 h to dislodge and remove the dyes on the surface. The cleaned membranes (Fig. S6A) were physically examined for attachment of dye solute on membrane surface and subjected to SEM mapping (Fig. S5A) for the same purpose. The baseline PES membrane displayed the highest residual deposits of the dye molecules on the membrane surface (Fig. S6A). Among the composite membranes, high residual deposits after washing of the pollutants were observed on the surface of P1 membrane series (GO/PES membranes), next was the P3 membrane series (Ag@HPEI@GO/PES membranes). Very little attachment of the dye molecules were observed on the P2 membranes series (HPEI@GO/PES membranes). It was further observed that increasing concentration of the GO-based fillers in the PES matrix decreased the extent of dye molecules attachment on the membrane surface (P1a to P1c, P2a to P2c and P3a to P3c membranes). The results further demonstrate that the incorporation of tailored fillers in the membrane matrix improved their antifouling properties.

### 4.10. SEM-EDS analysis after organic dyes fouling

The analysis of the membrane surfaces after dye fouling indicated that the baseline membranes had the highest residual solute on the surface (Fig. S5A). The EDS results were in line with the physical examination of the membrane surfaces. Among the composite membrane, the
P1 and P3 membrane series showed the highest retention of dye molecules whilst P2 membrane series displayed the least attachment. The mapping analysis is in similitude to the obtained result from the physical inspection of the fouled membrane (Fig. S6). Increasing the concentration of the fillers in the PES matrix plays effective role in decreasing the attachment of the dye molecules on the membrane surface which is attributed to increased hydrophilicity of the fabricated membranes. The reduction of foulant attachment to membrane surface could be attributed to the effects of increased hydrophilic and charge functionalities in the PES matrix [48, 66, 67]. Furthermore, the presence of Ag NPs on the P3 membrane series (P3a to P3c) in the EDS micrograms after the extended filtration and washing indicated minimum or no leaching of Ag.

4.11. Fouling comparison due to BSA compared to dye solutes

The FRR of the PES membranes was also determined using organic dye solutions and the results are presented in Figure 6A-B. Like observations found for BSA studies, the baseline PES membranes again displayed the lowest FRR value of 43% \(\pm\) 0.69 (Figure 6B), which is about 2% less compared to the pristine PES membrane fouled with BSA solution. The

Figure 5. Antifouling studies: A): antifouling parameters of the PES membranes during and after BSA fouling, B): FRR of the PES membranes after BSA fouling and C-E): total fouling studies of the Pristine PES, P1a membrane series, P2a membrane series and P3a membrane series respectively.
antifouling propensity of the PES membrane improved with the incorporation of GO as the FRR increased to the range of 80 ± 1.28–85% ± 1.36 for the P1 membrane series. This lower recovery observed for dye solutions compared to the BSA fouling can be attributed to the high attachment of the dye molecules due to charge effects onto the membrane surface resulting to cake layer formation (Fig. S6) as well as pores blockage. Higher recovery ratios were obtained for the HPEI@GO/PES membrane P2 series (between 76 ± 1.22–80% ± 1.30) for the dye solutions compared to the BSA solution. This was attributed to the weaker attachment of the dye molecules with the membrane surface (Fig. S6) due to improvements resulting from the increased hydrophilic modification of the fillers (HPEI on GO). Lastly, a comparable improvement of 76 ± 1.18–77% ± 1.23 in FRR during dye rejection were observed for the Ag@HPEI@GO/PES membrane P3 series as for the P2 series, which was about 6% improvement when compared to the BSA fouling. The slightly lower overall increase in FRR was attributed to the further decoration of Ag NPs on the HPEI@GO composite which led to slight decrease in hydrophilicity, which is considered the dominant mechanism of fouling resistance in these membranes. The obtained results indicates that the series of HPEI@GO/PES and Ag@HPEI@GO/PES composite membranes displayed better antifouling behaviour for the organics (coloured dye wastewater) compared to protein (BSA solution) fouling.

4.12. Dyes rejection

Three organic dyes were utilised for membrane rejection assessments (Fig. 7A-C), CR (696.7 g mol⁻¹) which is an anionic type of dye, AR dye (604.5 g mol⁻¹) which is also an anionic dye and the relatively smaller
cationic MB (319.85 g mol⁻¹) dye. Generally, CR is also used to confirm the UF nature of filtration membranes at above 95% rejection rates [67]. All the fabricated membranes showed CR rejection of above 95% confirming the UF nature. For all the prepared membrane series, it was observed that increasing the quantity of the fillers in the PES matrix amount to reversal in rejection ability of AR dye (604.5 g mol⁻¹) due increased membrane pore sizes (Figure 3 and Fig. S3A), despite it’s cationic MB (319.85 g mol⁻¹). This clearly indicated that rejections was affected by size exclusion [68]. Whilst the MB solution rejection improved with improved fillers modifications (from GO, to HPEI@GO and Ag@HPEI@GO) as well as increased fillers quantity in the PES matrix, indicating clearly that rejection was more affected by the surface charge properties of the solute, the membrane surface in contact with the solute and size exclusion [65, 66, 67, 68, 69, 70]. The rejection ability of the smaller MB dye by the baseline membrane was 90% ± 1.53. This was enhanced to the range of 94 ± 1.60–97% ± 1.65 by the HPEI@GO/PES membrane series, indicating an improve difference of 4–7%. The Ag@HPEI@GO/PES and GO/PES membrane series maintained a difference of 5 and 4% respectively compared to the baseline PES membranes. The obtained result was attributed to improve in the surface properties of the PES membrane viz. improve modifications of the membrane fillers. As observed in Figure 7B and D, the enhanced rejection ability by HPEI@GO/PES composite membrane was attributed to the less attachment of the dyes molecule on the membrane surface resulting to less cake formation and pores blockage.

The low rejection rate observed for the negatively charge AR dye (70–75%) which became worse with increasing filler content in the PES matrix despite its size indicates that AR dye solute rejection was also affected by the surface charge properties of the solute, the membrane surface in contact with it and size exclusion as stated earlier. The result obtained in this study is in good agreement with the recent results of Rambabu et al., (the surface properties of membranes in the removal of dyes) [68]. Membrane surface charge, molecular weight cut off (MWCO), particle charge, and size influences the membranes ability to exclude organic dye contaminants from wastewater [69, 70, 71, 72, 73].

5. Conclusion

Graphene oxide nanosheets modified with HPEI and doped with AgNPs were prepared and fully characterised utilising a suite of techniques such as TEM, SEM, EDS, XRD, and FTIR analysis. The synthesised GO-based fillers were subsequently incorporated into PES membrane matrix. The resulting membranes were characterised using SEM, EDS, AFM and water contact angle whilst the performances were assessed through pure water flux, BSA and dye fouling propensity and dye rejection studies. The composite PES UF membranes were positively impacted by the introduction of the fillers as demonstrated by improved performance in relative to the baseline PES membrane. For instance, the water flux, flux recovery ratio and solute rejection were greatly improved in the composite, flux increased by over three folds from 35 ± 0.52 L m⁻² h⁻¹ to 120 ± 1.44 L m⁻² h⁻¹, FRR increased by two folds from 45% ± 0.9–90% ± 1.8 and dye (MB) rejection also increased from 90% ± 1.53–97% ± 1.65 in the composite membranes. These observations are credited to the positively charged composite PES membranes due to the presence of HPEI@GO and AgNPs/HPEI@GO composites within the PES matrices. The positively charged HPEI/GO@PES and AgNPs/HPEI/GO@PES membrane surfaces enhanced solute rejection due to electrostatic effects.

Declarations

Author contribution statement

Chukwuati N. Christopher: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Richard M. Moutloali: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

Christopher Chukwuati and Prof Richard Moutloali were supported by Department of Science and Innovation/Mintek Nanotechnology Innovation Centre.

Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2022.e11825.

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