Leaching of CuO Nanoparticles from PES Ultrafiltration Membranes

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ABSTRACT: Recent studies have incorporated nanoparticles such as CuO, ZnO, and TiO2 to improve membrane physical and filtration properties. However, one of the major concerns about membrane modification with nanoparticles is the possible leaching of the nanoparticles leading to further contamination of source waters. Therefore, this study investigated the effects of prolonged exposure of polyethersulfone (PES) membranes incorporated with CuO nanoparticles, to different cleaning solutions. The cleaned membranes were extensively characterized for both material properties and separation performance, which enabled a closer look at particle leaching effect through a prolonged exposure. After 840 h of exposure, the presence of CuO in the cleaning solutions was confirmed using dynamic light scattering (DLS), energy-dispersive X-ray spectroscopy (EDS), and inductively coupled plasma mass spectroscopy (ICP-MS) techniques. Nanoparticle leaching resulted in changes in membrane hydrophobicity, surface roughness, pure water permeability, and salt rejection properties. Through a prolonged exposure of polyethersulfone (PES) membranes incorporated with CuO nanoparticles, it was shown that cleaning solutions also degraded the membrane polymer. However, the marked effect was less pronounced compared to combined leaching of nanoparticles and degradation of the polymer noted with PES membranes incorporated with CuO nanoparticles. Therefore, when membranes incorporated with nanoparticles are used, a polishing step may be required to remove potentially leached nanoparticles. Leached nanoparticles may result in secondary pollution and pose a health risk concern to nontarget organisms. This work provides insights into the stability of nanocomposite membranes, and the achieved results can be extrapolated to other nanoparticles such as TiO2 and ZnO because they possess similar physicochemical behavior.

INTRODUCTION

In recent years, there has been an increase in research on polymeric ultrafiltration (UF) membranes incorporated with nanomaterials where graphene oxide (GO), copper oxide (CuO), titanium oxide (TiO2), zinc oxide (ZnO), tungsten oxide (WO3), iron oxide (FeO3), and other materials have been used to improve the physical properties of membranes.1−6 In some instances, these materials are often blended to form composites to reap the benefits of synergistic effects of the different materials used.5−8 The membranes modified with nanoparticles have often shown improved properties that include but not limited to hydrophilicity, high fluxes, resistance to fouling, photocatalytic properties, and rejection of the target pollutants.

Although the incorporation of nanomaterials into the membrane polymer matrix has shown positive results, membranes incorporated with nanoparticles have not yet made a breakthrough in the commercial market. This is mainly attributed to the high cost of synthesizing the nanomaterials. Not only is the synthesis costly, but also the methods commonly adopted when fabricating nanomaterials are not environmentally friendly and unsustainable. In addition, the reproducible scaled-up production of most nanoparticles has been extremely difficult to achieve and presents environmental health concerns. There are only a handful of reports on the green synthesis of nanoparticles, even these approaches are not entirely proven.9−12 The mass production of nanomaterials following green synthesis techniques has not yet been reported. Generally, polymers are immiscible in the absence of specific interactions between them. However, miscible systems have been reported with copolymer−copolymer and copolymer−homopolymer blends in the absence of specific interactions.13 Binary interaction parameters for a blend of a random copolymer A constituting monomer residues 1 and 2 with a homopolymer B with monomer residue 3 can be estimated from the relation $X_{\text{blend}} = X_1i + X_2j - X_{i,j}$, where $i,j$ are the volume fraction of the monomer residue $i$ in the copolymer and $X_{i,j}$ are the interaction parameters between monomer residue $i$ and $j$. When $X_{\text{blend}}$ is less than $X_{\text{critical}}$, then the blend is miscible. $X_{\text{blend}}$ is close to zero for polymer−polymer systems. Further details on the miscibility of polymers can be found in...
the literature. In most instances, the miscibility of polymers and interactions between polymers and nanoparticles is not evaluated when incorporating nanoparticles into the membrane matrix for improved performance. Miscibility information is important because it gives an indication of polymer–filler compatibility, in this case the interactions that determine the dispersion of CuO on the polyethersulfone matrix (thermodynamic compatibility).

There are serious engineering concerns about the possibility of the nanomaterials leaching from the polymeric membranes (such as polyethersulfone (PES) UF membranes) during filtration leading to secondary pollution. Though this has not been widely reported, there are studies that have shown that nanoparticles have the potential to leach from the membrane polymer matrix. For example, Zhang et al. investigated the antibacterial and antifouling properties of PES membranes modified with biogenic silver nanoparticles. The presence of silver nanoparticles improved membrane hydrophilicity and permeate flux. However, the nanoparticles were found to leach from the polymer matrix and the maximum leaching rate was 92.0 μg m⁻² h⁻¹. In another study, Liu et al. used a quartz crystal microbalance with dissipation to investigate silver leaching from nanocomposite membranes. The authors found that silver leached from the nanocomposite membrane with the initial leaching rate reaching 800 ng cm⁻² h⁻¹ but decreased over time. Leaching of nanomaterials may pose a health concern as the toxicity of nanomaterials to humans and other organisms remains unknown. Some studies have shown that nanoparticles anchored in graphene oxide (GO) sheets do not leach from the membrane polymer matrix. However, in most instances, the nanoparticles are incorporated into the membrane matrix directly without anchoring them in GO.

There is still a plethora of studies on the incorporation of nanoparticles on membranes, and the focus is only on improving separation properties rather than permanent adhesion of the nanoparticles onto the membrane polymer. Leaching could result from membrane cleaning, where the cleaning solution may weaken interactions between the membrane polymer and nanoparticles, but also long-term application as the retentate washes on the membrane surface during filtration in cross-flow mode. During membrane filtration, the effluent (permeate) from the membrane filtration system directly enters the water distribution system. Such an effluent may contain nanoparticles and lead to secondary pollution should they find their way through the membrane during filtration. Even if the nanoparticles do not pass through the membrane, they may be introduced into the retentate water causing further pollution. It is believed that leaching of nanoparticles from the membrane surface would be evident through changes in the membrane surface properties together with membrane filtration performance. For instance, a change in the membrane surface morphology, hydrophobicity, roughness, and pure water permeability is expected after the nanoparticles have leached from the membrane matrix. Previous studies have already shown that the permeability of polymeric membranes increased to about twice of its initial value after the membranes were exposed to sodium hypochlorite (NaClO) at pH 8 for 144 h. The effect of membrane wearing out due to cleaning has been reported where the membrane pore size increased from about 200 to 640 nm after cleaning with NaClO and NaOH. A recent publication by Ding et al. has warned about leaching of nanoplastics and microplastics from membrane systems due to physical flushing, chemical agents, mechanical stress, aging, wear, and other factors. This is problematic as toxic organic compounds may adsorb onto the hydrophobic plastic materials. The presence of nanoparticles in polymer matrix creates a serious disposal challenge of old membranes.

The aim of this work was to investigate the possible leaching of CuO nanoparticles from PES UF membranes incorporated with CuO nanoparticles. CuO nanoparticles were chosen for membrane modification because the nanoparticles attract great interest due to their excellent features in electronics, catalysis, and photonics. Further, CuO nanoparticles are chemically stable under atmospheric conditions and during photocatalytic reactions. Similarly, PES was selected as a polymer of choice because it has excellent properties such as chemical inertness as well as high chemical and thermal stabilities. The synthesized membranes were characterized for various properties and kept in different cleaning solutions for a predetermined time frame. This was followed by further characterization of the membranes for similar characteristics where attention was paid to changes in surface morphology and filtration properties. Characterization was also performed...
on the cleaning solutions where the presence of CuO was determined using dynamic light scattering (DLS) and inductively coupled plasma mass spectroscopy (ICP-MS) techniques. Results of this study will be very useful in shedding some light/insight into the future of other membrane materials incorporated with nanoparticles, which have similar characteristics to those of CuO. They will also provide warning about potential secondary contamination of water sources by nanoparticles leached from polymeric membranes.

RESULTS AND DISCUSSION

Morphology and Functionality of the Prepared CuO Nanoparticles. Figure 1 shows SEM micrographs of agglomerated CuO nanoparticles that were confirmed using energy-dispersive spectroscopy (EDS). The EDS spectrum showed that the composition of the nanoparticles mainly consisted of Cu (82.1%) and O (17.3%), thereby verifying the successful synthesis of CuO nanoparticles. Very small amounts of calcium impurities were detected but only covered less than 1% of the total composition, and this signifies the high purity of the prepared sample.

Dynamic light scattering results revealed that the size of the CuO nanoparticles ranged between 17.43 and 21.43 nm while streaming potential analysis results showed that the CuO nanoparticles had ζ potential in the range 23.1–23.8 mV.

Figure 2 further verifies the functionality of the CuO nanoparticles. From the FTIR spectra, peaks characteristic of the formation of CuO from its precursors and the presence of CuO in the analyzed sample. Given that pure CuO nanoparticles only show these prominent peaks, the remaining peaks are due to impurities within the analyzed sample.29 The broad peak at 3442 cm⁻¹ is a suitable example of the impurities as this is a peak signifying O–H stretching,30 which is due to adsorbed water molecules in the sample.

Membrane Morphology and Filtration Properties. Table 1 presents the membrane physical properties as well as the filtration properties of the PES + CuO membranes. The membranes are porous, hydrophilic (water contact angle <90°), and poorly reject MgSO₄. The addition of CuO decreased the membrane’s pure water permeability (Lp). PES membranes without CuO had Lp values of 17.9 L m⁻² h⁻¹ bar⁻¹, while the Lp value for the CuO membrane was 3.0 L m⁻² h⁻¹ bar⁻¹.

Figure 3 shows cross-sectional micrographs and EDS spectra of neat and modified PES membranes. The membranes have uniform finger-like pores as internal structures (Figure 3). The membranes’ cross sections comprise a mixture of small and larger microvoids. The microvoids of the PES + CuO membrane (Figure 3B) did not seem to differ from that of the PES membrane without the nanoparticles (Figure 3A) in terms of size. However, there was an obvious evolution in the geometry of the outermost lower layer of the membrane resulting in almost horizontal layers compared to the mixture of tear droplike macrovoids and spongy morphology observed on the neat membrane (see circled areas). The larger microvoids were due to the delay in the onset of solvent (NMP) and nonsolvent (water) demixing resulting in the formation of larger pores.² From the EDS spectra, it is evident that the neat membrane comprised mainly C, S, and O (Figure 3C), while Cu represents a small proportion of the total weight of the CuO-modified PES membrane (Figure 3D). The detection of the CuO particles was a bit cumbersome because the particles were embedded within the polymer and had minimal exposure to the surface.

AFM micrographs of the PES and PES + CuO membranes are presented in Figure 4. Compared to the PES membrane without the addition of CuO (Figure 4A), the addition of CuO particles increased the membrane surface roughness from the average arithmetic roughness (Sa) of 4.2–7.1 nm and the root-mean-square roughness (Sq) from 5.2 to 8.9 nm. Therefore, the addition of CuO nanoparticles resulted in the membrane surface/topology becoming rougher.

Furthermore, the surface functionality of the membranes was probed with Raman spectroscopy, and as shown, Figure 5 presents the Raman spectra of PES and PES + CuO membranes. The peaks located at 285, 340, and 618 cm⁻¹ are characteristic of CuO.31 These results symbolize the presence of CuO in the polymer matrix.

Confirmation of Nanoparticle Leaching. While investigating the leaching of CuO nanoparticles from the membranes, control experiments were also conducted with a bare/neat PES membrane. The aim was to monitor the effect

Table 1. Physical and Filtration Properties of Neat and Modified PES Membranes

| membrane type | pure water permeability (L m⁻² h⁻¹ bar⁻¹) | MgSO₄ rejection (%) | roughness (nm) | contact angle (deg) | porosity (%) |
|---------------|------------------------------------------|---------------------|----------------|---------------------|--------------|
| PES           | 17.9 ± 0.8                               | 7.1 ± 0.4           | 4.2 ± 0.5      | 85.7 ± 0.6          | 18.4 ± 0.6   |
| PES + CuO     | 3.0 ± 0.1                                | 7.2 ± 0.2           | 7.1 ± 0.9      | 63.2 ± 0.5          | 8.3 ± 0.4    |

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of chemical cleaning on membrane surface and filtration properties. The investigation needed to verify whether the changes in membrane properties were due to the leaching of CuO nanoparticles, degradation of the polymer by the cleaning solutions, or a combination of both factors.

**Dynamic Light Scattering (DLS) Results.** Dynamic light scattering techniques were used to determine the particle size distribution of the CuO nanoparticles assumed to have leached from PES + CuO membranes after 5 weeks of exposure to different cleaning solutions. The presumably leached CuO nanoparticles were detected in all cleaning solutions. The size of the measured nanoparticles ranged between 100 and 500 nm, while the $\zeta$ potential was between 20 and 25 mV (Figure S1). It was expected that the nanoparticles would not be in...
their pristine structure after being exposed to the solvent and polymer matrix, resulting in the observed increase in nanoparticle size. This observation could be attributed to various factors/processes. First, the measurement of the nanoparticles prior to their addition into the dope solution was controlled. A certain concentration was added to enable particle stability and proper measurement under carefully controlled background electrolyte concentration, thus resulting in the narrow size distribution range. Although the measurement of the leached nanoparticles in the permeate was robust, the main aim was to indicate the presence of particles. The nanoparticles in the cleaning solutions may have aggregated as it is a common feature when nanoparticles are added to polymer matrices. Often, the polymer–nanoparticle compatibility is poor, which leads to polymer- and nanoparticle-rich regions. Second, it is believed that the leached nanoparticles had already nucleated themselves with coagulated microfractions of the polymer, and this assumption is a cause for further investigations.

Confirmation of nanoparticle leaching for PES membranes without CuO (results not presented) did not show the presence of nanoparticles in the solutions. These results provided an indication that particles in similar size and charge ranges were present in the cleaning solutions, which subsequently confirmed that the CuO particles leached out of the polymer matrix. Further verification was required to validate if the measured particles were CuO or polymer fragments. However, from our previous work, PES membranes without nanoparticles had a ζ-potential of −27.4 mV (SurPASS Electrokinetic Analyzer, Anton Paar GmbH, Austria).²

**ICP-MS Results.** Table 2 presents ICP-MS results of cleaning solutions used in the leaching experiments. From all of the cleaning solutions, traces of CuO were detected collaborating DLS results and confirming that the measured nanoparticles were indeed CuO. Based on the measured CuO concentration, 0.1 M HCl resulted in more leaching of the nanoparticles and the leaching order was 0.1 M HCl > 0.5% NaClO > 0.1 M NaOH > 0.1 M NaCl > water. The leaching order makes sense, considering that the PES polymer has a limited working pH range (3.5–10) outside of which it is prone to chemical alterations. The polymer in particular is known to be susceptible to chloride attack, and the use of hypochlorite solutions for cleaning is never recommended. This has led to the development/coating with polyamide layers because they have shown remarkable stability and resistance to chloride attack. CuO leaching as a result of membrane cleaning with NaOH was attributed to partial hydrolysis of the PES polymer, which led to the dislodge of nanoparticles during physical abrasion. These results reveal that nanoparticle leaching could have been an interplay of chemical and physical interactions during stirring to maintain solution homogeneity. It was expected that the nanoparticles were leaching from the membrane surface.¹⁷

**EDS Results for Dead-End Experiments.** Figure 6 shows the EDS spectra of neat PES membranes after deposition (in dead-end filtration mode) of solutions used to clean or leach CuO from PES + CuO. The presence of CuO was confirmed, and it only contributed to less than 0.5% of the elemental composition according to the presented spectra. It was believed that some of the leached CuO nanoparticles permeated through the neat PES membrane when the cleaning solution was filtered under applied pressure. Also detected by the EDS technique were Na and Cl, which were believed to originate from the cleaning solutions.

Based on the DLS, ICP-MS, and EDS results, it was believed that indeed the CuO nanoparticles leached from the membrane polymer. Elemental components of the cleaning solutions were determined in solutions used to clean neat PES membranes (see Figure S2 in the Supporting Information). Release of CuO nanoparticles from long-term continuous application and/or during membrane cleaning may cause secondary pollution of water.¹⁹ At elevated concentrations, the leached CuO nanoparticles may cause serious safety problems.

**Influence of Nanoparticle Leaching on the Membrane Physical Properties.** Figure 7 shows the cross-sectional micrographs of PES + CuO membranes after 840 h of exposure to different cleaning solutions. Micropores of the leached membranes appeared more open compared to those of the membranes not exposed to cleaning solutions (Figure 3B). It was also noted that the uniformity in membrane micropores was lost due to nanoparticle leaching and possible degradation of the membrane polymer. Therefore, the membranes after leaching experiments are expected to have higher pure water fluxes and even lower rejection properties. An increase in membrane pore size and porosity due to hypochlorite aging has been reported. An increase in membrane pore size leads to a decrease in membrane resistance, as well as weakens the membrane’s mechanical strength.²³,²⁴ The presented SEM micrographs are sensitive to parameters including imaging angle and coating materials;²⁵ thus, the comparison of membranes before and after exposure to the cleaning solutions can be biased as measurements are not done on the same spot despite applying the same imaging variables. In addition, SEM as a surface technique is ineffective in differentiating between surface pits and true pores. Deformation of the neat PES membrane micropores due to prolonged exposure to cleaning solutions was also noted (Figure S3). This showed that in addition to leaching nanoparticles, cleaning solutions have the
potential to degrade the membrane polymer as previously explained in the preceding section.

Generally, membrane exposure to different cleaning solutions resulted in an overall increase in membrane roughness. This was observed as an increase in both $S_a$ and $S_q$ values of the leached membranes (Figure 8) compared to a similar membrane coupon that had not been exposed to the cleaning solutions (Figure 4B). The exception was for PES + CuO membranes cleaned with 0.1 M NaCl and 0.5% NaClO where the roughness parameters remained almost the same. Generally, the increase in surface roughness as observed using AFM techniques can be attributed to the elimination of preservation residues in the bulk polymer. AFM analysis of PES membranes without CuO also showed an increase in surface roughness due to the degradation of the polymer matrix (Figure S4). While the membrane coupons were in the cleaning solutions, the swollen selective layer can relax the undulated surface topological features, resulting in structural rearrangement and therefore changes in the surface roughness.

A general increase in membrane water contact angle was noted due to prolonged exposure of the membrane coupons to different cleaning solutions (Figure 9A). Prior to exposing membranes to cleaning solutions, it was noted that the addition of CuO nanoparticles improved membrane hydrophilicity, and this observation was consistent with findings from the literature. It was therefore believed that leaching of the nanoparticles (which has been verified through EDS, DLS, and ICP-MS techniques) resulted in the membranes becoming less hydrophilic due to the removal of hydrophilic additives. Even though the membrane hydrophilicity decreased after nanoparticle leaching, it was noted that the contact angles were still lower than those of the PES membrane without the addition of CuO ($85.7 \pm 0.6^\circ$). This showed incomplete leaching of the CuO nanoparticles. Contrarily, prolonged exposure of PES membranes without

Figure 6. EDS spectra of neat PES membranes after deposition (in dead-end filtration mode) of solutions used to clean or leach CuO from PES + CuO: (A) 0.1 M NaCl; (B) 0.1 M HCl; (C) 0.1 M NaOH; (D) 0.5% NaClO; and (E) water.
CuO to the cleaning solutions resulted in a slight decrease in water contact angles, and this could be due to wearing out of the polymer matrix (Figure S5A). It was noted that contact angles of PES membranes that were exposed to water remained almost the same, showing a negligible influence of polymer degradation by water.

Figure 7. SEM micrographs of the PES + CuO membranes after 840 h of exposure to different cleaning solutions. (A) Not cleaned; (B) cleaned with 0.1 M NaCl; (C) cleaned with 0.1 M HCl; (D) cleaned with 0.1 M NaOH; (E) cleaned with 0.5% NaClO; and (F) cleaned with water.
Nanoparticle leaching appeared to increase membrane porosity (Figure 9B) due to the removal of surface modifiers.38 The higher porosity of the membranes implied higher pure water fluxes of the leached membranes compared to the control membrane, which had not been exposed to cleaning solutions. Similar trends of increasing membrane porosity were also noted for PES membranes without the addition of CuO nanoparticles (Figure S5B), showing that the cleaning solutions also acted on the polymer. However, for PES membranes, the increase in membrane porosity was not remarkable. These results further complemented the explanations provided on the previous sections on the role of the cleaning solutions in nanoparticle leaching rate.

Influence of Leaching on Membrane Performance. Table 3 presents filtration results of the PES + CuO membranes after exposure to different cleaning solutions. Leaching of CuO resulted in an increase in membrane pure water permeability ($L_p$) but reduced salt rejection. The increase in $L_p$ can be attributed to the deformation of membrane microvoids, increase in membrane roughness as well as increase in membrane porosity.38 The decline in salt rejection could therefore be due to the membrane microvoids becoming larger hence increasing the membrane porosity since solute rejection is also through size exclusion.32 The trend of increasing pure water permeability and decreasing salt rejection was also noted for PES membranes without the addition of CuO nanoparticles.

Limitations of the Study. This study used high nanoparticle loading than mostly reported in the literature. This implies that the nanoparticle leaching rate may be lower compared to that reported in this study. However, as per the aim, it was mainly focused at demonstrating the behavior of nanoparticles when incorporated into a polymer matrix with the intention of water filtration. Second, some of the characterization techniques used (such as SEM) are destructive, making it difficult to determine membrane properties at the same spot. Inconsistencies in membrane morphology may lead to deviations from the observed results. However, it is expected that changes in membrane properties would still be noted due to nanoparticle leaching. To ensure reproducible results, all experiments were conducted in triplicate.

Nanoparticle leaching appeared to increase membrane porosity (Figure 9B) due to the removal of surface modifiers.38 The higher porosity of the membranes implied higher pure water fluxes of the leached membranes compared to the control membrane, which had not been exposed to cleaning solutions. Similar trends of increasing membrane porosity were

![Figure 8. AFM micrographs of the PES + CuO membrane after 840 h of exposure to different cleaning solutions.](image1)

![Figure 9. Contact angle measurements (A) and membrane porosity (B) of PES + CuO membranes before and after 840 h of exposure to cleaning solutions.](image2)
to membranes with the intent of improving their separation properties. The aim was to build/develop/lay fundamental information on the fate/behavior of nanoparticles in polymer matrices upon extended exposure to usage as well as cleaning. Copper was used as a representative of those metals with known toxic effect on animal health.

■ CONCLUSIONS

This work has shown that prolonged exposure of membranes incorporated with nanoparticles leads to leaching of the nanoparticles from the membrane matrix. The rate of nanoparticle leaching may depend on the type of cleaning solution and the strength of the cleaning solution. Leaching of nanoparticles results in changes in membrane properties such as hydrophilicity, pure water permeability, porosity, and salt rejection properties. Not only does changes in membrane properties result from nanoparticle leaching, but also prolonged exposure of PES membranes (without nanoparticles) to cleaning solutions leads to degradation of the polymer matrix, and this results in noticeable changes in membrane physical and filtration properties. Some membrane materials such as PES are known to be relatively sensitive to oxidation effects, and this may enhance leaching of nanoparticles. Nanoparticle leaching may limit the long-term applicability of the membranes as nanoparticle release results in a loss in the desired morphological and filtration properties of the membranes. In addition, leaching of nanoparticles from the membrane polymer may result in secondary pollution of environmental water causing a health concern to humans and other organisms.

■ MATERIALS AND METHODS

Synthesis and Characterization of CuO Nanoparticles. Synthesis of CuO. CuO nanoparticles were synthesized using 0.1 M solutions of copper (II) sulfate (Sigma-Aldrich, South Africa) and sodium hydroxide (Sigma-Aldrich, South Africa). The copper (II) sulfate reagent was prepared by dissolving 1.6 g of anhydrous copper (II) sulfate in 100 mL of deionized water, while for the sodium hydroxide reagent, 2.0 g of sodium hydroxide was dissolved in 500 mL of deionized water. Drops of the sodium hydroxide solution (400 mL) were added slowly to 100 mL of the copper (II) sulfate solution under constant stirring.

The pH was monitored continuously, and the reaction was stopped at pH 11 when a black precipitate formed. This precipitate was then washed using a vacuum filtration apparatus and deionized water, until the filtrate reached a neutral pH of 7. The cleaned precipitate was then dried at 80 °C for 12 h in an oven. After drying, the precipitate was then calcined at 500 °C for 3 h in a muffle furnace. A mortar and pestle was then used to grind the final product into a fine powder that was stored in an airtight container to avoid moisture adsorption from the atmosphere.27

Characterization of CuO Nanoparticles. The surface morphology of the nanoparticles was analyzed by scanning electron microscopy (SEM) (Jeol JSM IT300, Tokyo, Japan). The SEM is coupled with energy-dispersive spectroscopy (EDS, Jeol JSM IT300, Tokyo, Japan) that was used to confirm the elemental composition of the prepared CuO nanoparticles. A 0.01 wt % CuO dispersed in deionized water was first prepared and sonicated for 30 min before spotting on a glass slide with the sample. This was then dried in an oven at 110 °C, affixed to a sample stub, and then coated with gold to improve conductivity before analysis.

A Fourier transform infrared (FTIR) spectrophotometer (PerkinElmer) with attenuated total reflectance accessory (ATR) was used to determine the surface functionality of the nanomaterials. The synthesized CuO nanoparticles were analyzed without any sample preparation step. Prior to conducting FTIR analysis, a background scan was performed, and measurements were done under the following equipment parameters: scan from 4000 to 650 cm⁻¹ with a resolution of 4 cm⁻¹ and 4 scans per sample.

A Malvern Zetasizer nano range (U.K.) was used to determine the size and surface ζ potential of the CuO nanoparticles. A 0.01 wt % dispersion of CuO nanoparticles in deionized water was prepared and sonicated for 30 min before analysis. The background electrolyte concentration was maintained at 10 mM using KCl (Sigma-Aldrich, South Africa). The dispersion (10 mL) was then transferred into DTS0012 disposable cuvettes to determine the size of the CuO nanoparticles, and measurements were performed using the dynamic light scattering method with a 173° backscatter (NIJS default). A dip cell (DTS1070, Malvern Instruments) was used for measuring the ζ potential of the nanoparticles. All measurements were performed at 25 °C, neutral pH, and an equilibrium time of 120 s.

Membrane Synthesis and Characterization. Preparation of Casting Solutions. Casting solutions were prepared using polyethersulfone (PES, Solvay, Belgium) as the polymer and N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, South Africa) as the solvent. Table 4 shows the content of the casting solutions where the values represent the weight percentage (wt %) of each component in the total weight of the casting solution.

### Table 4. Composition of Casting Solutions (wt %)

| membrane type          | PES | NMP | CuO |
|------------------------|-----|-----|-----|
| PES membrane           | 22  | 78  | 0   |
| PES + CuO membrane     | 22  | 77  | 1.0 |
The polymer was dissolved in the solvent overnight by stirring under a fume hood. For the synthesis of PES + CuO membranes, 1% CuO nanoparticles were first dispersed in 10 mL of NMP, ultrasonicated for 30 min, and continuously stirred vigorously. A high nanoparticle loading was chosen to enable quantification of small amounts of leached CuO nanoparticles by various techniques. The solution was then added to the previously prepared PES solution and stirred for an additional 2 h to mix well. Prior to membrane casting, the casting solutions were kept in the dark for 12 h to ensure complete release of bubbles (degassing) before casting.

**Membrane Synthesis.** Membrane synthesis commenced with cleaning and drying of the casting knife and glass using water and acetone (Sigma-Aldrich, South Africa). This was followed by adjusting the casting knife gap clearance to 150 μm and the casting solution for the neat membrane (PES membrane without CuO nanoparticles) was hand-cast on the glass plate. The glass was then placed in a coagulation bath with water to allow coagulation to take place at room temperature for 30 min. After coagulation, the membranes were heat-treated at 50 °C for 5 min, placed in plastic bags with water, and kept at 5 °C to complete the phase inversion process. Similar synthesis steps were repeated for the preparation of PES membranes with CuO.

**Membrane Characterization.** In this study, the fabricated membranes were characterized for selected parameters according to the experimental design and objectives of the study. It was expected that the leaching of nanoparticles would change the membrane’s surface morphology and filtration properties. Therefore, surface imaging, elemental analysis, and filtration properties were characterized for the membranes before and after the leaching experiments.

A scanning electron microscope (SEM, IT 300, JEOL, Tokyo, Japan) was used to characterize the membranes for cross-sectional morphology. The irradiation beam was maintained at 15 kV. Prior to cross-sectional imaging, the membranes were coated with gold to improve the conductivity of the membranes. Coating was done at a current of 25 μA for 50 s using an SCD 005 Cool Sputter Coater (Bal-Tec, Germany). The membranes were further characterized for their quality of dispersion by evaluating the energy of dispersion of X-ray (EDX, IT 300, JEOL, Tokyo, Japan).

The presence of CuO nanoparticles in the membranes was further verified using Raman spectroscopy. A Raman Micro200 microscope (PerkinElmer) with a 750 nm laser was used to perform the measurement. The membrane 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 at 532 nm.

The membranes were further characterized for atomic force micrographs utilizing a WITec α 300 atomic force microscope (AFM) (WITec, GmbH, Germany). Measurements were done in noncontact mode using reflex-coated FM (AC), 2.8 N/m, 75 kHz AFM Arrow cantilevers. Prior to AFM imaging, the membrane samples were dried in a desiccator. The presence of nanoparticles on the membrane surface influences the membrane surface roughness; therefore, membrane surface roughness parameters before and after leaching experiments were estimated using Control FOUR software (WITec, GmbH, Germany).

Changes in membrane hydrophobicity due to the addition of nanoparticle were determined by measuring contact angles of the membranes with deionized water. Contact angle measurements were based on the sessile drop method, where analysis was performed on surfaces of membranes previously dried overnight. The measurements were performed at room temperature, where 15 drops of deionized water (drop volume of 5 μL) were placed on the membrane surface using a microliter syringe (DSA 10-MK2, Kruss, Kruss, Germany).

The porosity of the synthesized membranes was determined based on the dry–wet weight approach following our previous works. Briefly, small portions of the different membrane types were soaked in water overnight and the masses of the wet membranes were measured after wiping off superficial water on the membrane surfaces. The wet membranes were then dried in an oven at 45 °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), weight of the dry membrane (Wd), membrane area (A), membrane thickness (δ), and density of water (ρw) according to the following relationship (eq 1)

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

A cross-flow filtration setup with six membrane cells was used to measure membrane pure water fluxes (Jw, L m⁻² h⁻¹) at 500
kPa (Figure 10). Each cell (Sterlitech, Sterlitech Corporation, Kent, Washington, DC) had the following channel dimensions: channel width of 4.2 cm, channel length of 8.7 cm, and channel height of 0.1 cm. The six membrane cells were used simultaneously to determine the reproducibility of the test results.

During filtration, the feed flow rate was kept constant at 0.2 ms⁻¹ and filtration was performed in recycling mode, where the permeate and concentrate were recycled into the feed. Prior to conducting membrane pure water flux experiments, the membranes were compacted at 600 kPa until stable fluxes were reached. The water flux (Jw) was calculated from eq 2 based on the volume of water collected (V, L) at specific time (t, s) and membrane area (A, m²).

\[ J_w = \frac{V}{At} \]  

Salt rejection properties of the PES membranes were investigated by filtering 2000 mg/L MgSO₄ (Sigma-Aldrich, South Africa). Observed rejection percentage Rᵢ (%) was calculated from the salt concentration in the feed (Cᵢ) and permeate (Cᵢₚ) according to eq 3. MgSO₄ concentration was measured as electrical conductivity using a portable Consort C6010 conductivity meter (Consort, Turnhout, Belgium). All measurements were performed after the membranes were allowed to equilibrate with the salt solution for 2 h.

\[ Rᵢ(\%) = (1 - \frac{Cᵢₚ}{Cᵢ}) \times 100 \]  

Investigation of Nanoparticle Release. Preparation of the Cleaning Solution. Sodium hydroxide (Sigma-Aldrich, South Africa), water, sodium chloride (Sigma-Aldrich, South Africa), sodium hypochlorite (Spar, South Africa), and hydrochloric acid (Sigma-Aldrich, South Africa) were selected and prepared as cleaning solutions (Table 5). After preparation, the cleaning solutions were kept at room temperature until further experiments.

### Table 5. Cleaning Solutions and Their Properties

| no | solution name       | concentration | pH  |
|----|---------------------|---------------|-----|
| 1  | sodium chloride (NaCl) | 0.1 M         | 7.7 |
| 2  | hydrochloric acid (HCl) | 0.1 M         | 1.2 |
| 3  | sodium hydroxide (NaOH)  | 0.1 M         | 12.5|
| 4  | sodium hypochlorite (NaClO) | 0.5%       | 12.4|
| 5  | water               | n.a           | 7.5 |

The membrane coupons were cut into a rectangular shape with an area of 32 cm² and individually placed in 350 mL of the respective cleaning solutions in 500 mL beakers. The solutions with the membrane coupons were slowly stirred at 10 rpm without interruption for 5 weeks (840 h), after which the membranes were removed, cleaned with deionized water, and characterized for pure water fluxes, SEM cross-sectional micrographs and AFM micrographs for changes in surface morphology, and roughness and contact angles for changes in hydrophobicity following similar procedures as explained in the Membrane Characterization section. Analysis of the Presence of CuO in the Cleaning Solutions. After conducting leaching experiments, 50 mL of the cleaning solution was withdrawn and analyzed for the presence of nanoparticles using the DLS technique (Malvern Zetasizer Nano series, Malvern, U.K.) without changing the background electrolyte. Prior to measurements, the cleaning solutions were sonicated to prevent the nanoparticles from coagulating. From each solution, three measurements were taken, and the results were averages (±standard deviation) from the measured values.

Another 10 mL of the individual cleaning solutions were taken for copper analysis using inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS analysis was done under controlled operational conditions (Table S1). The average rate of leaching of CuO nanoparticles was estimated based on eq 4.

\[ \text{average leaching rate} = \frac{m}{At} \]  

where \( m (\mu g) \) is the mass of silver in the cleaning solution, \( A \) (m²) is the membrane area, and \( t \) (h) is the total time of exposure.

The remaining cleaning solutions were individually filtered through neat PES membrane coupons to deposit the supposedly leached CuO nanoparticles onto the membrane surface. This would permit the determination of the quality of dispersion through EDX analysis. Filtration was done using a batch cell dead-end filtration unit with a capacity of 300 mL (Sterlitech, Sterlitech Corporation, Kent, Washington, DC) (Figure 11). The disk membrane had a diameter of 32 mm with an area of 8.04 × 10⁻⁴ m². Filtration experiments were conducted under a fully conditioned environment to maintain a constant temperature of 25 °C and an applied pressure of 500 kPa.

After the filtration experiments, the membrane samples were dried in a desiccator overnight and characterized for the presence of nanoparticles on the membrane surface using EDS (EDX, VEGA3 TESCAN, TESCAN, Orsay, France).

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04431.

DLS results of cleaning solutions, parameters for ICP-MS operational conditions, EDS spectra of cleaning solutions from PES membranes without CuO, SEM and AFM micrographs of neat PES membranes, as well as contact angles and porosity results of neat PES
membranes after exposure to the cleaning solutions (PDF)

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**Author Contributions**
A.K., O.M., and M.M. contributed equally in guiding the experiments, and preparing the first draft of the manuscript. B.B.M. conducted reviews and editing as well as project administration. All authors have read and agreed to the final version of the manuscript and have declared no conflict of interest.

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