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Heavy metals removal from mine wastewater using polysulfone membrane infused with waste plastic-derived carbon nanotubes as filler

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ABSTRACT

The study focuses on "treating waste with waste" through the removal of toxic metals from gold mine wastewater using polysulfone (PSF) membrane infused with waste plastic derived-multi-walled carbon nanotube (MWCNTs) as an innovative approach. MWCNTs synthesized from waste polypropylene (PP) plastics by the chemical vapour deposition (CVD) method were purified in oxidizing acid, and different loadings (0, 0.05, 0.10, and 0.15 wt%) were incorporated into the PSF membrane to form mixed matrix membranes (MMM) via phase inversion technique. Fabricated pristine and nanocomposite membranes' properties: hydrophilicity, thermal stability, and morphology, were ascertained by the water contact angle measurement, thermogravimetry analysis, and scanning electron microscopy, respectively. Results show that incorporating plastic-derived-MWCNTs into the matrices of PSF polymer significantly enhanced the properties of all fabricated MWCNTs/PSF nanocomposite membranes compared to pristine PSF. The flux and rejection of metals increased with MWCNTs loading. Iron (Fe) and nickel (Ni) removal by pristine PSF were 70.2% and 11.4%, respectively, while optimal Fe and Ni rejection of 91% and 74%, respectively, were obtained with 0.10 wt% MWCNT loading. The results obtained in this work revealed that incorporating different loadings of plastic-derived-MWCNTs onto the PSF polymer matrix impacted its surface properties, and improved flux, and removal efficiency. Therefore, utilizing waste plastics as a precursor in CNTs production will save on the cost of CNTs and provide a sustainable plastic waste management option, as well as open up vast prospects at the industrial scale in the potential for application in environmental remediation (such as in membrane separation).

Introduction

The rapid economic development and advancement in modernization and industrialization, have resulted in the release of large quantities of untreated and partially treated wastewater containing numerous heavy metal contaminants. Wastewater from mining, tannery and textile dyeing, fertilizers, pesticides, smelting, pharmaceutical and battery industries, etc. contain considerable amounts of heavy metal ions which are directly discharged into aquatic environments posing significant severe toxicological and environmental hazards (Hosseini et al., 2016). Heavy metal contaminants are usually not biodegradable, and over time gradually accumulate in living organisms giving rise to serious environmental and irreversible health complications (Wang and Wu, 2018). Acid mine drainage (AMD) is an effluent created by the mining industry, from tailings, or abandoned mines due to the atmospheric exposure/oxidation of minerals containing sulphide-rich ores to form sulfates at a very low pH range (Akcil and Koldas, 2006; Aguiar et al., 2016; Fornarelli et al., 2013). Common metals normally found in AMD in addition to dissolved Fe^{2+} and SO_4^{2-} are Pb, Au, Ar, Mn, Ca, Zn, Cu, Ni, Co, Al, Hg, etc. However, the characteristics of AMD vary from site to site depending on the availability of water, oxygen, naturally occurring bacteria, and mineralogy features of local rock as well as the quantity of exposed sulphide-bearing rocks (Akcil and Koldas, 2006; Al-Zoubi et al., 2010; Naicker et al., 2003).

Consequently, the elimination of toxic metal ions from contaminated water is necessary before their discharge. Various technologies such as coagulation, electrochemical processes, floatation, ion exchange, adsorption, membrane separation, etc. have been renowned for

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wastewater treatment (Hosseini et al., 2016). Earlier traditional AMD treatments like lime or limestone neutralization resulted in the generation of massive sludge and possible loss or little recovered metals, limiting the application of this method in treating AMD (Al-Zoubi et al., 2010). When compared to other treatment methods, membrane separation has become known as one of the propitious approaches given its superior efficiency, low energy demand, affordable, ease of operation and maintenance, minimal supervision, small sludge (environmental) footprint, and flexibility in design, etc. compared to other treatment methods (Kheirieh et al., 2018). Several studies have succeeded in treating real and stimulated AMD using the membrane separation technique. Aguiar et al. (Aguiar et al., 2018) utilized the NF270 nanofiltration membrane in treating AMD, and from their study, high $MgSO_4$ rejection was achieved after 270 days of exposure. Similarly, Lopez et al. (Lopez et al., 2018) employed NF270 and sulfonated polyethersulfone (HydraCoRe 70pHT) nanofiltration membranes in treating AMD containing Na_2SO4, Fe, Zn, and Cu ions under different transmembrane pressures and pH. According to their study, the NF270 nanofiltration membrane performed better with metal rejection of over 90 % than the sulfonated PES whose rejection was around 60–70 %.

PSF membranes have drawn a lot of attention due to their outstanding characteristics in terms of their good solubility in a large aprotic polar solvent, good thermal, chemical, and mechanical properties, tolerance in a wide range of pH, etc. (Nechifor et al., 2009). However, PSF membranes result in low water flux and membrane fouling as a result of their hydrophobic nature (Habibi et al., 2015).

As such several attempts have been devoted to incorporating organic or inorganic sorbents such as activated carbon (Goswami et al., 2021), graphene oxide (Zhang et al., 2015), chitosan (Mathaba and Daramola, 2020), carbon nanotubes (Rashed et al., 2020; Sianipar et al., 2016; Altaf et al., 2021), etc. into the polymeric matrix forming MMM. The introduction of these adsorbent materials into the solution used for casting improved the adsorption capacity and physicochemical features of the MMM when compared to the pure polymeric membrane (Ma et al., 2017). Shah and Murthy (Shah and Murthy, 2013) have demonstrated that MWCNTs/PSF composite membranes showed enhanced stability and increased heavy metal rejection compared to unblended plain PSF membranes. Rashed et al. (Rashed et al., 2020) examined the effect of incorporating different loading of carboxylated CNT on the forward osmosis performance of the thin film nanocomposite (TFN) and blank thin film composite (TFC) during the desalination of wastewater. Their investigation showed that a high flux of about 73.15 $L/m^{-2}h$ was achieved with TFN compared to TFC. The salt rejection for TFN was 13 % higher than that obtained with the TFC membrane.

CNTs are one-dimensional allotropes of carbon, they possess very large surface area and nano-sized diameter with excellent mechanical, thermal, and electrical properties, and their tensile strength and elastic modulus were up to 100 GPa and 1000 GPa, respectively (Deng et al., 2016). CNTs have demonstrated superior performance with controllable properties as reinforced material and filler in composites, however, the associated high cost of CNTs has limited its applications and expansion of CNTs end-user markets. Alternatively, low-cost feedstock based on waste plastics has been widely studied as a hydrocarbon starting material for CNTs synthesis (Modekwe et al., 2021; Modekwe et al., 2021; Mishra et al., 2012; Yao et al., 2018; Tripathi et al., 2017) instead of pure industrial chemicals and gases namely methane, acetylene, benzene, etc., as a way of reducing the cost of producing CNTs and by extension the unit cost of CNTs (Modekwe et al., 2024).

Globally, huge quantities of plastic waste are produced annually. Due to their inability to degrade biologically, their improper disposal in landfills and open spaces has posed serious environmental problems around the globe (Geyer et al., 2017). There is a growing interest in other recycling technologies such as chemical recycling through pyrolysis/gasification of waste plastics, which has proven to be a promising sustainable option for waste management. Hence, cheaply available waste polymer could be used as hydrocarbon feedstock for value-added CNTs synthesis, thereby reducing market prices of CNTs.

Some of the setbacks in the potential utilization of plastic derived-CNTs revolve around whether the produced CNTs can be employed in purity-sensitive applications such as membrane technology and other industrial materials (Borsodi et al., 2016; Wu et al., 2016). This is owing to the low crystalline quality of CNTs arising from the abundance of amorphous carbon, metallic impurities, defects, etc. (Das et al., 2015), in addition to the non-uniform structure and properties (such as diameter) distribution of CNTs especially the plastic-derived-CNTs. A previous study (Modekwe et al., 2021) compared the crystallinity of waste plastics-derived MWCNTs and commercially available (sourced) MWCNTs produced via the catalytic chemical vapour deposition (CCVD) method. This study validated and proved that the alignment degree and crystallinity of waste plastics-derived MWCNTs and commercially sourced MWCNTs are comparable.

From a waste management and environmental standpoint, recycling waste plastics into value-added products and applying the obtained materials as a resource in treating mine wastewater aligns with and integrates into the circular economy scheme as a waste reduction and management strategy. This also tackles its environmental impacts while creating and developing innovative technology for their application in industrial wastewater treatment, thereby, supporting the concept of using “waste-to-treat-waste”. Waste management is an effective key to achieving the United Nations (UN) Sustainable Development Goals (SDGs). The study herein directly promotes the attainment of SDG 6 (clean water and sanitation), SDG 12 (responsible consumption and production), and SDG 13 (climate action), and indirectly addresses SDG 3 (Good health and well-being), SDG 14 (life below water), SDG 15 (life on land) and SDG 9 (industry, innovation, and infrastructure) (de Sousa, 2021).

Therefore, in this study, waste plastic-derived MWCNTs obtained from the decomposition of waste PP plastics were utilized as a filler (additive) material and incorporated into the PSF membrane to form a mixed matrix MWCNTs/PSF composite membrane. The influence of varying CNTs loading on the separation efficiency of the developed MMM in removing heavy metals (iron and nickel) from simulated gold mine wastewater was reported. The current study showcased the potential of utilizing and applying waste plastic-derived MWCNTs as filler material in purity-sensitive applications such as membrane fabrication technology for AMD treatment. Hence, value-added materials obtained from waste plastics were in turn utilized in eliminating toxic metals from wastewater. Furthermore, the impact of varied loadings of plastic derived-CNTs on the characteristics (morphology, stability, hydrophilicity, and mechanical strength) and the separation activity of prepared membranes were also investigated and compared with unmodified and commercially available membrane materials.

Materials and methods

Materials

The transparent polysulfone (PSF) beads (molecular weight = 44,000 Da) were obtained from Sigma-Aldrich, South Africa, and were firstly oven-dried at 100 ℃ for 24 h before usage. N-methyl-2-pyrrolidinone (NMP, 99.5 % used as solvent), nitric acid (65 %), sulphuric acid (98 %), $FeSO_4{\cdot}6H_2O$ and $NiSO_4{\cdot}6H_2O$ (obtained from Rochelle Chem. & Lab Equipment C.C., South Africa). Deionized water (DI) was obtained from our laboratory and was utilized during filtration study and solution preparation. All utilized chemicals were of analytical grade and required no further purification. Waste plastic derived-MWNTs (outer diameter 5–35 nm, length in few microns) were obtained from the previous study (Modekwe et al., 2020), where, as-synthesized MWCNTs and their characterization were extensively discussed. In summary, waste plastic-derived MWCNTs were produced from waste polypropylene plastic as carbon precursor and $NiMo/CaTiO_3$ as the catalyst using the chemical vapour deposition technique (single-stage CVD) at 700 ℃ ramped at 10

Table 1
Formulation of the dope solutions of PSF and MWCNTs/PSF mixed matrix membranes.

PSF (wt.%)	NMP (wt.%)	MWCNTs (wt. %)	Notation
18	82	–	MMM-00
18	81.95	0.05	MMM-05
18	81.90	0.10	MMM-10
18	81.85	0.15	MMM-15

℃/min under nitrogen atmosphere (Modekwe et al., 2020).

Purification of MWCNTs

Synthesized MWCNTs were purified using a two-stage oxidation procedure (Modekwe and Ramatsa, 2024): (i) by air oxidation, the synthesized MWCNTs were first milled into powder via an agate mortar. The powdered sample underwent thermal air oxidation in a tube furnace at 450℃ and held for 1 h. (ii) by acid oxidation treatment adopting the method reported by Zhao et al. (Zhao et al., 2006). The sample treated thermally was then refluxed in nitric acid for 2 h at 80 ℃, washed until the solution pH = 7, and later vacuum dried in an oven at 60 ℃ for 24 h.

Production of pristine PSF and MWCNTs/PSF membranes

The PSF and MWCNTs/PSF membranes were produced using the phase inversion approach according to the described procedure by Sianipar et al. (Sianipar et al., 2016). The formulation of the cast mixture is depicted in Table 1. Typically, PSF was dissolved in NMP and stirred for about 5 h until a homogeneous solution was obtained. The obtained homogenous polymer solution was degassed naturally for 24 h and then spread through the glass plate with the aid of a machine (Elecometer 3545 casting blade) at a casting speed of 150 mm/sec with a knife gap setting of 200 µm. The glass plate was immediately dipped in a deionized water bath and washed severally to obtain a defect-free membrane and ensure complete phase separation. The obtained membrane was denoted as MMM-00.

To prepare the MWCNTs/PSF MMM cast solutions, a designated amount of MWNTs (see Table 1 for the mass ratios of MWCNTs used) were dissolved in NMP (the solvent) and sonicated for 12 min, then PSF was vigorously stirred into the solution mixture and allowed to agitate for 5 h to form the dope solution. The formed semi-viscous solution was degassed naturally for 24 h at room temperature, and afterward, cast on a plate using a casting machine (Elecometer 3545 casting blade) at a similar casting speed and knife gap of 150 mm/sec and 200 µm, respectively. The glass plates were immediately plunged in a water bath, thereafter, the formed membrane was washed several times with fresh DI water to ensure that all solvents were totally removed, and then kept in DI water for future use. All obtained MWCNTs/PSF MMM using different loadings of MWCNTs (0.05, 0.1, and 0.15 wt%) were denoted as MMM-05, MMM-10, and MMM-15, respectively, as illustrated in Table 1.

Characterization of purified MWCNT and fabricated membranes

The microstructure of purified and oxidized MWCNTs was checked using a JEM 2100 Transmission Electron Microscope (TEM) operated at 200 kV.

The membrane's cross-section was characterized by Scanning Electron Microscopy (SEM) (VEGA3 TESCAN). Some portions of membrane samples were fractured in liquid nitrogen, and using carbon tape, a piece of each of the fractured membranes was fastened on a sample holder and carbon-coated before scanning.

Hydrophilicity or hydrophobicity of fabricated membranes was determined at room temperature by the sessile drop method using DataPhysics Optical Contact Angle (OCA) 15 EC (G10, KRUSS, Germany). The average value was noted from five different contact angle measurements obtained at different spots on each fabricated membrane sample surface.

HITACHI STA-7200RV Thermal Analysis System was employed to obtain the thermal stability of all fabricated membranes.

The tensile strength of all produced membranes was obtained using a nano-tensile tester for membrane dimensions of 20 mm × 14 mm.

Table 2
AAS result of gold mine wastewater (pH = 2.7) collected from Randfontein, South Africa.

Compositions	Ca^{2+}	Fe^{2+}	Mg^{2+}	Mn^{2+}	Na^{2+}	Ni^{2+}	SO_4^{2-}
Concentration (mg/L)	483	895	308	195	153	2.8	3680
Std. Dev.	2.65	4.52	3.95	4.89	1.38	2.57	3.28

Testing of fabricated membranes using synthesized gold-mining wastewater

Synthetic wastewater was prepared by mimicking similar Fe and Ni contents of real gold mine wastewater as shown in Table 2. The synthetic wastewater was employed as the feed solution during the treatment operation. The calculated amount of Ni and Fe sulfate salts were dissolved and agitated in 1000 mL of DI water (to make 895 mg/L Fe and 2.8 mg/L Ni). Also, 0.1 M sulphuric acid was utilized in adjusting the pH of the feed solution until a pH of 2.7 was achieved. Ni and Fe metals were chosen to portray the membranes' selectivity and effectiveness in removing low and high metal content in the wastewater. Again, Ni and Fe were amongst the most hazardous pollutants in AMD, in addition to the economic values that could be obtained from the recovery of these metal ions from AMD wastewater.

Filtration experiments were conducted using a laboratory-scale dead-end stirred filtration cell (Sterlitech, Kent, OH, USA) pressurized by nitrogen gas, with an effective membrane filtration area of 14.6 cm^2. An average membrane thickness of 0.074 mm was obtained using a digital micrometer. Membrane samples were initially pre-compacted at a pre-compacting pressure of 9 bar for 1 h to obtain constant flux and then further reduced to 6 bar. From each membrane sample, the average value from three measurements was taken for the water flux and rejection experiments at 6 bar. From each produced membrane sample, the average value from three (3) measurements was taken for water flux and membrane rejection. The original flux through the membranes (PWF, L $m^{-2}h^{-1}$) was evaluated by permeating DI water via the membrane at the same pressure and room temperature to get the original flux through the membranes. The permeate flux was calculated as follows:

$$PWF = \frac{V}{A \times t} \quad (1)$$

where V is the volume of permeate (L), while A is the effective surface area of the membrane (m^2), and t the permeation time (h).

The metal content in the filtrates was analyzed using GBC 909 AA atomic absorption spectrophotometer (Wirsam Scientific & Precision Equipment (Pty) Ltd, South Africa), at operating wavelengths of 246 and 232 nm and lamp current of 15 and 5 mA for Fe and Ni, respectively.

Metal Rejection (%) for each of the fabricated membranes was evaluated using equation (2):

$$R(\%) = \frac{C_{feed} - C_{permeate}}{C_{feed}} \times 100 \quad (2)$$

where R is the metal % rejection while, C_{feed} and $C_{permeate}$ (mg/L) are feed and permeate concentrations, respectively.

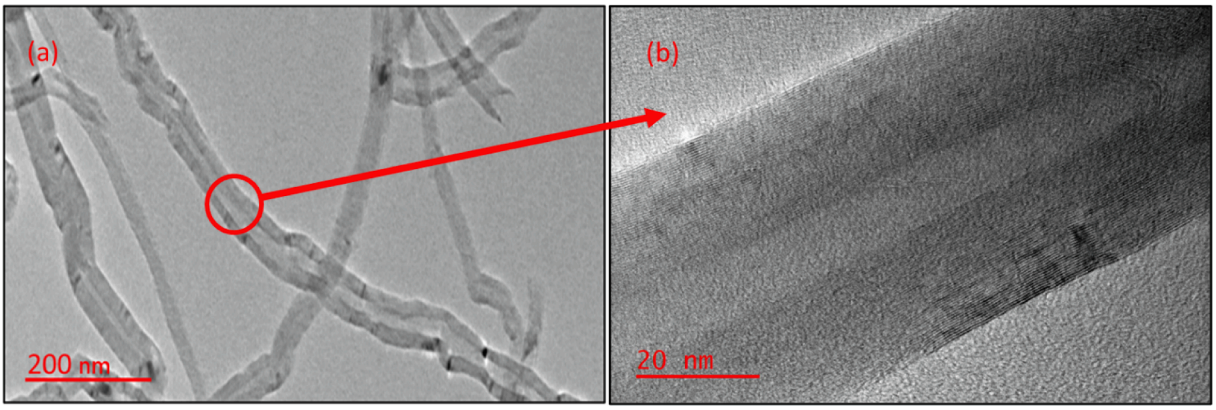

Fig. 1. TEM images of oxidized MWCNTs.

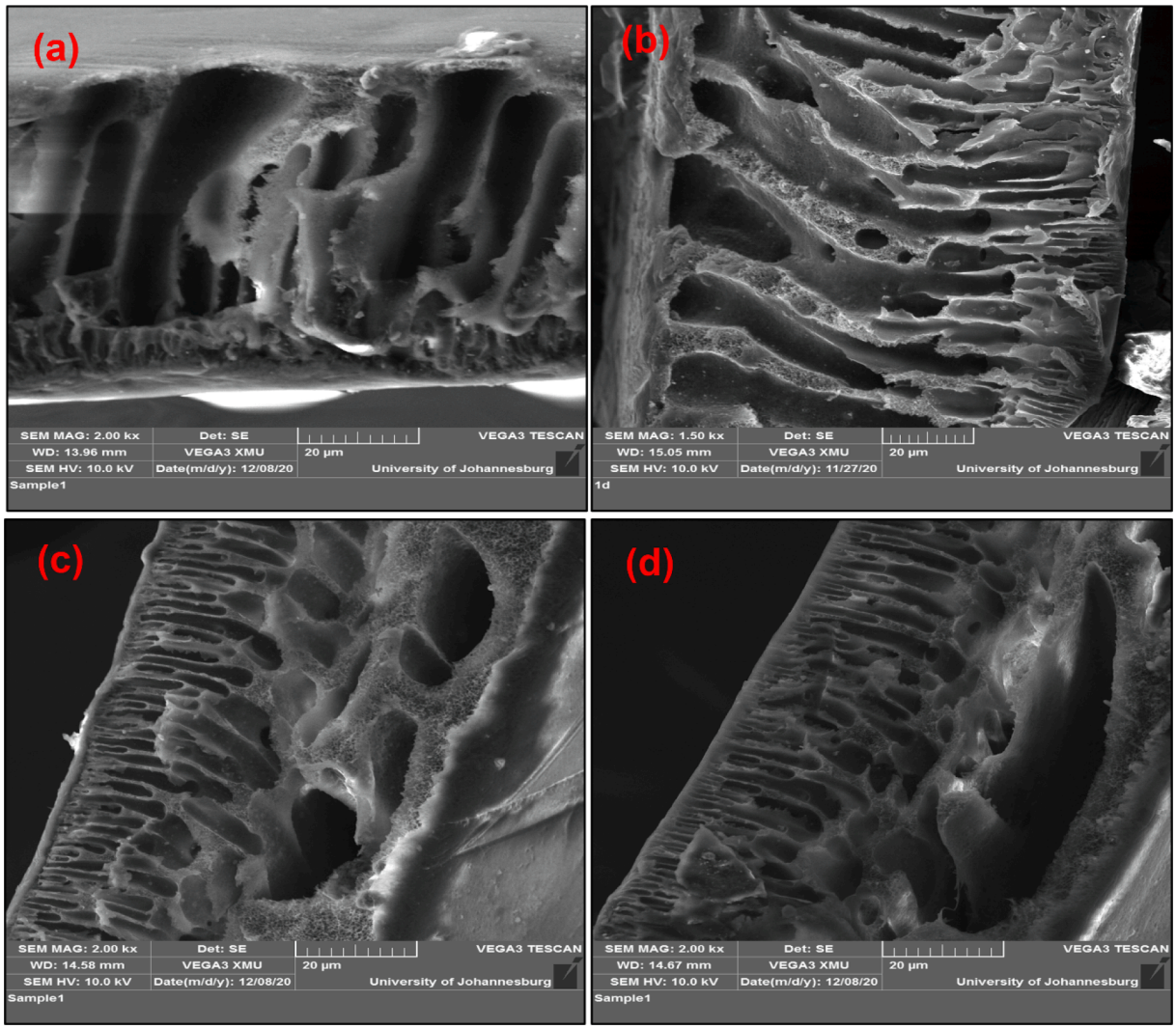

Fig. 2. SEM cross-sectional micrographs of fabricated mixed matrix membranes. (A) MMM-00; (B) MMM-05; (C) MMM-10 and (D) MMM-15.

Results and discussion

Characterization of purified CNTs and fabricated membranes

Fig. 1 depicts the microstructure of purified and oxidized MWCNTs. As could be observed, purified CNTs revealed a smooth and clear wall surface, while the diameter and length are shorter due to the oxidation treatment with HNO_3. Some of the tips of oxidized CNTs are open, and some defect sites (floccules) around the walls of oxidized CNTs likely to arise from the spots of amorphous carbon or metal residues peeled from CNTs' surface. These open tips activate the CNTs surface by grafting active functional groups which are beneficial during the fabrication of CNTs-based composite membranes (Ma et al., 2017).

The cross-section of fabricated nanocomposite and pristine PSF

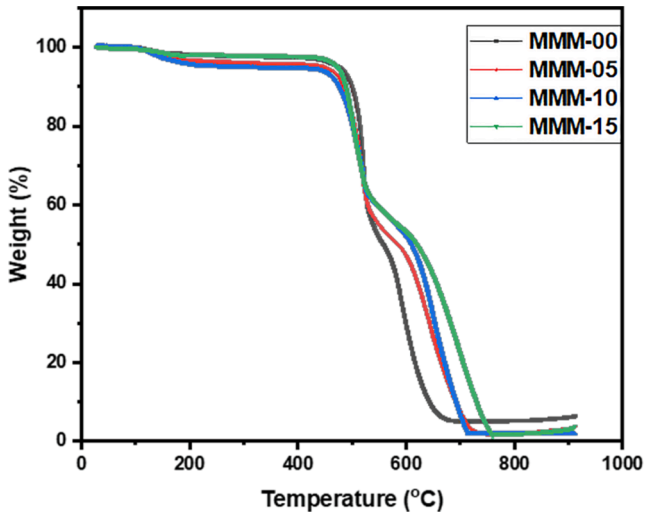

Fig. 3. Thermal analysis plot of all fabricated PSF/MWCNTs mixed matric membranes.

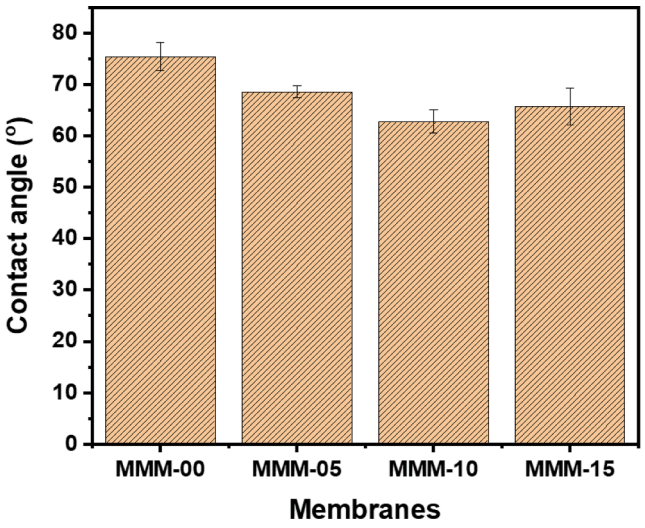

Fig. 4. The water contact angle of synthesized PSF/MWCNTs mixed-matrix membranes with different loading of MWCNTs.

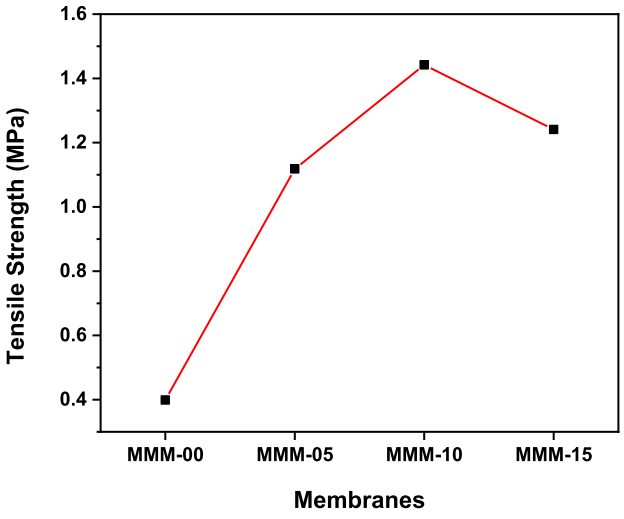

Fig. 5. Tensile strength of pristine and all fabricated mixed-matrix membranes.

membranes are shown in Fig. 2. The cross-section revealed a characteristic morphology of finger-like macropores with microvoids of varying shapes. There is a noticeable transformation in the morphology of the pores into vascularized microporous voids which could change the rate of mass transfer through the membrane (Fallahnejad et al., 2022). As the amount of nanocarbon increases, the emergence of compacted selective thin layer and sublayer porous structure increases (Altaf et al., 2021; Nayak et al., 2020). Generally, the inclusion of nano-additives into the polymer framework causes the creation of free voids due to the interaction between the polymer and nanofiller (Khanlari et al., 2020). Consequently, the integration of MWCNTs into the PSF polymer matrix influenced the membrane formation mechanism with increased pore density and pore size. Ultimately, the structure of fabricated membranes showed increased pore density compared to unmodified PSF (MMM-00). Hence, increasing the MWCNTs loadings resulted in varying surface and structural properties of fabricated membranes.

The thermographs of all fabricated membranes with varying loadings of MWCNTs and unmodified PSF are presented in Fig. 3. It could be observed that all fabricated membranes undergo recognisable weight loss and degradation of the membrane polymeric chain as the temperature increases. At the onset of thermal degradation, no significant difference could be observed in the thermograms, all membranes begin to decompose at relatively high temperatures, at approximately 520 ℃. Unmodified PSF membrane showed the least stability at 628 ℃ while modified membranes, MMM-05, MMM-10, and MMM-15 showed to be more thermally stable than MMM-00. MMM-15 with the highest MWCNTs loading presented the highest thermal stability at 751 ℃ than other fabricated MMMs. The increasing thermal stability of all fabricated MMM as compared to unmodified PSF membrane could be ascribed to the incorporation of CNTs into the PSF matrix which resulted in their increased stability properties, as CNTs loadings were increased from 0.05 to 0.15 wt%. This could be due to the increased strong interaction between the hydrogen bonding between the free hydroxylic groups of the oxidized CNTs and the sulfonic group within the PSF membrane skeleton. This result is consistent with studies reported by (Shah and Murthy, 2013; Celik et al., 2010).

The water contact angle (WCA) of a membrane is a measure of its wettability and surface interfacial energy. A low water contact angle is suggestive of the membrane's high hydrophilicity (the capability to attract water molecules while rejecting the foulants on the membrane surface) (Vatanpour et al., 2014; Covaliu-Mierlă et al., 2023). Ideally, MMMs with lower contact angles and higher surface hydrophilicity would pose a higher affinity towards water molecules. This parameter is generally used in evaluating membrane antifouling properties and water flux (Mahmoud and Mostafa, 2023). Fig. 4 depicts the water contact angle measurements of all membranes under investigation. Unmodified PSF (MMM-00) exhibited the highest water contact angle value of 75.4 ± 2.7 of all fabricated membranes suggesting its relative hydrophobic nature while MMM-10 showed the least WCA (62.8 ± 2.2) indicative of its greatest tendency to attract more water molecules and reject foulants than other fabricated MMMs. The incorporation of CNTs enhanced the surface hydrophilicity, hence, hydrophilicity improved with increasing CNTs loading. Therefore, increasing CNTs loading resulted in increased hydrophilic properties of fabricated MMM, and could be ascribed to the abundance of oxygen-containing functional groups from the oxidized CNTs available on the membrane surface as CNTs loading increases (Costa et al., 2019; Ali et al., 2019). As could be confirmed from the SEM cross-sectional image, increasing CNTs loading from 0.05 to 0.15 wt% resulted in increased pore density and thinner pore skin-like layers. It is also worth mentioning that a further increase in CNTs loading above 0.10 wt% increased WCA, which could be ascribed to an increase in CNTs agglomeration or poor dispersion and compatibility between PSF and CNTs during phase inversion resulting in increased viscosity and interfacial energy between the polymer and nanomaterial in the casting

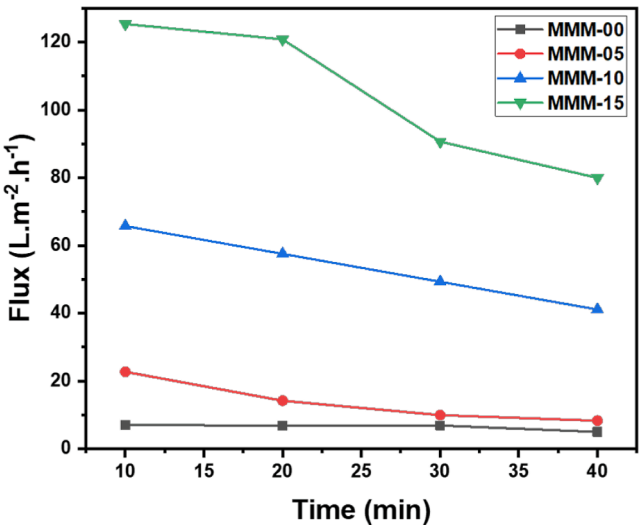

Fig. 6. Pure water flux performance of pristine and all fabricated mixed-matrix membranes.

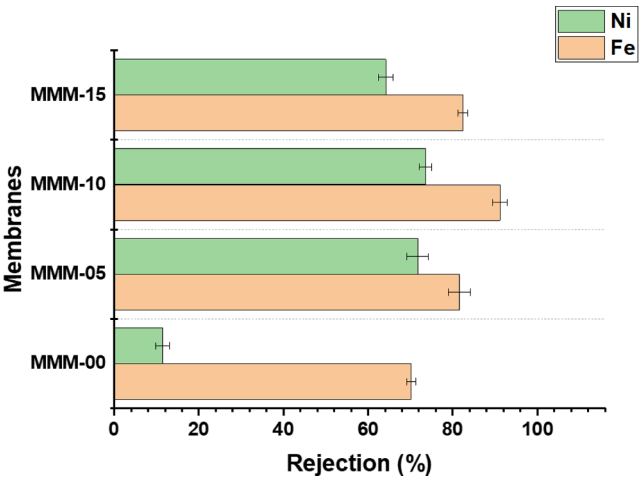

Fig. 7. Metal percentage rejection performance of pristine and all fabricated mixed matrix membranes.

solution (Rahimpour et al., 2012; Yin et al., 2013; Lee et al., 2017).

Incorporating CNTs into the matrices of polymeric membranes improved the mechanical properties of the mixed matric membrane due to the inherent high mechanical properties of CNTs (Ma et al., 2017). Mechanical properties such as tensile strength are very important characteristics of membranes utilized for pressure-driven processes/separation (Ma et al., 2017; Ali et al., 2019). Fig. 5 shows the tensile strength of the pristine membrane and all fabricated PSF/MWCNTs mixed matrix membranes with different MWCNTs loadings. It could be noticed that the tensile strength enhanced with increasing MWCNTs loading. MMM-10 (0.1 wt% MWCNTs) depicts the highest mechanical property with about 28 % improved strength compared to unmodified PSF polymer (MMM-00). These results are in agreement with some other studies reporting the potential of CNTs as promising fillers in enhancing the mechanical properties of polymeric membranes (Feng et al., 2015; Singh et al., 2021). However, MMM-15 showed a slight reduction in tensile strength which could be attributed to the agglomeration of the filler material (MWCNTs) leading to the formation of voids within the membrane matrices. The formation of these voids reduces the interfacial interaction between the polymeric membrane and the CNTs (Feng et al., 2015; Singh et al., 2021).

Membranes performance assessment

The membrane performance indicators (pure water flux and metal % rejection) of all fabricated membranes with 0.05 to 0.15 wt% MWCNTs loadings and unmodified PSF membrane are shown in Fig. 6 and Fig. 7.

Pure water flux

Pure water flux (PWF) through all fabricated mixed matrix nanocomposite and pristine PSF membranes were assessed for filtration flow measurements as shown in Fig. 6 using deionized water under 60 min experimental time at 6 bar and room temperature. The water flux values for both pristine and fabricated MMMs follow a pattern and tend to gradually decline over time, this behaviour is due to the hydration of the membrane pores resulting in the reduction in the passage of water molecules through the membrane-free pores volume (Dias and Ferreira, 2023). Again, the restructuring of the polymer chains in the membranes could result in less dense and closer pore walls (Khalid et al., 2017) which could also affect the flow of water through the membrane. The lowest flux values were observed with unmodified PSF membrane and increased with increasing filler (MWCNTs) loadings. For example, the unmodified PSF membrane (MMM-00), showed the least flux value at 7.0 L $m^{-2}h^{-1}$ and increased CNTs loading from 0.05 wt% to 0.15 wt% under the same pressure, flux through the membranes also increases from 22.7 L $m^{-2}h^{-1}$ to 125.3 L $m^{-2}h^{-1}$. A comparable result trend was also reported by Nayak et al. (Nayak et al., 2020). This shows that the incorporation of CNTs into the polymeric membrane alters its surface properties by changing the pore sizes of the polymeric membranes such that the permeability capacity of the membranes (due to additional flow routes created) was greater than the unmodified membrane. Thus, membranes with high hydrophilicity showed relatively high flux as expected, this is in good agreement with the WCA result as shown in Fig. 4.

Again, the degree to which flux decreases is an indicator of the membrane's fouling resistance capacity (hydrophilicity), surface pore size, porosity, and pore interconnectivity (Yin et al., 2013). As could be observed from Fig. 6, MMM-10 showed a somewhat less steady decrease in flux over time (after the first 40 min of testing time) before attaining a steady state unlike MMM-15 which showed a drastic flux reduction of about 30 L$m^{-2}h^{-1}$ within the first 30 min of filtration. According to Shah and Murthy (Shah and Murthy, 2013), high CNTs loadings in membranes could reduce membrane porosity caused by the steric hindrance and also the electrostatic interaction between CNTs and PSF polymer or between CNTs particles as a result of irregular/poor dispersion and aggregation during phase inversion.

Metal rejection

The separation performance investigation was conducted to assess the effect of MWCNTs loadings on the separation performance of all fabricated MMM in comparison with pristine (unmodified) PSF membrane in treating synthetic goldmine wastewater. The separation performance experiment was conducted using simulated wastewater containing 895 mg/L Fe and 2.8 mg/L Ni at a pH range of 2.7 and a transmembrane pressure of 6 bar. As can be observed in Fig. 7, both Fe and Ni percentage rejections were enhanced for all MWCNTs/PSF nanocomposite membranes compared to the unmodified pristine PSF membrane. Integrating CNTs into the PSF polymer matrix resulted in improved target metals removal efficiency. MMM-10 (with 0.10 wt% CNTs loading) showed the highest Fe and Ni rejection of 91.2 ± 1.7 % and 74.0 ± 1.44 %, respectively, compared to MMM-05 (81.6 ± 2.6 % Fe and 72.0 ± 2.5 % Ni) and MMM-15 (82.4 ± 1.1 % Fe and 64.3 ± 1.7 % Ni). Unmodified PSF showed a very low % rejection for Ni (11.4 ± 1.6 %) than Fe cation (70.2 ± 1.03 %) which may be due to the chargeless electrostatic interaction between the charges of the solute (feed stream) in contact with the top surface part of the membrane and/or its pore size (ionic radius of Ni^{2+} 0.069 nm; is smaller than 0.076 nm of Fe^{2+}) which pushes metal ions to be absorbed and entrapped inside the membranes porous structure (Mahmoud and Mostafa, 2023; Wanjiya et al., 2024).

Table 3
Performance summary of this work compared to other reported studies that used commercial NF membranes in the literature.

Membrane type	Initial concentration and pH	Feed solution	Rejection (%)	Flux/permeability	Reference
Commercial NF membranes: TFC-SR3	Fe −7.15 mg/L pH = 3	Groundwater	~70 %	4.68 $L.m^{-2}.h^{-1}.bar^{-1}$	(Kasim et al., 2016)
Commercial NF Membranes (DK4040F)	Ni – 16.6 mg/L pH = 3	AMD	92.45 %	55 $L.m^{-2}.h^{-1}$	(Zhong et al., 2007)
Commercial NF membrane(1) NF270 (2) HydraCoRe 70pHT	Fe – 4330 mg/L Fe – 3610 mg/L pH = 2.95	Synthetic AMD	Fe – 89.1–92.7 % Fe – 39.9–60.7 %	–	(Lopez et al., 2018)
Plastic-derived MWCNTs modified PSF membranes	Fe – 895 mg/L Ni – 2.8 mg/L pH = 2.7	Synthetic AMD (Ni & Fe)	Fe – 91.2 % Ni – 73.6 %	22.7 – 125.3 $L.m^{-2}.h^{-1}$	This study

The isoelectric potential of PSF membrane is between a pH value of 3 and 4 (Martín et al., 2003) and membrane charge is usually zero at the Isoelectric point (IEP) or zero potential charge effect (Fornarelli et al., 2013). To achieve good membrane selectivity for metals, membrane IEP needs to be higher than feed pH (Zhao, 2014). The pH of the feed is an essential factor that affects the performance of the membrane. At a lower pH, membrane performance declines due to the presence of more H^+ ions resulting in the change of membrane surface charges and cross-linking of the polymer network which alters the pore properties and affects the removal efficiency (Machodi and Daramola, 2019; Dong et al., 2022). Generally, Donnan exclusion (the repulsion between the charged membrane surface and the metal ions) or the size exclusion (based on the dissimilarity in the pore size of the membrane and permeate) are the two major mechanisms that determine the overall membrane performance in the removal of heavy metals (Wanjiya et al., 2024; Zhong et al., 2007); although, the membranes pore size of all prepared membranes was not measured. The separation (rejection) mechanism for the separation of divalent metal (Fe and Ni) ions from simulated gold mine wastewater in this study was mostly controlled by the Donnan exclusion effect, that is, the electrostatic interactive (repulsive) force between the charged membrane and the feed solution (Mahmoud and Mostafa, 2023; Zhao, 2014; Zhong et al., 2007). Due to the low pH of the feed solution (pH = 2.7), the membrane surface is filled with positively charged hydronium ions (H_3O^-), therefore, repulsive force arises between the hydronium ion and the positively charged metal ions (Mahmoud and Mostafa, 2023). The rejection efficiency exhibited by all prepared nanocomposite membranes decreases for Fe in the order of MMM-10 > MMM-15 > MMM-05 and for Ni metal in the sequence of MMM-10 > MMM-05 > MMM-15.

Table 3 presents a summary of some reported results in the literature compared to the results obtained in this study. Improved flux through the fabricated membranes was accomplished in this work compared to some of the reported studies with commercially available NF membrane materials. For the removal of Ni and Fe metals at a comparable low pH value, good rejection performance was achieved in this study. However, there is a considerable decline in the % rejection for Ni metal.

Conclusion

MWCNTs obtained from waste polypropylene plastics were successfully incorporated into a polysulfone (PSF) polymer matrix to develop an innovative PSF-MWCNTs MMM fabricated via the phase inversion method. Fabricated PSF-MWCNTs MMM were tested in the removal of Fe and Ni metals from gold mine wastewater. The obtained results revealed that the incorporation of plastic derived-MWCNTs significantly affected the surface structure properties of PSF membranes and improved their thermal stability, surface hydrophilicity, and flux through the membranes. The filtration treatment demonstrated that all fabricated MMM had great selectivity for divalent cations compared to unmodified pristine membrane whose % rejection for Fe and Ni cations were 70 and 11 %, respectively. The metal removal performance of all fabricated PSF-MWCNTs MMM was 81–91 % rejection for Fe and 64–74 % rejection for Ni metals. The performance of this study could be improved by functionalizing the surfaces of the plastic-derived nanotubes with more hydrophilic materials, such as strong oxidizing acids, primary/secondary amine-containing groups, ionic liquids, etc. Results presented herein confirm that the membrane separation performance of waste plastic derived-MWCNTs could be a technological solution in the field of membrane technology and a viable environmental sustainability approach to solid waste management and wastewater remediation.

CRediT authorship contribution statement

H.U. Modekwe: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **I.M. Ramatsa:** Writing – review & editing, Supervision, Resources. **M.A. Mamo:** Writing – review & editing, Supervision, Resources. **O.O. Sadare:** Writing – review & editing, Resources. **M.O. Daramola:** Writing – review & editing, Supervision, Resources. **K. Moothi:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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