**Fe₂O₃ NANOCOMPOSITE PVC MEMBRANE WITH ENHANCED PROPERTIES
AND SEPARATION PERFORMANCE**

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ABSTRACT

Organic and inorganic mixed matrix membranes are one of the most promising new membrane materials for ultrafiltration (UF) separation applications. In this study, PVC/Fe₂O₃-mixed UF membranes were fabricated at different nano-Fe₂O₃ loading levels (0–2 wt. %) using the phase inversion method. Surface chemical compositions, surface and cross-section morphologies and characteristics, hydrophilicity and mechanical strength of the membranes were characterized using several analytical techniques and instruments such as scanning electron microscopy (SEM), atomic force microscopy (AFM), a contact angle goniometer, dynamic mechanical analyzer (DMA) and a nanoindenter. Membrane performance was also tested in terms of water flux, solute rejection, and anti-fouling characteristics. The experimental results demonstrated that the overall membrane structure was remarkably enhanced with the addition of Fe₂O₃ nanoparticles up to a loading of 1%. This was due to the membrane's more hydrophilic and smoother surface and a more elongated finger-like structure as well as higher porosity and pore size. The nanoindentation experiments indicated that Fe₂O₃ incorporation greatly enhanced the hardness of the membranes providing a higher pore integrity degree. However, higher Fe₂O₃ content caused a nanoparticle aggregation resulting in a decline in the performance of the composite membranes. Compared with the pristine PVC membrane, the membrane containing 1% Fe₂O₃ exhibited better capabilities such as the enhanced water flux (782 L/m²h), higher

sodium alginate (SA) rejection rate (91.9%) and better antifouling properties. The PVC/Fe₂O₃ nanocomposite membranes may have applicable potential in water and wastewater treatment applications based on their low price, enhanced mechanical strength, high permeability, high removal efficiency, and good antifouling performance.

Keywords: Ultrafiltration, nanocomposite membranes, mechanical strength, PVC/Fe₂O₃, antifouling.

1. Introduction

Over the past few decades, ultrafiltration (UF) membranes have gained widespread implementation in the treatment of groundwater, surface water and wastewater owing to their ability to remove a variety of particulates and macromolecules to produce high quality potable water [1]. Because of this increasing demand, many efforts have been devoted to enhancing the performance of UF membranes such as feed pretreatment, module design, process optimization and membrane materials, among which, the latter is still the key factor affecting overall membrane performance [2]. The most commonly used commercial UF membranes are being fabricated using polymers such as polyvinylidene fluoride (PVDF), cellulose acetate (CA), polyacrylonitrile (PAN), polyether imide (PEI), polysulfone (PS), polyethersulfone (PES), polysulfone (PSF), polypropylene (PP) and polyvinyl chloride (PVC) as well as ceramic membranes, which have also gained popularity in recent years [3–6]. However, all these backbone polymer-based materials are highly hydrophobic and susceptible to extensive fouling which is mainly caused by the sorption or aggradation of contaminants such as natural organic matter (NOM), colloidal and particulate matter, and microorganisms at the membrane surface or pores, which in turn causes a decline in flux, increases the operational costs for clean-up and reduces the membrane lifetime; hence, these contaminants can even cause the replacement of the membrane [5, 7, 8]. Moreover, the mechanical strength of the polymeric membrane, especially, indentation, is another important concern for pressure-driven UF separation processes in terms of long-duration stable performance. High transmembrane pressure differentials bring about irreversible changes in the macrovoid structure of the membranes, in which the polymeric matrix is slightly reorganized and may be internally deformed or damaged due to physical compaction, resulting in a decreased pore volume, a higher membrane resistance and a non-recoverable

loss of water flux [9–11]. Although methods such as membrane polymer modification, blending the polymer with an additive, surface coating and grafting have been employed to enhance membrane properties in terms of fouling resistance and hydrophilicity, their applications remain limited due to some drawbacks, such as the lack of stability and adaptation to larger scale processes [2, 4, 12]. Accordingly, efforts have been devoted to the development of ultrafiltration membranes with better anti-fouling property and mechanical strength using more viable techniques [13].

As modification of membranes by incorporating commercial nanoparticles gained acceptance in the industry [14], membrane performance was enhanced through research. Researchers improved permeability, resistance to fouling and deferred deformation making substantial alterations in the structure of membrane matrices. These changes and advancements included inhibited macrovoid formation, increased pore connectivity and enhanced mechanical strength owing to the porous nature of the nanofillers in the polymeric matrix [15]. These morphological changes in membrane structure also made it easier for researchers to suppress compaction and reduce structural losses, which can occur in the bulk macrovoid region of asymmetric membranes [16]. Compaction resistance in membranes are usually overcome by reducing the membrane porosity or increasing the membrane hydrophobicity, which in turn causes a decrease in flux rate; however, incorporation of nanomaterials into the polymeric matrix may have paved the way for achieving the goal without sacrificing other desirable characteristics [17]. These improvements in the membrane structure are attributed to enhanced localized interactions between the membrane polymer chains and well-distributed particles, which lead to a change in the microstructural properties of the fabricated membrane such as pore size, pore structure, and distribution [12, 15]. The existence of nanoparticles can speed up water diffusion into the membrane matrix due to their higher hydrophilic nature and weaken the interaction between the polymer and solvent molecules, which helps to delay the swelling degree and dissolution of the polymeric matrix by inhibiting the collapse of the porous support layer. Another concern is the loading amount of nanoparticles since the optimum dose may change depending on the types of nanoparticle and backbone material to be used. Low nanoparticle loading may not be sufficient to enhance the membrane properties whereas high loading may cause aggregation of the nanoparticles during immersion precipitation. High loading can also plug the membrane pores which can greatly affect the membrane morphology and filtration ability, suppressing all positive effects rather than improving them [17].

Recently, extensive efforts have been devoted to incorporating inorganic nanoparticles into the membrane polymeric matrix. Various types of inorganic nanoparticles such as titanium oxide (TiO_2) [18–22], alumina (Al_2O_3) [19, 23, 24], zirconium (ZrO_2) [19, 25], silica (SiO_2) [14, 26], zinc oxide (ZnO) [5, 6, 27–29], copper (II) oxide (CuO) [30], graphene oxide [31, 32], zeolite [33], silver (Ag) [34], iron oxide Fe_2O_3 [35] and multi-walled carbon nanotubes (MWCNTs) [36–38] have been used as a bulk material to fabricate organic and inorganic composite membranes, which were endowed with more hydrophilic surfaces with nanoparticle incorporation. Alpatova et al. [35] fabricated PVDF membranes using MWCNT and Fe_2O_3 simultaneously. They concluded that using only MWCNTs did not change the membrane hydrophilicity; however, with the addition of Fe_2O_3 , hydrophilicity and the flux rate both increased. The optimum combination was found as 0.2% MWCNTs and 1% Fe_2O_3 [35]. Arsuaga et al. [15] fabricated PES membranes by adding TiO_2 , Al_2O_3 , and ZrO_2 nanoparticles and reported that the membrane structures were positively impacted in terms of porosity, antifouling property and long-term flux stability with the addition of nanoparticles. Low et al. modified PES UF membranes by incorporating nanoporous titania nanoparticles (NTNs) with amounts ranging from 0.1–1 wt. % and indicated that the modified membranes showed increased wettability as well as reduced surface energy and pore size. Moreover, Arsuaga et al. [15] also reported that the modified membranes with an optimized nanoparticle dose of 0.5 wt. % NTN showed a 20% increase in water flux and exhibited improved fouling resistance with 80% water flux recovery compared to bare PES membranes. Yang et al. fabricated PSF composite UF membranes incorporated with TiO_2 nanoparticles and stated that up to 2 wt. % of nanoparticles in fabricated membranes exhibited excellent water permeability, hydrophilicity with good mechanical strength and anti-fouling property. However, the properties of the membrane were negatively affected with the further increase in nanoparticle loading due to the serious aggregation of particles. [20, 21]. Cao et al. [18] fabricated PVDF/ TiO_2 UF membranes and investigated the effect of nanoparticle size on the performance of the resultant composite membranes and reported that smaller size nanoparticles (10 nm) had better antifouling properties compared to PVDF/ TiO_2 membranes with bigger particle sizes (26–30 nm). Oh et al. [22] synthesized PVDF-UF membranes by dispersing nano- TiO_2 into the casting solution and using both nonwoven fabric and PET films as support layers on the fabricated membranes. Based on the MFI fouling index, they concluded that the addition of TiO_2 nanoparticles into the casting solution improved membrane fouling resistance. Liu et al. [23]

fabricated PVDF/ γ -Al₂O₃ composite membranes and demonstrated that modified membrane with 2 wt.% γ -Al₂O₃ nanoparticle showed better separation performance over the neat PVDF membranes.

Several studies have reported on the fabrication of ultrafiltration membranes using a different type of particles. However, as of this writing, no detailed work has been published in the literature concerning the use of Fe₂O₃ particles in the synthesis of UF membranes. The main motivation of this study is to investigate the influence of Fe₂O₃ nanoparticles dispersed in PVC polymer on the membrane performance and to determine the optimum Fe₂O₃ dose. Pressure dependent flux values, pore integrity degree and mechanical strength of the modified PVC membranes were evaluated relative to the pristine PVC membrane to help understand the effects of nanoparticle dispersion on compaction behavior and deformation of the membrane. The morphologies of cast membranes in terms of pore structure, pore size and distribution, and nanoparticle distribution as well as membrane hydrophilicity and surface roughness were studied to monitor the changes in the modified membrane structure. Moreover, rejection abilities and antifouling performance of the membranes were investigated for sodium alginate removal.

2. Materials and Methods

2.1. Chemicals and materials

High molecular weight polyvinyl chloride (PVC), polyethylene glycol (PEG 6000), 1-methyl-2-pyrrolidone (NMP), iron (III) oxide (Fe₂O₃) in nanopowder form (<50 nm), organic model foulant sodium alginate (SA) and sodium chloride (NaCl) were purchased from Sigma-Aldrich, USA. All reagents and chemicals, unless otherwise stated, were supplied from commercial sources and used as received.

2.2. Preparation of PVC and PVC/Fe₂O₃ ultrafiltration membranes

The PVC and PVC/Fe₂O₃ composite membranes were prepared by the phase inversion method. The experimental steps used to prepare PVC membranes have been described in detail elsewhere [5, 7]. First, Fe₂O₃ with varying amounts (0–2.0% by wt.) were added to NMP solvent and the resultant mixture was stirred for two hours to ensure good dispersion of the nanoparticles in the solvent. For higher amounts of Fe₂O₃ beyond 1.0%, the mixture was sonicated for at least two hours to get a good dispersion of nanoparticles in the solution. After that, PEG was added to the mixture, which was then heated to 60 °C under rapid stirring for two hours and finally, after adding PVC to the solution, the final mixture

continued to be stirred for 24 hours until a homogenous solution was formed. Subsequently, polymer suspension was held static for at least two hours to get rid of the air bubbles prior to use. Table 1 shows the composition of each casting solution. The membranes were cast on a glass plate to a thickness of 200 μm using an adjustable casting blade, referred to as a Universal blade applicator (Paul N. Gardner Company Inc., Pompano Beach, FL, USA). The cast membranes were left in air for about 15 s and then immersed in a deionized water coagulation bed at room temperature to conduct the phase inversion step. After 30 min, the membranes were placed in another fresh water bath and left for about 48 hours to get rid of the remaining solvent. All the fabricated membranes were air dried for 24 hours prior to getting tested.

Table 1. Compositions of the casting solutions for PVC and PVC/Fe₂O₃ nanocomposite membranes.

Membrane ID	PVC (g)	PEG (g)	NMP (g)	Fe ₂ O ₃ (g)	Fe ₂ O ₃ /PVC (wt/wt. %)
PVC	12.8	3.2	84.000	0	0
PVC/0.2Fe ₂ O ₃	12.8	3.2	83.974	0.0256	0.2
PVC/0.6Fe ₂ O ₃	12.8	3.2	83.232	0.0768	0.6
PVC/1.0Fe ₂ O ₃	12.8	3.2	83.872	0.1280	1.0
PVC/1.6Fe ₂ O ₃	12.8	3.2	83.795	0.2048	1.6
PVC/2.0Fe ₂ O ₃	12.8	3.2	83.744	0.2560	2.0

2.3. Flux performance and pressure stability experiments

Membrane flux performance tests were conducted using a dead-end filtration cell (Millipore, USA). In a typical test, a membrane sample with an effective area of 28.7 cm² was placed into a filtration cell having a volume of 200 mL. The feed solution was poured into a 5.0 L dispensing vessel connected to the filtration cell. The solution in the cell was stirred at 300 rpm to minimize concentration polarization. Permeate was weighed in one minute time intervals using a balance, and the data was collected and stored using Collect 6.1 software (Fig. 1).

Fig. 1. Schematic view of the dead-end ultrafiltration system.

The transmembrane pressure (TMP) was kept constant at 0.14 MPa during the runs by using compressed nitrogen gas. The pure water flux was determined by measuring the mass of permeate collected over specific time intervals and was calculated as:

$$J_w = \frac{Q}{A \Delta t} \quad (1)$$

where Q is the mass of the permeate, A is the membrane effective area, and Δt is the time interval for the measurement. Moreover, pure water flux values of some membrane samples were measured at different transmembrane pressures (0.07–0.34 MPa) to ascertain the deformation of membranes.

2.4. Mechanical property analysis

2.4.1. Mechanical strength

Nanoindentation measurements were performed using a Ubi-1 Nanoindenter (Hysitron, Inc., Minneapolis, MN, USA) to determine the hardness (H) of the fabricated membranes. The test was performed by applying a load on the sample with a Berkovich diamond tip. The displacement of the diamond tip was recorded continuously to produce a force versus displacement curve. This serves as the 'mechanical fingerprint' of the material allowing the quantitative nanoscale material properties such as hardness to be determined.

Indentations were conducted at three different locations on the surface of each sample with a 3 by 3 matrix of test points (9 points) at each location, which corresponds to 27 measurements for each membrane sample. Average values of all three measurements were calculated and reported.

2.4.2. Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) tests were performed using a DMA machine (Q800, TA Instruments Inc., New Castle, DE, USA) in film tension mode. The membrane samples (dimension 10mm×3mm×1mm) were first heated to 28°C in the DMA machine and stabilized for 5 minutes to reach thermal equilibrium. A preload of 0.005 N was applied to keep the samples straight during the test and the strain was oscillated at a frequency of 1 Hz with peak amplitude of 0.1%. Meanwhile, the temperature was increased from 28°C to 120°C with a rate of 3°C/min.

2.5. Contact angle analysis

Dynamic water contact angles of the fabricated membranes were measured using a Model 250 contact angle goniometer (ramé-hart Instrument Co., Succasunna, NJ, USA). The membrane samples were dried in an oven for 24 hours prior to measurements. Distilled water was dropped on three different parts of the membrane surface and the contact angles were measured at 30 s intervals over a total 180 s. Average values of all three measurements were calculated and reported.

2.6. Morphology observation

Field emission scanning electron microscopy (FE-SEM) (Zeiss Ultra 60; Carl Zeiss NTS, LLC North America) has been used to elucidate the cross-sectional and surface morphological structures of fabricated membranes. For cross-section imaging, the flat membranes were subjected to propyl alcohol and then immersed in liquid nitrogen to get the membrane frozen so that it could be fractured properly and distortion of the membrane could be avoided. Then the membranes were fixed on copper stubs before the analysis. For surface imaging, membrane samples were positioned on stubs with carbon dots. A 5.0 kV acceleration voltage was applied at different magnifications. Energy dispersive X-ray spectroscopy (EDX) coupled to SEM was applied to monitor the dispersion of the nanoparticles on the surface and through the cross section of the membrane matrix. AZtec

software, version 3.0 (Oxford Instruments Nanotechnology Tools Ltd.) was used to interpret the results.

2.7. Porosity and water uptake measurements and mean pore diameter determination

Porosity measurements were conducted by calculating the volume fraction of each membrane [28]. Membrane samples were kept in fresh distilled water and weighed carefully after getting rid of the excess water on the surface and bottom parts of the membranes. Afterward, the membrane samples were dried in a vacuum oven overnight to remove all the water inside the pores and weighed. The thickness of the membranes was measured with a micrometer. Porosities and water uptake values of each membrane were calculated using the following equations, respectively.

$$\varepsilon = \frac{W_w - W_d}{\rho_w(\pi r^2 l)} \times 100\% \quad (2)$$

$$\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100\% \quad (3)$$

where W_w and W_d are the weights of the wet and dry membranes (g), respectively, ρ_w is the density of the water at room temperature (g/cm^3), r is the radius (cm) and l is the thickness (cm) of the membrane.

Mean pore diameters of the fabricated membranes were calculated using the measured water flux values of each membrane at constant pressure and the other individual membrane properties using the Guerout-Elford-Ferry equation below [39, 40].

$$a = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times (8\mu l Q_w)}{\varepsilon A \Delta P}} \quad (4)$$

where a denotes the mean pore diameter (m), ε is the porosity, μ is the viscosity of the water to be filtrated at room temperature (Pa.s), l is the thickness of the membrane (m), Q_w is the water flux (m^3/s), A is the filtration area of the membrane (m^2), and ΔP is the transmembrane pressure (Pa).

2.8. Viscosity measurement

Viscosity measurement of each casting solution was conducted using a viscometer (DV2T, Brookfield, AMETEK, Massachusetts, USA). Experiments were performed at room temperature using a CPA-41Z spindle with a speed of 0.8 rpm.

2.9. Surface roughness

An Agilent 5500 atomic force microscope (AFM) (Agilent Technologies, Santa Clara, CA, USA) was employed to analyze the surface morphology and roughness of the fabricated membranes. Approximately 1 cm² of the prepared membrane was cut and fixed on the copper stub and further scanned with a 5 x 5 μm² scan size and 0.5 line/s rate. Imaging was performed in the non-contact mode using a silicon cantilever probe (Budget Sensors, Bulgaria). PicoView software (Version 6.1.3) was used for image acquisition and processing. At least five measurements were taken from different positions on the membrane surface and average values were reported.

2.10. Rejection and antifouling performance

After each water flux test, membranes were conditioned using 2 L of NaCl solution with an ionic strength of 10 mM. Sodium alginate (SA), which is a hydrophilic microbial polysaccharide, was used in the fouling experiments to represent an extracellular polymeric substance [41]. After the conditioning of membranes, fouling experiments using a solution of 20 mg/L SA and 10 mM NaCl were performed for at least eight hours until the flux was almost stable. In the very first 10 min of the fouling test, a permeate sample was taken to calculate the rejection. The concentrations of the collected permeate and feed for each membrane was determined quantitatively using a TOC-L Analyzer (Shimadzu, Japan). The instrument uses the National Environmental Methods Index High-Temperature Combustion Method 5310B. The instrument was calibrated using a series of potassium hydrogen phthalate (KHP) and sodium hydrogen carbonate (NaHCO₃) and the calibration curve was used to calculate the TOC values of unknown samples. These concentrations were then used to calculate the percentage rejection (R) of each membrane.

$$R(\%) = 1 - \left(\frac{C_p}{C_f} \right) \times 100 \quad (5)$$

where C_p and C_f denote the concentrations of permeate and feed solutions, respectively.

At the end of each fouling experiment, all parts of the flux device were cleaned with DI water and the membranes were also physically cleaned. After each fouling experiment and subsequent physical cleaning, the feed tank was filled with 4 L of DI water in order to measure the flux. Flux recovery ratio (FRR) was calculated as:

$$FRR(\%) = \left(\frac{J_{w,2}}{J_{w,1}} \right) \times 100 \quad (6)$$

where $J_{w,1}$ and $J_{w,2}$ denote the pure water flux and water flux after the SA fouling test, respectively.

A previously defined membrane fouling index for ultrafiltration membranes (MFI-UF) was used to measure the degree of particulate membrane fouling since the deposition of particulates during membrane filtration causes a decline of the permeate flux and, hence, affects the reusability of the membranes.

Deposition of particulates during membrane filtration is being measured using the Membrane Fouling Index ($MF_{0.45}$), which uses 0.45 μm membrane. However, since $MF_{0.45}$ is not sensitive to the presence of smaller particles, a more recent MFI using ultrafiltration membranes was developed to include smaller particles into the fouling measurement and a polyacrylonitrile 13 kDa membrane (PAN 13 kDa) has been proposed as the reference membrane for the MFI-UF test [42].

MFI is based on a cake filtration mechanism and is calculated from the gradient of the general cake filtration equation at constant pressure in a plot of t/V versus V :

$$MFI - UF = \frac{\eta_{20^\circ\text{C}}}{\eta_T} \frac{\Delta P}{\Delta P_0} \left(\frac{A}{A_0} \right)^2 \frac{d\left(\frac{t}{V}\right)}{dV} \quad (7)$$

where $\eta_{20^\circ\text{C}}$ and η_T are the viscosities of the water to be filtrated at a reference temperature of 20 °C and filtration temperatures, respectively; ΔP is the transmembrane pressures at the operating condition and ΔP_0 is the reference transmembrane pressure (2 bars), and A and A_0 are the ultrafiltration membrane area and the reference surface area ($13.8 \times 10^{-4} \text{ m}^2$), respectively. $d(t/V)/dV$ are the gradient of two data points in the plot of t/V versus V , and this value was calculated by plotting t/V versus V and calculating the derivative from the slope of the corresponding curve. Therefore, the MFI-UF value is directly comparable with the $MF_{0.45}$.

3. Results and Discussion

3.1. Flux performance and pressure stability tests

Pure water flux values of the PVC and PVC/ Fe_2O_3 nanocomposite membranes were measured at varying transmembrane pressures to monitor the compaction behaviors of the modified membranes relative to that of the pristine membranes, as shown in Fig. 2.

Fig. 2. Variation of water flux under different applied transmembrane pressures.

Fig. 2 shows the pure water flux of the PVC membranes measured at 0.14 MPa TMP increasing from 522 L/m² h to 712 L/m² h with the addition of 0.2% Fe₂O₃. The highest value was observed with 1.0% Fe₂O₃ (782 L/m² h) at the same TMP, which means that the nanocomposite membranes exhibited an improvement of approximately 50% in flux relative to that of the pristine membranes. Water flux profiles of the fabricated membranes at 0.14 MPa TMP as a function of Fe₂O₃ loading can be found in the Supporting information. The highest pure water flux obtained at 0.2 MPa was markedly higher (1181 L/m² h in the case of 1% Fe₂O₃ nanocomposite membranes) when compared to the previous work [6] performed with PVC and ZnO nanoparticles. In [6], the highest flux of DI water was 401.9 L/m²h at the same applied pressure of 0.2 MPa. Wu et al. [43] claimed that hydrophilicity and pore structure of the membrane were the most significant factors that affect permeation rate. Moreover, the adsorption effects together with hydrophilicity enhanced the exchange between solvent and water during the phase inversion and resulted in an increment in the pore size, amount and the interconnectivity between the upper and sublayer [43, 44]. The highest flux was reached in the case of 1% Fe₂O₃ due to the hydrophilic groups of nanoparticles, which were evenly distributed both on the surface and through the finger-like pores of the membrane matrix (Figs. 6 and 8). Further loading of Fe₂O₃ nanoparticles led to

a change in the structure and size of the finger-like pores which, in turn, resulted in an increase of membrane resistance and a decrease in water permeability. The decline of flux in the presence of greater amounts of nanoparticles may be attributed to the higher density of nanoparticles in the casting solution. When the density of the casting solution increases, the interchange process between the solvent and water will slow down the precipitation of the membrane, which in turn will induce a lower porous membrane, resulting in the decline of water flux.

Flux values measured at different applied pressures give insight about the compaction behavior of the membrane since the flux always reaches a steady value as soon as the membrane compacts to the extent at which it can resist the applied pressure [45]. Fig. 2 shows how the flux values of all membranes were linear with regard to applied TMP up to the point where flux values start to decrease due to pore deformation. PVC membranes have a lower resistance to compaction than nanocomposite membranes because the flux did not increase linearly and became stable above a pressure of 0.24 MPa. All the modified membranes appeared more resistant to deformation compared to the PVC membrane during filtration at higher pressures. It can be inferred from the figure that the PVC/1.0Fe₂O₃ membrane could resist the impact of compaction at pressures higher than 0.34 MPa. Ebert et al. [46] also found that the stability of PVDF membranes will increase when incorporated with titanium dioxide nanoparticles, and that modified membranes will exhibit less compaction, which was demonstrated by the minimal structural changes after exposure to pressure [46]. In order to verify the maintenance of pristine and nanocomposite membranes with varying Fe₂O₃ loadings (1% and 2%) after the UF tests at high transmembrane pressures were shown using SEM images, which can be found in the Supporting information. As it is seen in Figure S5 (in the Supplementary data document), the structure of pristine membrane was not stable under high pressure demonstrating a clear compression of the substructure and a decrease in the thickness of active layer, which is also supported by the dramatic flux loss at high pressures (Fig. 2). For the case of PVC/1.0 Fe₂O₃ and PVC/2.0 Fe₂O₃ membranes, the compaction effects are less pronounced since the substructures and thicknesses of the active layers remain almost unchanged.

3.2. Mechanical property analysis

Mechanical strength is a very significant characteristic since it indicates the long-term stability performance of a membrane when subjected to high pressure [17]. The

mechanical strength of the fabricated membranes in terms of hardness of the selective layer is depicted as a function of membrane pore integrity degree in Fig. 3.

Fig. 3. Variation of hardness with membrane pore integrity degree (the percentage values shown in the figure correspond to Fe₂O₃ loading for each membrane).

The indentation hardness can quantify the membrane resistance to plastic deformation, i.e., compaction resistance under a compressive applied force. Membrane pore integrity degree ($dJ_w/d\Delta P$) gives information about the variation of hardness regarding the extent where the membrane begins to deform due to pore collapse and flux loss under an applied pressure, as plotted in Fig. 3. The pore integrity degree of the pristine PVC membrane was lower compared to the nanocomposite membranes since it had the lowest level of hardness (8.364 MPa). The pore integrity degree increased for higher loadings of Fe₂O₃ due to the enhanced mechanical strength of the support structure imparted by the nanoparticles. The ultimate hardness (10.160 MPa) was reached in the case of 1% Fe₂O₃ due to the highest resistance to deformation and showed a marked decrease with a loading above 1.0% Fe₂O₃, which may be attributed to membrane instability caused by Fe₂O₃ aggregates. The lowest hardness among the nanocomposite membranes was obtained in the case of 2% Fe₂O₃ loading despite having higher pore integrity degree than 0.2% Fe₂O₃ doped membrane since a serious agglomeration developed, which was also observed in surface EDX images (Fig. 8). In the paper [14], it was reported that increasing the nanofiller concentration would

enhance the mechanical strength of the nanocomposite membranes up to a threshold loading and after exceeding this optimum value, the aggregation of nanoparticles would endanger the uniform dispersion. This post-threshold nanoparticle aggregation overload could result in stress convergence points in the membrane matrix due to applied external force and, hence, lead to weakened mechanical strength [17]. The reinforcement effect on mechanical strength may be attributed to nanoparticles serving as cross-linking agents to link polymer chains, which in turn provides extra stiffness to the polymeric matrix. The interfacial interaction between the polymer chains and nanoparticles should be enough to ensure the high mechanical strength of the nanocomposite membranes; otherwise, the insufficient load transfer between the nanoparticles and polymer chains may reduce the impact strength and related mechanical properties [17, 20]. Another reason for the enhanced mechanical properties was due to the suppression of the macrovoids in the membrane matrix by introducing nanoparticles, which was also proved by the SEM cross-section images. This mechanical contribution enabled the membrane to resist compaction, which occurred during the initial stages of the membrane operation and induced better recoverable flux during high-pressure separation. The macrovoid suppression also delayed deformation of the membrane matrix producing a more mechanically robust membrane structure.

Moreover, the DMA of the fabricated membranes were investigated in order to monitor the viscoelastic properties of membranes and address the difference between the pristine and the nanocomposite membranes in terms of their stiffness or resistances to deformation. Variation of storage modulus and loss modulus as a function of the applied temperature for different loadings of Fe_2O_3 is given in Fig. 4. This representation allows the determination of relaxation processes, which are characterized by a decrease of storage modulus and a peak of loss modulus.

Fig. 4. Variation of (a) storage modulus, (b) loss modulus with temperature at different Fe_2O_3 loadings.

DMA technique, which is applied to measure the modulus (stiffness) and damping properties (energy dissipation) of materials as the materials are deformed under periodic stress, separates the dynamic response of materials into two distinct parts: an elastic part represented by storage modulus and a viscous or damping component which is depicted by loss modulus [47, 48]. The variation of storage modulus and loss modulus with temperature could give insight about the viscoelastic property of a polymer as well as the glass transition temperature, which depicts the transition of the polymeric material from glassy behavior to rubbery property and in turn results in a dramatic decrease in the stiffness of the material. However, it is difficult to assign a single glass transition temperature since the transition occurs over a range of temperatures and the glass transition temperature determined from storage modulus might differ from what is determined from loss modulus spectrum; in the former, the onset of the transition is said to be the glass transition temperature, while in the latter the temperature of the maximum loss modulus is assigned as the glass transition temperature. A slight increase of storage modulus in the case of PVC/1.0% Fe_2O_3 nanocomposite membrane after around 75 $^{\circ}\text{C}$ may be attributed to the removal of some residual casting solvent (NMP) and water, which had a plasticizing effect [49]. According to Fig. 4a, the storage modulus values of all the membranes decreased slightly and in the vicinity of glass transition temperature, a considerable drop was observed indicating that the membrane material was experiencing a transition from glassy to rubbery state [50]. Furthermore, the storage modulus data showed that the nanocomposite membranes exhibited improvements over the pristine PVC membrane, especially in the case of 1% and 1.6%

Fe₂O₃ membranes, 1% showing the best performance, which reflected an increased intermolecular association after adding Fe₂O₃ nanoparticles [51]. According to Fig. 4b, the glass transition temperature of the pristine membrane was 86.5°C, while that of PVC-1.0%Fe₂O₃ membrane was found to be 94°C, which was the highest value reached among the fabricated membranes. Thus, the presence of nanoparticles generated stronger interfacial bonds within polymer matrix and produced a much stiffer structure [48]. The trends of variation of moduli values with temperature as well as the glass transition temperature values of all the fabricated membranes are in good consistency with the nanoindentation data, which shows that the highest resistance to deformation was reached with PVC/1.0% Fe₂O₃ nanocomposite membrane.

3.3. Contact angle measurement

Surface hydrophilicity is an important parameter since it can directly affect the flux and fouling tendency of the membrane. A dynamic contact angle test was applied at 25 °C to analyze changes in surface hydrophilicity of the PVC and PVC/Fe₂O₃ nanocomposite membranes. The results are shown in Fig. 5.

Fig. 5. Dynamic contact angles of the fabricated membranes with varying loadings of Fe₂O₃.

As shown in Fig. 5, the water contact angle of the PVC membrane decreased by 22% with the addition of Fe_2O_3 up to a final concentration of 1 wt. % due to the hydrophilic nature of the Fe_2O_3 nanoparticles [52], and this indicates that the hydrophilicity of the PVC membrane improved substantially by the addition of Fe_2O_3 . The reduction in contact angles was insignificant at lower Fe_2O_3 loadings and increased gradually as higher loadings were added into the casting solution. Moreover, contact angle values decreased after the Fe_2O_3 content exceeded 1%, which may be attributed to an increase in the viscosity of the casting solution and the reunion of the nanoparticles with a reduced effective area on the surface of the membrane matrix [22]. To show the evidence, viscosity of each casting solution was measured. As it can be seen in the Fig. S3 in the Supporting Information, the viscosity of the casting solution continuously increases up to 1.6% Fe_2O_3 loading. These results proved that at higher nanoparticle loadings, viscosity effect is more pronounced, which is the expected outcome of nanoparticle agglomeration at higher nanoparticle loadings (also clearly shown in Figures 7f and 9f). Moreover, water uptake values of the fabricated membranes that were also tested in Fig. S4 in the Supporting Information in order to show the hydrophilic difference.

3.4. Membrane morphology

SEM imaging and EDX analysis were utilized to investigate the changes in cross-section and surface morphology of the composite membranes after the addition of Fe_2O_3 and the results are given through Figs. 6–9.

The cross-sectional SEM images of the fabricated membranes are given in Fig. 6.

Fig. 6. Cross-sectional SEM images of PVC and PVC/Fe₂O₃ nanocomposite membranes: (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.6 wt. %, (d) 1.0 wt. %, (e) 1.6 wt. %, and (f) 2.0 wt. %.

As illustrated in Fig. 6, the cross-section structures of all the membranes were asymmetric, including a denser skin layer on the surface and a finger-like pore structure in the upper layer followed by a macrovoid structure observed in the sub-layer. The finger-like structure of all the composite membranes incorporated with Fe₂O₃ appeared to be larger than that of a PVC membrane. This structure was due to the higher solvent-water exchange rate during the phase-inversion process, which may be attributed to the high affinity of nanoparticles towards water [19]. Pore connectivity and the enlargement of finger-like microvoids improved across the membrane thickness as the loading increased up to 1.0% [6]. Further loading of Fe₂O₃ nanoparticles led to a change in the structure and size reduction of the finger-like pores, which may be attributed to the viscosity increase of the modified casting solutions delaying the exchange rate between solvent and nonsolvent during the phase inversion process. Similar findings were also demonstrated by Huang et al., who fabricated PES/SiO₂ composite membranes and noted that although the modified membranes had similar finger-like structure as pure PES membrane, the macrovoids and finger-like pores were almost joined together (in the case of 1% SiO₂ loading) showing no boundaries between sub and bottom layers [53].

It is a known fact that the resistance through a membrane is inversely proportional to the thickness of the active layer, which is responsible for permeation and rejection. It can be inferred from the images that the thickness of the active layer decreased with Fe_2O_3 addition up to 1% and increased for further nanoparticle loading [20], which could explicitly be observed for PVC/ $1.6\text{Fe}_2\text{O}_3$ and PVC/ $2.0\text{Fe}_2\text{O}_3$ membranes. The reason for the increase in thickness may be attributed to the viscosity increase of the casting solution, which likely reduced the diffusion rate between the solvent and water leading to a thicker top layer [14]. These findings indicate that the addition of Fe_2O_3 nanoparticles has a large effect on the membrane cross-section structure.

The cross-sectional EDX topologies of the pristine PVC and Fe_2O_3 modified PVC membranes are depicted in Fig. 7.

Fig. 7. Cross-sectional EDX images of PVC and PVC/Fe₂O₃ nanocomposite membranes: (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.6 wt. %, (d) 1.0 wt. %, (e) 1.6 wt., and (f) 2.0 wt. %. Left image shows the distribution of all the elements including C, O, Cl and Fe; right image refers to Fe distribution on the membrane cross-section.

According to Fig. 7, nanoparticles were scattered throughout the entire cross-section of all of the modified membranes and the Fe₂O₃ content continuously increased with the increasing amount of added Fe₂O₃. The amount of Fe in the fabricated membranes increased with serious agglomeration, which started to develop after the 1% Fe₂O₃ addition.

Surface SEM images of the fabricated membranes are illustrated in Fig. 8.

Fig. 8. Surface SEM images of PVC and PVC/Fe₂O₃ nanocomposite membranes: (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.6 wt. %, (d) 1.0 wt. %, (e) 1.6 wt. %, and (f) 2.0 wt. %.

As illustrated in Fig. 8, all the membranes had a porous skin with interconnected surface pores ranging from 15–40 nm in size. The PVC/1.0Fe₂O₃ membrane had a bigger pore size distribution compared to other composite membranes and also the pristine membrane. The pore sizes tended to decrease to accommodate nanoparticle addition beyond 1% due to the blocking of some pores by agglomerated nanoparticles.

The surface EDX images of the PVC and modified membranes showing the distribution of Fe₂O₃ nanoparticles on the surface are given in Fig. 9.

Fig. 9. Surface EDX images of PVC and PVC/Fe₂O₃ nanocomposite membranes: (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.6 wt. %, (d) 1.0 wt. %, (e) 1.6 wt. %, and (f) 2.0 wt. Left column images show the distribution of all the elements including C, O, Cl and Fe. Right column images refer to Fe distribution on the membrane surface.

The EDX analysis was applied to further confirm the distribution of Fe₂O₃ nanoparticles on the top surface of the PVC/Fe₂O₃ composite membranes. The EDX mapping analysis demonstrated that nanocomposite membranes had a good Fe₂O₃ distribution and particle aggregation was negligible. However, at higher loadings of over 1%, the aggregation became serious especially in the case of 2% Fe₂O₃ loading giving rise to pore blockage and hence, decreasing the permeability (Fig. 9).

Table 2 represents the porosities, thickness values and mean pore diameters of the fabricated membranes.

Table 2. Morphological properties of the PVC and PVC/Fe₂O₃ nanocomposite membranes.

Fe ₂ O ₃ loading (%)	Porosity (%)	Thickness (μm)	Mean pore diameter (nm)
0	84.0±0.7	73±2	28.6
0.2	87.1±1.2	74±2	33.3
0.6	88.0±1.1	73±2	33.8
1.0	90.2±1.7	72±2	34.6
1.6	86.4±1.3	74±2	33.6
2.0	80.2±2.2	72±2	33.2

According to Table 2, the porosity of the PVC membrane was found as 84.0%, which was due to the existence of pores forming PEG in the casting solution [6] and this value increased up to 90.2% with the addition of Fe₂O₃ leading to more porous membrane structures. Also, the mean pore diameter of the PVC membrane increased from 28.6 nm to 34.6 nm (in the case of 1% Fe₂O₃). However, there was a reduction in both porosity and mean pore diameter values of the modified membranes as higher loadings of Fe₂O₃ occurred at the same time that porosity experienced a rapid decline. The reduction in porosity was due to the change in finger-like structures with a reduced pore connectivity in the bottom and in the sublayers. The reason why the mean pore diameter decreased after achieving a 1% Fe₂O₃ content could be attributed to the agglomeration of the nanoparticles on the surface of the membrane leading to pore blockage. This result is in accordance with the SEM surface image data presented in Fig. 8.

3.5. Surface Roughness

Determining surface roughness and monitoring the topology of membranes are crucial tasks since they give insight into the anti-fouling behavior of the membrane. Average surface roughness values and three-dimensional AFM images of the external surfaces of fabricated membranes are given in Table 3 and Fig. 10, respectively.

Table 3. The mean surface roughness of the PVC and PVC/Fe₂O₃ nanocomposite membranes.

Fe ₂ O ₃ loading (%)	0	0.2	0.6	1.0	1.6	2.0
Mean surface roughness (nm)	15.9±0.6	10.2±0.5	8.1±0.7	8.3±0.4	10.6±0.6	10.2±0.7

Fig. 10. AFM topography images of the PVC and PVC/Fe₂O₃ nanocomposite membranes: (a) 0 wt. %, (b) 0.2 wt. %, (c) 0.6 wt. %, (d) 1.0 wt. %, (e) 1.6 wt. %, and (f) 2.0 wt. %.

According to Table 3 and Fig. 10, the surface roughness of the pristine membrane was apparently higher than that of the modified nanocomposite PVC/Fe₂O₃ membranes and decreased gradually with the increasing loading of Fe₂O₃ up to 1%, which revealed that the embedment of nanoparticles led to a smoother membrane surface. It was reported that a membrane with a smoother surface had greater fouling resistance since the foulants in water were less prone to adsorb on smoother surfaces. In addition, nanoparticles provided a smoother surface by self-assembling or collocating on the membrane surface [21, 22, 54]. The higher surface roughness when the Fe₂O₃ content exceeded 1% was due to the agglomeration of the nanoparticles before they were embedded into the membrane surface, which is consistent with the data reported for PVDF/ZnO nanocomposite membranes by previous researchers [55].

3.6. Rejection and antifouling behavior

The rejection of PVC and modified membranes with Fe₂O₃ nanoparticles is depicted in Fig. 11.

Fig. 11. Rejections of the PVC and PVC/Fe₂O₃ nanocomposite membranes.

SA rejection of the nanocomposite membranes was higher than that of PVC membrane, which could be attributed to a greater hydrophilic effect disclosed by the Fe₂O₃ addition, which is located at the surface and within the cross-section of the modified

membranes. The rejection value increased with the addition of nanoparticles up to 1.0% Fe_2O_3 having the highest level of rejection (91.9%). The rejection values tended to decrease with more Fe_2O_3 loading due to the ineffective dispersion of nanoparticles in the membrane polymer (Fig. 10). This was also indicated in the literature where dispersion was one of the limiting factors in the incorporation of nanoparticles into polymeric matrices, especially nanoparticles of less than 100 nm in diameter having large surface interactions (Van der Waals forces and inter-planar stacking), which could bring about inhomogeneities and defects in the membrane morphology. Therefore, it becomes difficult to control the aggregation and dispersion behavior in the polymeric membrane matrix, which may induce pore blockage and deposition of nanoparticles on the membrane surface, which inevitably influences the rejection [56]. SA filtration profiles of the fabricated membranes at 0.14 MPa TMP with varying loadings of Fe_2O_3 were included in the Supporting information.

The antifouling characteristics of the pristine PVC membrane and the modified nanocomposite membranes were evaluated in terms of the flux recovery ratio (FRR), and the membrane fouling index for the ultrafiltration membranes (MFI-UF), which are presented in Fig. 12.

Fig. 12. (a) Water flux recovery and (b) membrane fouling index of the PVC and PVC/ Fe_2O_3 nanocomposite membranes after SA fouling.

According to Fig. 12a, the FRR value for a pristine PVC membrane was calculated to be 78.7% after an 8-hour SA fouling test indicating that a substantial amount of membrane fouling occurred due to the adsorption of SA on the membrane surface. The FRR increased to 87.7% with the addition of 0.2% Fe_2O_3 to the casting solution and reached a maximum value of 91.5% in the case of PVC/1.0 Fe_2O_3 . The improvement of the FRR was mainly due to the hydrophilic sites of the nanocomposite membrane, which inhibited the hydrophobic

interaction between the foulant and the membrane surface. The FRR value tended to decline with further Fe_2O_3 addition, which could be attributed to particle aggregation blocking the pores of the membrane. The results are consistent with the surface roughness data, which revealed that the ridge and valley morphology of the PVC membrane induced the accumulation of particles in the valleys; hence, the membrane fouling became more serious than the modified membranes [31]. Moreover, [57] reported that surface roughness could give some insights about the flux rate trend, i.e., membranes with smoother surfaces tended to have less flux decline, which also supports the results presented in this study.

The MFI-UF value indicates the contamination rate of membranes. As shown in Fig. 12b, the pristine membrane had the highest MFI value, which confirms the fact that it had the lowest resistance to contamination. The addition of Fe_2O_3 nanoparticles into the dope solution gradually enhanced the antifouling potential, which had its lowest value with the PVC/1.0 Fe_2O_3 membrane, which tended to increase in value with the further addition of nanoparticles. The MFI value trend was quite consistent with the contact angle of the corresponding membranes, which supported the fact that membranes with more hydrophilic surfaces were less susceptible to fouling.

4. Conclusions

In the present study, PVC membranes were modified by dispersing Fe_2O_3 nanoparticles into the casting solution, and the overall structures of the modified membranes were investigated in terms of morphological characteristics such as porosity, mean pore size, thickness, Fe_2O_3 distribution, hydrophilicity, surface roughness, mechanical strength and membrane performance such as water flux, rejection and anti-fouling ability. The SEM results indicated that the structure of the modified nanocomposite membrane was altered through the interconnectivity of the pores in the porous substrate between the sublayer and bottom layer, which led to a longer finger-like pore structure as well as a larger pore size. Based on the EDX results, Fe_2O_3 nanoparticles were evenly distributed along the cross-section and on the surface of the membranes with serious particle agglomeration beyond 1% nanoparticle loading, which brought about defects to membrane structure rather than an improvement. Filtration performance tests revealed that pure water flux and rejection of the nanocomposite membranes were enhanced significantly with the addition of Fe_2O_3 in comparison with the PVC membrane due to higher porosity and pore size as well as a more hydrophilic surface of the modified membranes. The pure water flux of the membrane with a 1% Fe_2O_3 loading reached 782 $\text{L}/\text{m}^2\text{h}$ with an SA rejection of 91.9%. The antifouling

performance demonstrated that the modified membranes exhibited better antifouling properties with a 91.5% flux recovery ratio and lower fouling index. Moreover, nanocomposite membranes held better mechanical strength in terms of hardness, which showed that membrane compaction resistance could be achieved by incorporating Fe_2O_3 nanoparticles into the polymeric matrix extending the lifespan of the membrane without sacrificing other desirable properties.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

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