Development of hydrophilic GO-ZnO/PES membranes for treatment of pharmaceutical wastewater
O. T. Mahlangu, R. Nackaerts, B. B. Mamba and A. R. D. Verliefde

ABSTRACT
Membrane application in water reclamation is challenged by fouling which deteriorates membrane performance in terms of permeate flux and solute rejection. Several studies focusing on antifouling membranes incorporated with nanoparticles have been carried out, but these membranes are not yet a viable solution due to their high energy requirements and inability to completely remove or degrade trace organic compounds (TOrCs). Therefore, this study aims at fabricating polyethersulfone (PES) membranes for treatment of pharmaceutical wastewater by using a unique membrane synthesis approach. PES membranes were synthesised by casting two different solutions before coagulation. Therefore, the synthesis technique was called ‘double-casting phase inversion’. The membranes were impregnated with nanohybrid graphene oxide-zinc oxide (GO-ZnO) to increase their hydrophilicity, rejection of pharmaceuticals (by decreasing membrane-solute hydrophobic interactions), resistance to organic fouling and photodegradation properties. The addition of GO-ZnO increased membrane hydrophilicity and pure water permeability. The rejection of TOrCs and antifouling properties were also improved due to a reduction in membrane-solute and membrane-foulant hydrophobic interactions, respectively. In addition to improved TOrC rejection properties and resistance to fouling, GO-ZnO/PES membranes degraded Brilliant Black.

Key words | anti-fouling, double-casting, graphene oxide, photodegradation, polyethersulfone

INTRODUCTION
Over the past few years, membranes have been successfully applied in treatment of wastewater contaminated with organic pollutants such as pharmaceuticals, steroids, pesticides etc. The major challenge in applying membranes for wastewater reclamation is fouling by organic and colloidal foulants (as well as their combinations). Fouling results in reduced membrane performance (i.e. reduces permeate flux). Fouling may potentially lead to a decline in rejection of trace organic compounds (TOrCs) and salts (Verliefde et al. 2009; Mahlangu et al. 2014). Most materials used for membrane synthesis (e.g. polysulfone and polyethersulfone (PES)) are hydrophobic. Previous studies have shown that hydrophobic membranes are more prone to fouling compared to hydrophilic membranes, due to long range hydrophobic attractions between the membrane and foulants (Kim & Fane 1995; Koehler et al. 1997). Therefore, current studies have paid attention to fabricating membranes with antifouling properties (Koseoglu-Imer et al. 2013; Lee et al. 2013; Gohari et al. 2014; Mahlambi et al. 2014; Mahlangu et al. 2017). In order to overcome this challenge, hydrophilic materials such as TiO2, Al2O3, zeolites, manganese dioxide, hydrophilic cellulose fibrils and ZnO have been incorporated onto the hydrophobic membranes to increase their hydrophilicity. For instance, the resistance of ZnO/PES membranes to fouling by bovine serum albumin has been studied by Shen and co-workers (Shen et al. 2009). The modified membranes showed resistance to fouling compared to the bare PES membranes. Similar observations were made by Maximous and co-workers, who filtered activated sludge through Al2O3/PES membranes (Maximous et al. 2009). Many other studies focusing on PES membranes with modified top layers have also shown that the addition of nanoparticles results in membranes that are resistant to fouling due to improvement in membrane hydrophilicity. In addition, the membrane’s thermal stability and chemical strength is also improved (Wu et al. 2008; Li et al. 2012).

There are other materials such as graphene oxide (GO) which have been shown to have interesting physical and
chemical properties. GO has been used as an additive to achieve high adsorption of micropollutants. It has also been applied in the drug delivery and biosensing processes (Hong et al. 2011). GO has reactive functional groups such as hydroxyl and carboxyl groups on its surface. Zinc oxide (ZnO) is another material that has very good physico-chemical properties. ZnO has optical absorption in the UV region, high photosensitivity, high thermal stability and antimicrobial activity (Moezzi et al. 2012). It has therefore been used as a photocatalyst to degrade organic pollutants in water and air (Li et al. 2012).

This work is based on the incorporation of a GO-ZnO blend in PES membranes with the aim of improving: (1) pure water fluxes; (2) rejection of TOrCs; (3) anti-fouling properties by making the membrane surfaces hydrophilic; and (4) photocatalytic properties. Based on the membrane test performance results, the synthesised membranes may be applied in tertiary treatment for the removal of organic micro-pollutants and/or membrane bioreactors (MBRs) for photo degradation of dyes (due to the longer residence time in an MBR).

### MATERIALS AND METHODS

The experimental design follows a series of steps in the following sequence: (1) synthesis and characterisation of GO and nanohybrid GO-ZnO; (2) fabrication and characterisation of modified GO-ZnO/PES membranes; and (3) membrane application for the removal of trace organic pollutants and degradation of dyes.

#### Synthesis of GO-ZnO nanohybrid

For the synthesis of GO, the Hummers method was adopted with minor modifications following the works of Li and co-workers (Hummers & Offeman 1958; Li et al. 2012). The synthesis approach involves oxidation and exfoliation of graphite powder. All chemicals used in this study were purchased from Sigma Aldrich, South Africa. Graphite powder (8 g) and sodium nitrate (6 g) were successfully dissolved in 95% sulfuric acid (270 ml). This was followed by slow addition of potassium permanganate (KMnO₄, 36 g), stirring for 2 h in an ice bath and further stirring at room temperature for 5 days. The solution was heated gradually to 98 °C and stirred for an additional 2 h. The solution was then cooled to room temperature and 30 wt% hydrogen peroxide (H₂O₂) solution was added. The mixture was then centrifuged and washed several times with 5% hydrochloric acid (HCl) and deionised water and kept in an oven at 60 °C for 18 h to dry.

The nanohybrid material was synthesised as follows: 0.5 g GO was dispersed in 200 ml deionised water and exfoliated for 30 min by ultracentrifugation. Thereafter, zinc nitrate (Zn(NO₃)₂) solution was added under vigorous stirring. The suspension was further ultrasonicated for an additional 30 min and stirred for 2 h with the pH of the solution maintained at pH 7 by adding a 25% ammonia solution (NH₃). The suspension was kept in an oven at 90 °C for 9 h and centrifuged for 30 min. The GO-ZnO product was dried overnight at 80 °C and calcined in a muffle furnace for 2.5 h at 500 °C to crystallise the ZnO on the GO.

#### Characterisation of GO and GO-ZnO nanohybrid

The GO and GO-ZnO nanohybrids were characterised using a transmission electron microscope (TEM) and Raman spectroscope in order to estimate the size and shape of the GO-ZnO hybrid and also assure the presence of Zn, O and C in the nanohybrid. The samples were coated with copper (Quorum Q150R ES Rotary-Pumped Sputter Coater/Carbon Coater, Quorum Technologies, UK) prior to TEM analysis. TEM measurements were done with an FEI Tecnai T12 TEM (USA).

Raman characterisation of the GO and GO-ZnO nanohybrids was performed using a Raman Micro200 microscope (Perkin Elmer, USA) with a 750 nm laser. GO and GO-ZnO samples were placed on glass slides and viewed under an Olympus BX51 (Japan) microscope. The laser beam was focused on the sample and Raman scattering spectra were measured.

A Zetasizer 2C (Malvern Instruments, UK) was used to characterise the surface zeta potentials of the GO, ZnO and GO-ZnO hybrid at pH 6.8 and 10 mM KCl background electrolyte (Sigma Aldrich, South Africa). Particle zeta potential measurements were based on the electrophoretic mobility of the particles. The size of the particles was determined by means of dynamic light scattering techniques using a photon correlation spectroscope (PCS 100M, Zetasizer 2C, Malvern Instruments, UK). Detailed information about zeta potential and size measurements can be found in our previous works (Mahlangu et al. 2014).

#### Preparation of casting solutions and synthesis of membranes

In this study, two casting solutions were prepared for membrane synthesis. The solutions were to form the

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Table 1 | Composition of casting solutions (wt%)

<table>
<thead>
<tr>
<th>Solution A</th>
<th>Solution B</th>
</tr>
</thead>
<tbody>
<tr>
<td>22% PES</td>
<td>22% PES + 0.0125% GO-ZnO</td>
</tr>
<tr>
<td>22% PES</td>
<td>22% PES + 0.05% GO-ZnO</td>
</tr>
<tr>
<td>22% PES</td>
<td>22% PES + 0.2% GO-ZnO</td>
</tr>
</tbody>
</table>

base (solution A) and top layer (solution B). Table 1 shows the content (in weight percentage or wt%) of the casting solutions used in this study. The content of GO-ZnO was varied from 0% to 0.2% to obtain the desired membrane type. N-Methyl-2-pyrrolidone or NMP (Sigma Aldrich, South Africa) was added as solvent to achieve 100% base on an initial set weight of the casting solution. All casting solutions were kept in the dark overnight to ensure complete release of air bubbles before membrane preparation.

PES membranes were fabricated and blended with GO-ZnO hybrid following a modified phase inversion technique (Mahlangu et al. 2017). This method involves casting two solutions with different additives on a glass plate before coagulation. Therefore, the method is called double-casting phase inversion or double-casting phase inversion (DCPI). Briefly, the membranes were synthesised as follows: the casting knife gap clearance was first adjusted to 180 μm, and solution A was cast on the glass plate. The glass plate with cast solution A was not removed from the film applicator. The casting knife was quickly cleaned and the gap clearance was adjusted to 200 μm, and solution B was then cast on top of the previously cast solution A to obtain a thin film containing the hybrid nanoparticles. This was followed by coagulation at room temperature for 15 min. After coagulation, the membranes were stored in plastic bags with seals and kept wet in the refrigerator overnight. The synthesis steps were repeated for the other casting solutions with different GO-ZnO concentrations.

**Characterisation of the nanohybrid membranes**

The membranes were characterised for hydrophilicity by measuring their contact angles (DSA 10-MK2, Kruss, Germany) with water at room temperature. The goniometer is equipped with a video camera, computer with monitor and image analysis software. The sessile drop method was adopted for the contact angle measurements. A minimum of 15 drops (drop volume of 10 μL) were placed on each membrane sample using a microlitre syringe. An average (+standard deviation) from the measured contact angles was calculated.

The porosity of the synthesised membranes was determined based on the dry-wet weight approach following previous reports (Zhang et al. 2014). Briefly, small portions of the different membrane types were soaked in water overnight and the mass of the wet membranes was measured after wiping superficial water on the membrane surfaces. The wet membranes were then dried in an oven at 80 °C for 24 h. This was followed by measuring the weight of the dry membranes. The porosity (P) of the membranes was then calculated from the weight of the wet membrane (Ww), the weight of the dry membrane (Wd), the membrane area (A), membrane thickness (δ) and density of water (ρw) according to the following relationship:

\[
P (\%) = \frac{W_w - W_d}{\rho_w A \delta} \times 100
\]  

Surface micrographs of the membranes were obtained using a scanning electron microscope (JSM 7600 FESEM, JEOL USA). The membranes were first dried in desiccators for 24 h and gold coated (to improve membrane conductivity for electrons) at a current of 25 μA for 50 s using an SCD 005 Cool Sputter Coater (Bal-Tec, Germany). An atomic force microscope (WITec Alpha 300 atomic force microscope or AFM (WITec, GnbH, Germany)) was used to investigate surface topography of the synthesised membranes. Measurements were done in non-contact mode using reflex coated FM (AC), 2.8 N/m, 75 kHz AFM Arrow cantilevers. All membrane samples were dried in desiccators before analysis and analysis was done in room temperature.

A SurPASS Electrokinetic Analyser (Anton Paar, Austria) was used to measure zeta potentials of the different types of membranes. Zeta potential measurements were determined at a background electrolyte of 10 mM KCl and pH 6.8. The tangential mode of analysis was adopted at an applied pressure of 200 mbar and gap height of 105 μm. Membrane zeta potential results were useful in determining the role of membrane-solute charge interactions in rejection of TOrCs.

An Instron (5900 Series Universal Testing Instruments) was used to measure the tensile strengths of the different membrane types. The dried membrane samples (width 10 mm and length 150 mm) were mounted on the grips, and tensile strength measurements were taken using Bluehill®3-Material and Component Testing software. The original length of the grips was 100 mm.
Membrane application for water treatment

Filtration experiments were carried out in a self-assembled cross-flow filtration setup. The membrane cell had a channel width of 4.2 cm, channel length of 8.7 cm and channel height of 0.1 cm. A high pressure pump (Hydra-Cell; Wanner Engineering, Minneapolis, Minnesota) was used to push water from the 10 L feed to the membrane cell. Inlet and outlet valves were used to control the feed pressure and cross-flow velocity. The feed flow was kept constant at 0.2 m/s for all the experiments. Feed pressure was measured using a pressure gauge (ERIKS, Belgium). Both permeate and concentrate were recycled into the feed.

The membranes were tested for the following properties: pure water permeability using Milli-Q water, salt rejection and concentrate were recycled into the feed. Salt rejection properties and rejection of trace organics. Salt rejection properties were evaluated using 2,000 mg/L MgSO₄ at 4 bar, 25 °C and 15% recovery, while the rejection of pharmaceuticals was quantified using a concoction of 9 model trace organics each maintained at a concentration of 5 μg/L. The concentrations of MgSO₄ and trace organics in both permeate and feed were measured using a conductivity meter and a Bench-top Exactive Orbitrap Mass Spectrometer U-HPLC-HRMS (Thermo-Scientific, San José, CA, USA), respectively.

The membranes were compacted at 5 bar to obtain constant fluxes before carrying out filtration experiments. Membrane flux was calculated from Equation (2):

\[
J_w = \frac{\nu}{A t} = \frac{\Delta P}{\mu R_m} = L_p \Delta P
\]

where \(J_w\) is membrane flux, \(\nu\) is volume of permeate collected, \(A\) is membrane area, \(t\) is time used for collecting specific volume, \(\Delta P\) is applied pressure, \(\mu\) is water viscosity, \(R_m\) is membrane hydraulic resistance and \(L_p\) is the membrane pure water permeability.

Observed rejection (\(R_o\)) was calculated from the solute concentration (conductivity in the case of salts) in the permeate (\(C_p\)) and feed (\(C_f\)) based on Equation (3). The influence of the GO-ZnO blend on TOrC rejection was also noted.

\[
R_o (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

Selection and analysis of trace organics

Trace organics (a total of nine) were selected based on size, charge and hydrophobicity (see Table 2) in order to investigate various interactions playing a role in rejection of TOrCs by the synthesised membranes. Figure 1 shows structural formulae for the selected trace organics. All solutes were dosed at concentrations of 5 μg/L. Rejection tests of trace organics were performed at an applied pressure of 4 bar, background electrolyte concentration of 10 mM NaCl and pH 7. Trace organics rejection was determined after 24 h of equilibration. Ideally, a longer equilibration time (48 h) is required to reach saturation before trace organic rejection is measured (Verliefsde et al. 2008). Therefore, rejection results presented in this work may be influenced by temporal adsorption of trace organics on the membrane surface.

After preparation of calibration standards, all feed and permeate samples were prepared for chromatographic analysis following solid phase extraction. Detailed information about sample preparation can be found in our previous works (Mahlangu et al. 2016).

The samples were analysed for trace organic content using a Bench-top Exactive Orbitrap Mass Spectrometer U-HPLC-HRMS (Thermo-Scientific, San José, CA, USA). The bench-top instrument consisted of an Accela autosampler (maintained at 15 °C), Accela degasser and an Accela 1250 pump, which injected the sample aliquot of 10 μL, and the compounds were eluted through the column at a flow rate of 300 μL/min. The extract was re-injected into a high-performance liquid chromatography (HPLC) system and segregated on a Nucleodur® C18 Pyramid column (100 mm × 2.1 mm, 1.8 μm, Macherey-Nagel, PA, USA) at 25 °C. The mobile phase consisted of 0.08% formic acid dissolved in ultra-pure water (solvent A) and methanol (solvent B). A linear gradient was used starting from 98% of solution A and 2% of solution B, which was held for 60 s. After 30 s, the proportion of solvent B was increased to 90%, and then increased further to 100% after 3 min and held for 1 min.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW (g/mol)</th>
<th>Formula</th>
<th>Charge (pH = 7)</th>
<th>Log D (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bezafibrate</td>
<td>361</td>
<td>C₁₃H₂₀ClNO₄</td>
<td>–</td>
<td>0.69</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>236</td>
<td>C₁₅H₁₁N₂O₂</td>
<td>Neutral</td>
<td>2.77</td>
</tr>
<tr>
<td>Chloridazon</td>
<td>221</td>
<td>C₁₀H₃ClN₃O₂</td>
<td>Neutral</td>
<td>–</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>296</td>
<td>C₁₄H₁₁ClNO₂</td>
<td>–</td>
<td>1.59</td>
</tr>
<tr>
<td>Diuron</td>
<td>233</td>
<td>C₆H₁₀Cl₂N₂O₂</td>
<td>Neutral</td>
<td>2.53</td>
</tr>
<tr>
<td>Lincomycin</td>
<td>406</td>
<td>C₁₈H₃₄N₅O₆S</td>
<td>+</td>
<td>–1.33</td>
</tr>
<tr>
<td>Metoprolol</td>
<td>267</td>
<td>C₁₅H₂₅NO₃</td>
<td>+</td>
<td>–0.61</td>
</tr>
<tr>
<td>Propranolol</td>
<td>259</td>
<td>C₁₈H₂₁NO₂</td>
<td>+</td>
<td>0.90</td>
</tr>
<tr>
<td>Theophylline</td>
<td>180</td>
<td>C₇H₈N₄O₂</td>
<td>–</td>
<td>–0.81</td>
</tr>
</tbody>
</table>

Table 2 | Trace organics and their selected physicochemical properties (Verliefsde 2008)
Equilibration at initial conditions was done for 90 s. The components were ionised with a heated electrospray ionisation probe (HESI-II) after segregation of the extract on the Nucleodur® C18 Pyramid column. Auxiliary and sweep gases were not used. Ionised components were then characterised using an Orbitrap-HRMS (Thermo Fisher Scientific, USA) at a polarity alternating from negative to positive ion mode. A scan range of 80.0–800.0 m/z was selected. For detection, a resolution of 50,000 FWHM (full width at half maximum) and an automatic gain control target of $5 \times 10^5$ were used. The option of ‘all-ion fragmentation’ using the High Energy Collision Dissociation cell was disabled. The Thermo Xcalibur 2.1.0.1140 software package (Thermo Fisher Scientific, USA) was used for data processing and interpretation. Every analyte of interest was detected based on the accurate mass of the precursor ions: [M + H]$^+$ and [M−H]$^-$. The maximum mass tolerance was set to 5.0 ppm. The following instrument settings were used: spray voltage of 4. kV; capillary temperature of 250°C; capillary voltage of 82.5 V; sheath gas flow rate of 30 AU; tube lens voltage of 120 V; skimmer voltage of 20 V and vaporiser heater temperature of 350°C.

Investigation of membrane ability to photo degrade dyes

The photocatalytic properties of the membranes modified with GO-ZnO nanoblend were evaluated by observing degradation of Brilliant Black (BB) dye solution. The process was carried out in a solar simulator (HAL-320), ASAHI SPECTRAL, Japan) equipped with a 300 W Xenon lamp. The solar simulator radiation spectrum output was set from 350 to 1,100 nm and an air mass filter of 1.5 G was used. The illuminance distance (i.e. distance from collimator lens to sample surface) was approximately 370 mm. This created an effective radial area of 50 mm$^2$ and an irradiance of 100 mWcm$^{-2}$ (1 sun). The simulator was warmed up for at least 30 min before the photodegradation experiments. The membranes (each with a surface area of $2.24 \times 10^{-4}$ m$^2$) were placed in glass beakers filled with 200 mL of 2 mg/L BB solution. At selected time intervals, 1 mL of the sample was withdrawn from the beaker and the BB concentration was analysed by measuring absorbance at 573 nm using a Lambda 650 UV-Vis spectrophotometer (PerkinElmer, USA). A higher dye concentration than could be measured in real wastewater samples was used in order to be able to measure 99.9% degradation of the dye. In order to factor out the effects of adsorption, the membranes were soaked in BB solution overnight prior to carrying out photodegradation experiments. To ascertain the photocatalytic properties of the modified membranes, experiments were carried out in the dark and also with PES membranes without GO-ZnO. All experiments were repeated for a BB concentration of 4 mg/L in order to investigate the effect of dye concentration on membrane photocatalytic performance.
RESULTS AND DISCUSSION

Figure 2(a) shows the transmission electron micrograph of GO-ZnO. The light-grey thin film is the GO, and ZnO nanoparticles are shown as dark regions on the surface of the exfoliated GO sheet. It was noted that the ZnO nanoparticles do not completely cover the surface of the GO. Furthermore, there was random crystallisation of ZnO on the surface of GO.

The Raman spectra of the GO and the GO-ZnO nanohybrid are shown in Figure 2(b). Three major bands are present in the spectrum: a broad band around 300 cm\(^{-1}\), two sharper bands at 1,350 cm\(^{-1}\) and one at 600 cm\(^{-1}\). The band at 1,600 cm\(^{-1}\) is the G-band resulting from the graphitic carbon in the structure. The band at 1,350 cm\(^{-1}\) is the D-band, which is associated with defects or disordered domains in the graphitic domain (Chen et al. 2013). The D-band is very strong, which confirms the structural defects of the basal planes by the presence of functional groups. The G and D bands are caused by first-order scattering from the E2g phonon of sp\(^2\) carbon atoms (Rattana et al. 2012). The band at 500 cm\(^{-1}\)–400 cm\(^{-1}\) for the nanohybrid can be assigned to the presence of ZnO crystals (Ameen et al. 2016). In the nanohybrid spectrum, one big band is showing in the range of 250 cm\(^{-1}\)–450 cm\(^{-1}\). This position of the broad peak is typical of ZnO. The lack of a dominating peak in this area of the spectrum shows that there is no clear morphology of the ZnO crystallised on the GO (Pant et al. 2013). The change in intensity of the D and G gap between the GO and the GO-ZnO can be attributed to the presence of ZnO on the surface of the GO sheets and a small red shift of 6 cm\(^{-1}\) in the bands. A change in the ratio of the intensities can indicate a change in the amount of graphitisation or the presence of sp\(^2\)-domains (Wang et al. 2011).

Table 3 shows the average size and zeta potentials of GO, ZnO and the GO-ZnO nanohybrid. The particle sizes of the synthesised particles were below 500 nm. The GO-ZnO nanohybrid was the largest, with a particle size of 380 nm. GO is negative with a zeta potential of −17.6 mV, while ZnO has a positive zeta potential of 30.8 mV. Modifying GO with ZnO results in a hybrid with a reduced zeta potential of −6.3 mV.

Membrane micrographs

Scanning electron microscopy (SEM) images of the membranes are shown in Figure 3. Membranes modified with GO-ZnO appear to have more pores (dark spots) than the PES membrane without GO-ZnO (Figure 3(a)). This signifies strong solvent (NMP) – additive (GO-ZnO) interactions, weak solvent – polymer (PES) interactions and weak additive – polymer interactions (Leo et al. 2015). Membranes with GO-ZnO incorporated are therefore expected to have high affinity for water molecules (hydrophilic) and fluxes. Cross-section images of the membranes (results not shown) showed that the membranes have finger-like microvoids as internal structures, and pores for the membranes with GO-ZnO are more uniform than those of the membrane without GO-ZnO. In addition, only one layer was visible, showing perfect adhesion of the ‘base’ and ‘top’ layer.

Figure 2 | TEM (a) and Raman (b) spectra for GO and GO-ZnO.
Figure 4 shows AFM images of the different membrane types. From the AFM results, surface roughness parameters (the average arithmetic roughness or $S_a$ and the root mean square roughness or $S_q$) were quantified using Control Four software (WITec, GmbF, Germany). Modifying the membranes with GO-ZnO increased the $S_a$ value from 12.8 nm to 34.8 nm, while the $S_q$ value increased from 18.7 nm to 44.3 nm. Increase in membrane surface roughness signifies enlargement of the effective membrane surface area. Therefore, membranes modified with GO-ZnO are expected to have higher permeability compared to the PES membrane without GO-ZnO.

Zeta potential and tensile strength measurements of the different membrane types are shown in Table 4. All the membranes had negative zeta potentials at neutral pH. The addition of GO-ZnO decreased membrane zeta potential while slightly increasing the tensile strength of the membranes. This shows that the membranes were successfully modified with the GO-ZnO nanohybrid.

Membrane contact angles and pure water permeability

Figure 5 shows water contact angles and pure water fluxes of the double-casted phase inversion or DCPI PES membranes. The PES membranes without GO-ZnO had the highest contact angles (average contact angles of 75°). A decrease in
Membrane contact angle was noted upon addition of GO-ZnO, showing that GO-ZnO improved the hydrophilicity of PES membranes. This was in agreement with observations made by other researchers (Shen et al. 2012; Lee et al. 2013; Wu et al. 2014). There was an increase in water flux upon addition of the GO-ZnO nanohybrid. A decrease in membrane water flux due to pore blocking by the nanoparticles and increase in solution viscosity were not noted (Lee et al. 2013; Wu et al. 2014). It is therefore confirmed that the addition of GO-ZnO increased membrane fluxes for PES membranes, thereby agreeing with previous reports (Shen et al. 2012; Lee et al. 2013; Wu et al. 2014).

Membrane porosity results revealed that the PES membrane without GO-ZnO has higher porosity than membranes modified with GO-ZnO (Table 5). The porosity decreased with increasing GO-ZnO concentration, showing similar variation with the membrane contact angle results presented in Figure 5. The addition of the GO-ZnO hybrid resulted in an increase in the membrane permeability to water flow by reducing the membrane hydraulic resistance (Table 5). However, the pure water permeability (PWP) results for the membranes were very low compared to those reported in the literature for microfiltration and ultrafiltration membranes (Veerasanmy & Ismail 2012; Koseoglu-Imer et al. 2013; Zhang et al. 2014), but comparable to the permeability of nanofiltration and reverse osmosis membranes (Padaki et al. 2012; Mahlangu et al. 2017). The increase in membrane permeability was also due to the enlargement of the effective membrane surface area as a result of the increase in membrane surface roughness upon addition of the GO-ZnO.

Table 4: Zeta potential and tensile strengths of the different membrane types

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Zeta potential (mV)</th>
<th>Tensile strength (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>-22.4 ± 1</td>
<td>2.7 ± 0.4</td>
</tr>
<tr>
<td>PES + 0.0125% GO-ZnO</td>
<td>-20.9 ± 3</td>
<td>3.1 ± 0.6</td>
</tr>
<tr>
<td>PES + 0.05% GO-ZnO</td>
<td>-20.4 ± 2</td>
<td>3.34 ± 0.3</td>
</tr>
<tr>
<td>PES + 0.2% GO-ZnO</td>
<td>-18.3 ± 4</td>
<td>3.55 ± 1.1</td>
</tr>
</tbody>
</table>

Table 5: Membrane porosity, pure water permeability, membrane resistance and salt rejection properties

<table>
<thead>
<tr>
<th></th>
<th>Porosity (%)</th>
<th>Lp (L/m².h. bar)</th>
<th>Rm (10⁻¹² 1/m)</th>
<th>Salt rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>84</td>
<td>2</td>
<td>18.4</td>
<td>9</td>
</tr>
<tr>
<td>PES + 0.0125% GO-ZnO</td>
<td>79</td>
<td>6</td>
<td>6.1</td>
<td>9</td>
</tr>
<tr>
<td>PES + 0.05% GO-ZnO</td>
<td>76</td>
<td>16</td>
<td>2.3</td>
<td>13</td>
</tr>
<tr>
<td>PES + 0.2% GO-ZnO</td>
<td>74</td>
<td>18</td>
<td>2.0</td>
<td>17</td>
</tr>
</tbody>
</table>
nanohybrid (Figure 4). In addition, the rejection of salts increased slightly with the PES +0.2% GO-ZnO membrane showing the highest salt rejection (27%). The increase in salt rejection can be ascribed to the improvement in water flux, which had a dilution effect (Verliefde et al. 2013). Overall, the membranes poorly rejected salts making them suitable for low-energy application due to the reduced influence of concentration polarisation.

Membrane trace organic rejection properties

As mentioned before, the trace organic rejection values presented in this work may be influenced by temporal adsorption of trace organics onto the membrane surfaces due to shorter equilibration time (24 h). However, for the membranes with GO-ZnO incorporated, the influence of hydrophobic attractions on trace organic rejection may be insignificant due to the reduction in membrane hydrophobicity upon addition of GO-ZnO. Figure 6 shows trace organic rejection values for the different membrane types. For the PES membrane without GO-ZnO, carbamazepine, metoprolol and theophylline were rejected below 40%. However, rejection values of about 60% were noted for the PES membranes modified with GO-ZnO. Generally, the addition of GO-ZnO improved the rejection of TOrCs. An increase in rejection with GO-ZnO concentration was noted. However, at the highest nanohybrid concentration (0.2% GO-ZnO), TOrC rejection declined. The increase in rejection for the membranes modified with GO-ZnO can be attributed to the reduction in hydrophobic interactions between the membranes and TOrCs (showing less influence of solute adsorption on the membrane surface on rejection). The influence of adsorption on trace organic rejection will be investigated in a separate section. On average, the PES +0.05% GO-ZnO membrane showed the highest rejection of trace organics. The trace organic rejection trend closely followed flux profiles where the addition of GO-ZnO improved fluxes. This shows that, to some extent, rejection was influenced by permeate flux.

In our previous works and also reports from the literature, it was shown that the rejection of a single compound can be influenced by a combination of various factors such as sieving effects (steric hindrance), electrostatic interactions as well as non-electrostatic interactions (van der Waals forces, hydrophobic attraction, hydrogen bonding and dielectric effects) (Hajibabania et al. 2011; Mahlangu et al. 2016, 2017). In order to investigate the role of these interactions on trace organics rejection, the rejection of trace organics is plotted as a function of solute molecular weight, solute charge and solute hydrophilicity (Figure 7).

For all the membrane types, trace organic rejection slightly increased with solute molecular weight (Figure 7(a)) and organics that are larger than the average membrane pore size were well rejected. These results are consistent with reports from the literature (Kiso et al. 2001; Nghiem et al. 2002; Schäfer et al. 2003), and show that to some extent steric hindrance was playing a role in the removal of trace organics. Repulsive charge interactions promote solute rejection if the membrane and trace organics have opposite charges. However, trace organics that have zeta potentials opposite to that of the membrane are poorly rejected as they are attracted to the membrane surface, leading to charge concentration polarisation and later partitioning to the permeate side of the membrane (Berg et al. 1997; Kimura et al. 2003). Experimental results showed no significant difference in trace organic rejection based on solute charge, when the rejection of trace organics was plotted as a function of charge. This showed that the influence of charge interactions on trace organic rejection did not play a major role for the synthesised membranes (Figure 7(b)). However, this does not mean membrane-solute charge interactions were insignificant for these membrane types. Previous reports have shown that hydrophobic solutes tend to partition into the membrane matrix due to their high affinity for hydrophobic membranes. The adsorbed solutes are easily transported to the permeate side of the membrane by diffusion and/or convection,
leading to poor rejections. This is contrary to hydrophilic trace organics, which are poorly adsorbed by hydrophobic membranes and therefore show high rejection (Braeken et al. 2005; Verliefde et al. 2006, 2013). Our results showed that hydrophobic TOrCs were rejected more than hydrophilic solutes (Figure 7(c)). This can be attributed to adsorption of hydrophobic solutes on the membrane surface. Membrane-solute hydrophobic interactions are temporal solute rejection mechanisms. Once the membrane surface becomes saturated with organics, rejection decreases as the solutes diffuse through the membrane to the permeate side.

In order to investigate the role of temporal adsorption of solute in rejection, long term trace organic rejection experiments (72 h) were conducted using 5 μg/L carbamazepine as the model solute. Concurrently, membrane permeate flux was monitored. Carbamazepine rejection as well as permeate flux were determined at selected time intervals, and the results are presented in Figure 8. A decline in carbamazepine rejection was noted for all the membrane types within the first 15 h of filtration (Figure 8(a)). The decline was significant for the PES membrane without GO-ZnO (30%) but less severe (less than 20%) for the PES membranes modified with nanohybrid GO-ZnO. After 15 h of filtration, carbamazepine rejection decreased
slightly and stabilised for the duration of the filtration run (72 h). The significant decrease in carbamazepine rejection for the PES membrane without GO-ZnO may be ascribed to membrane-solute hydrophobic interactions but not to the reduction in permeate flux as the flux remained relatively stable within the 72 h of filtration (Figure 8(b)). The flux stabilised due to prior membrane compaction before filtration. For the PES membranes modified with GO-ZnO, hydrophobic interactions were less pronounced due to the increase in membrane hydrophilicity upon addition of GO-ZnO (see Figure 5), which reduced solute-membrane hydrophobic interactions. These results indicate that trace organic rejection results presented in Figure 6 were not influenced by temporal adsorption of solutes on the membrane surface, as rejection stabilised after 24 h of filtration.

Membrane photocatalytic properties

BB was used as a model dye in order to investigate the photo-catalytic properties of the PES GO-ZnO membranes. The absorbance maximum of BB was obtained at 573 nm. Comparison of the degradation kinetics of BB by the different membrane types is shown in Figure 9. No degradation was noted in the dark for membranes with and without the GO-ZnO hybrid. In addition, the PES membrane without GO-ZnO was not able to degrade BB under illumination. A decrease in BB concentration was observed when a solution of BB was exposed to light in the presence of PES membranes with GO-ZnO. It can be observed from Figure 9 that GO-ZnO induced some photocatalytic properties to the PES membranes. Increasing nanohybrid concentration improved membrane photocatalytic properties. The degradation of BB by the different membrane types was higher for 2 mg/L BB compared to 4 mg/L BB, showing the influence of BB concentration on photocatalytic activity. It can therefore be concluded that incorporating GO-ZnO in polymeric membranes induces photocatalytic properties.

Figure 10 shows the relevant kinetic plots for the degradation of BB. The results show that photocatalytic degradation of BB by PES membranes incorporated with GO-ZnO follows first order kinetics for all membrane types. The rate constants for the different membrane types

**Figure 9** | Photo-catalytic degradation of BB: (a) 2 mg/L BB; (b) 4 mg/L BB.

**Figure 10** | First order kinetic plots for the degradation of: (a) 2 mg/L BB; (b) 4 mg/L BB.
are shown in Table 6. The results show that the rate constant was high at low concentrations of BB (i.e. 2 mg/L BB).

**Investigation of membrane resistance to organic fouling**

Figure 11 shows short term flux profiles for the PES membranes fouled with 50 mg/L alginate over a period of 4 h. The change in permeate flux is presented as $J / J_0$, where $J$ is flux at any time and $J_0$ is the initial flux. The bare membrane suffered more flux decline compared to PES membranes with GO-ZnO. Fouling decreased with an increasing concentration of GO-ZnO for all membrane types. This was due to the improvement in membrane hydrophilicity and reduced affinity of the foulants for the membrane surfaces. Therefore, the modified membranes showed some resistance to organic fouling by sodium alginate.

In order to closely investigate the influence of modifying the membranes with GO-ZnO on membrane anti-fouling properties, initial and later fouling rates were calculated from Figure 11. The initial fouling rate was defined as the change in permeate flux within the first hour of fouling, while the later fouling rate was defined as the change in permeate flux from 1 h to 4 h of filtration. For initial fouling, flux decline is due to membrane foulant interactions while later fouling is due to foulant-foulant interactions. It was noted that the addition of the GO-ZnO nanohybrid decreased the initial fouling rate (Figure 12). However, there was less influence of the addition of nanoparticles on later fouling rates as flux decline rates were similar for all membrane types. Later fouling rates were the same for all membrane types because subsequent fouling after initial deposition of foulants on the membrane surface is influenced by foulant-foulant interactions. It may therefore be concluded that the GO-ZnO nanohybrid increased membrane resistance to organic fouling by reducing foulant affinity for the membrane surfaces (i.e. reducing the initial fouling rate).

**CONCLUSIONS**

This work has shown that PES membranes can be synthesised using a two-step DCPI technique. Characterisation and filtration results showed the following: (1) the DCPI method produces membranes with reproducible results; (2) the modified membranes had high fluxes but poorly rejected salts; the increase in flux was due to improvement in membrane hydrophilicity; (3) addition of GO-ZnO resulted in improvement in trace organic rejection due to the decrease in membrane-solute hydrophobic attractions; (4) the membranes degraded BB dye; and (5) the modified membranes were less prone to organic fouling by sodium alginate. Due to the high fluxes, photocatalytic properties and rejection properties of the membranes at low applied pressures (4 bar), the membranes are suitable for low-energy application in rural areas of developing
countries where water is abstracted and used without any form of treatment.

REFERENCES


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