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Effect of TiO_2-MWCNTs Nanocomposite on the Performance of Mixed Matrix Nanofiltration Membranes: Manganese Ion Removal

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Abstract

This study aims to investigate the removal of manganese ions from aqueous residues of the chemical industries using neat and mixed matrix polyethersulfone (PES) membranes. Three types of fillers were incorporated into the mixed matrix membranes: functionalized multi-walled carbon nanotubes (MWCNTs), titanium dioxide nanoparticles (TiO_2), and a TiO_2-functionalized MWCNTs nanocomposite. Their purpose was to improve the overall performance of the membranes. MWCNTs were oxidized and functionalized using nitric acid. TiO_2 and TiO_2-functionalized MWCNTs nanoparticles were synthesized by the sol-gel method and Sun et al.'s method, respectively. These nanoparticles were characterized by transmission electron microscopy (TEM) and nitrogen adsorption/desorption isotherms (BET). Both neat and mixed matrix PES membranes were fabricated by the phase inversion method and characterized by SEM and contact angle measurement. They were further subjected to the filtration test for manganese removal. SEM images showed that all the tested membranes have an asymmetric structure with a top-dense layer supported by a sublayer with finger-like pores. Results of the contact angle test demonstrated adding each of these particles (functionalized MWCNTs, TiO_2, and TiO_2-functionalized MWCNTs) reduced the contact angle and, thus, increased the hydrophilicity of the membrane. The results of the filtration tests are as follows; Adding 0.1% functionalized MWCNTs could increase the membrane flux to 28.65 L/m^2h (with 89.3% manganese ions rejection), adding 0.1% TiO_2 increased the manganese ion rejection percentage to 92.06% (with a flux of 8.97 L/m^2h) and adding 0.1% TiO_2-functionalized MWCNTs nanocomposite increased the flux to 26 L/m^2h (with 87.04% manganese ions rejection).

Keywords: *Manganese, Nanofiltration, MWCNTs, TiO_2, TiO_2-MWCNTs nanocomposite, Wastewater treatment*

1. INTRODUCTION

Manganese is one of the most common heavy metals in wastewater and groundwater. The presence of the isotope Mn-54 in nuclear reactor water samples originating from steel equipment corrosion, has been confirmed [1–3]. Mn-54 removal is necessary due to its radioactive properties and its effect on the environment and living organisms [4, 5]. There are several techniques for removing manganese heavy metal from wastewater, such as chemical deposition [6–8], ion exchange [6, 9, 10], adsorption [11–13], and membrane filtration [11, 13].

Membrane processes are of great importance in the area of heavy metal removal, with advantages such as low energy consumption, high mass transfer rate, high efficiency, ease of use and scale-up, and so on [14,15]. Nanofiltration is one of the membrane processes with low energy consumption which has been used for bivalent and multivalent ions removal extensively [13, 17].

Polyethersulfone (PES) is one of the most popular polymers to fabricate membranes for filtration because of its chemical and thermal as well as mechanical strength [17,18]. However, PES membranes suffer from relatively high hydrophobicity and fouling tendency, for overcoming which researchers have proposed different methods. Fabrication of mixed matrix membranes, in which inorganic nanoparticles (such as MWCNTs, TiO_2, silica, MOFs, etc.) are embedded into the polymer matrix, is one of the techniques that are widely used to improve the performance of polymeric membranes [13, 19–22].

In recent years, MWCNTs have attracted much attention due to their unique properties such as high surface area, high mechanical strength, high length-to-diameter (aspect) ratio, high thermal stability, very soft internal surface, and nano-sized dimensions [23–28].

Carbon nanotubes (CNTs) are hollow cylinders with a diameter of nanometers and their structural uniformity and chemical inactivity make them relatively stable[29–31]. However, synthesized CNTs contain various impurities such as amorphous carbon, fullerene, and metal catalyst particles, and these impurities interfere with most of the desirable properties of CNTs [32, 33].In addition, in most applications, we need a stable and uniform dispersion of CNTs, which are insoluble in organic solvents and aqueous solutions in pristine form. Purification of CNTs has been considered by many researchers [34–36]. CNTs are usually purified with strong non-oxidizing acids such as HCL and HNO3 to remove metal residues without affecting carbon species [32, 37], Also, in recent years, amine-containing compounds have been used to modify CNTs [38–41]. By functionalizing CNTs and attaching functional groups on their surface, it is possible to achieve proper and homogeneous dispersion of CNTs in organic solvents and aqueous solutions and simultaneously activate their surfaces by creating active functional groups such as carboxylic acid or hydroxyl groups [42–44]. In addition, the purification of CNTs causes the opening of the tube caps [45].

The researchers showed that the addition of purified and functionalized MWCNTs to the polymer solution can affect the membrane structure and function. They found that the addition of these MWCNTs to the polymer solution can decrease the roughness of the membrane surface[38], increase porosity [39], change the shape of the channels and the size of the pores [23, 46], change the charge on the membrane surface [39, 41, 47], improve the anti-fouling properties [25, 40], increase the hydrophilicity and as a result increase the flux of the membrane [28, 41, 46, 48] and also increase the removal percentage of heavy metals [38, 40].

Titanium dioxide is one of the important titanium oxides that are used in various industries. This ion exchanger has attracted the attention of researchers due to its high thermal and radiation stability, good mechanical properties, high absorption power, and easy recovery for reuse. This metal oxide, which has photocatalytic properties, is known as an efficient adsorbent for removing heavy metals. Also, due to its extraordinary mechanical and chemical properties, this compound has been used to prepare various nanocomposites based on carbon nanotubes [49–51].

TiO_2 is one of the most widely used metal oxides to improve membrane performance for wastewater and sewerage treatment [51–57]. The researchers showed that adding TiO_2 nanoparticles to the polymer solution has different effects. They found that the amount of these nanoparticles in the polymer solution is an important factor [19, 58, 59], and adding the appropriate amount to the polymer solution can increase the hydrophilicity and flux of membranes[19, 59, 60], improve their anti-fouling [61, 62], and separation properties [60–62], change their morphology and mass transfer rate [57, 60, 63], and also reducing their roughness and free energy of the surface [64].

Recent studies have shown that the combination of TiO_2 nanoparticles with MWCNTs [65–68], graphite oxide [61, 62] or other nanoparticles [58, 59] can improve the functional and structural properties of the resulting membranes.

Considering the necessity of removing manganese ions from wastewater and the positive effects of MWCNTs and titanium oxide on the morphology and performance of the polymeric membranes, in the present work manganese ions removal from aqueous wastes by mixed matrix nanofiltration membranes using TiO_2 and MWCNTs nanoparticles was studied. It is necessary to note that the mixed matrix nanofiltration membrane containing TiO_2 and MWCNTs nanoparticles to filtrate manganese ions from wastewater has not been reported elsewhere. The membranes were fabricated by wet phase inversion technique and their morphology and separation properties were characterized by scanning electron microscopy, contact angle, and permeation tests. It is also worth noting that all the used nanoparticles (except pristine MWCNTs) were synthesized and characterized in this work.

2. MATERIALS AND METHODS

2.1. Materials

Polyethersulfone (Mw= 58,000 g/mol) was supplied by BASF, Germany. This material is white and scaly and its structure is shown in Figure 1-A [51]. N-methyl-2-pyrrolidone (NMP) is a polar solvent and has low toxicity and high boiling point. NMP used in this research has a molecular weight of 99.13 g/mol and was supplied by Merck, Germany. This solvent is a clear liquid with a yellowish color and its chemical formula is C5H9NO. A view of its structure is shown in Figure 1-B [69].

Polyvinylpyrrolidone (PVP) is a water-soluble white polymer with the chemical formula (C6H9NO)n. PVP used in this research has a molecular weight of 25,000 g/mol and was purchased from Merck, Germany. A view of PVP structure is shown in Figure 1-C [70]. The manganese ion source used in this research is manganese chloride with the chemical formula MnCl2.2H2O, which is a pink powder with a molecular weight of 161.87 g/mol and purity of 99%, supplied by Merck, Germany. MWCNTs (purity: 95%, outer diameter: 10-20 nm, length: 30 μm) were purchased from Chengdu Organic Chemicals Co. and used as the inorganic additive. Other used materials are listed in Table 1.

2.2. Purification and Functionalization of MWCNTs

Oxidation of MWCNTs with nitric acid leads to the formation of hydroxyl functional groups on the surface and increases the specific surface area, which further increases the surface hydrophilicity and enables their homogeneous mixing with the polymer. MWCNTs were functionalized as follows:

First, MWCNTs were added to 3M nitric acid solution and they were sonicated for 24 h in an ultrasonic bath (WUC-A03H, Daihan Scientific Co, South Korea). Then MWCNTs were separated by filtration and rinsed with demineralized water several times and finally, they were dried for 24 h in an oven at 50 °C. Then, 1.5 g of the dried MWCNTs was added to 600 mL of nitric acid 65%, and the mixture was refluxed for 3 h at 140 °C. After cooling, distilled water was added to the suspension, which was repeated several times. Then, the suspension was filtered and the filtrate MWCNTs were rinsed with distilled water until neutral pH was reached. Finally, functionalized MWCNTs were dried for 24 h at 80 °C [37, 54].

2.3. Synthesis of Titanium Dioxide (TiO_2) Nanoparticles

TiO_2 nanoparticles were synthesized by the sol-gel method [71], which is one of the most suitable methods for producing TiO_2 nanoparticles. For this purpose, 20 mL of 3 M titanium chloride solution was added to 180 ml distilled water and the solution was left for 3 h at room temperature. Then, the pH of the solution was adjusted to 7 by adding a 2.5 M ammonia solution. After the solution was left for 24 h to precipitate TiO_2, it was filtered with filter paper. TiO_2, the filtrate, was rinsed several times with distilled water to remove free chlorine and titanium ions. Finally, the sample was dried at 30 °C for 24 h. The

Table 1. *Other materials used in this research*

Chemical	Purity / Concentration (%)	Manufacturer
Titanium (III) chloride (TiCl3)	99	Merck
Ammonia (NH3)	25	Merck
Nitric acid (HNO3)	65	Merck
Hydrochloric acid (HCl)	37	Merck
Polyethylenimine (C2H5N)n	99.9	Sigma Aldrich

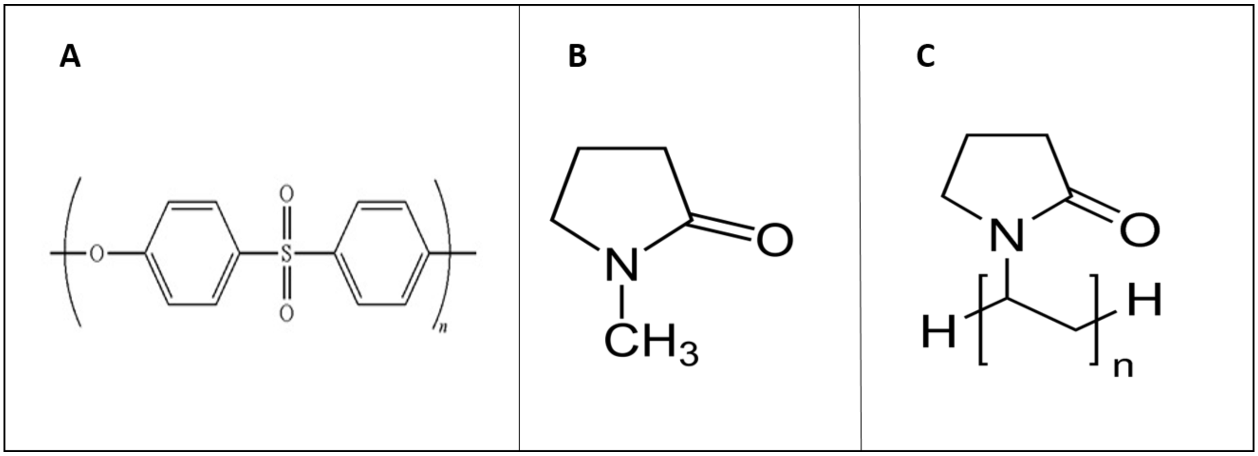

Figure 1*. Chemical structure of* ***A)*** *PES* [51] ***B)*** *NMP* [69] ***C)*** *PVP* [70]

synthesis process of TiO_2 nanoparticles is depicted in Figure 2.

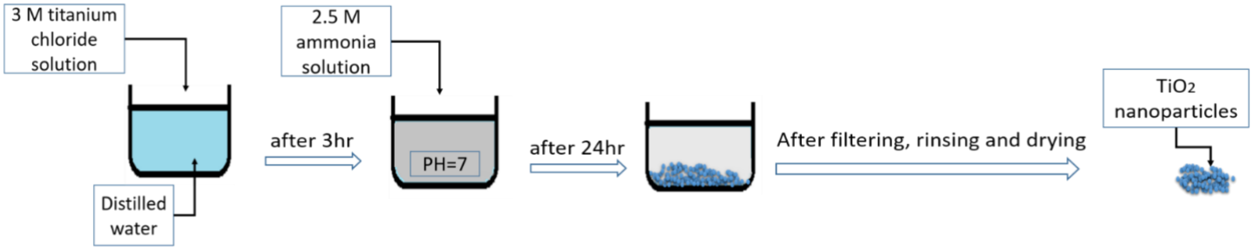

Figure 2. *Synthesis process of TiO_2 nanoparticles*

2.4. Synthesis of TiO_2-Functionalized MWCNTs Nanocomposite

TiO_2-functionalized MWCNTs nanocomposite was synthesized by Sun's technique [72]. 3 M titanium chloride solution was prepared by adding titanium tetrachloride ($TiCl_4$) to hydrochloric acid solution which was kept in an ice water bath. Then, 5 ml of the solution so prepared was transferred to a glass flask together with 1.5 ml of 50 ppm aqueous polyethyleneimine (PEI) solution and distilled water was added until the solution volume reached 300 ml. The flask was covered with aluminum foil and kept in an oven at 70 °C for 3 h until the white precipitate became visible. Then, 0.1 g of the functionalized MWCNTs were added into the flask, and the flask was kept in an ultrasonic bath for 10 min. The suspension was refluxed at 70 °C for 2 h and filtered. Then, the filtrate was rinsed with distilled water several times until neutral pH was reached. The synthesized nanocomposite (TiO_2-functionalized MWCNTs) was placed in an oven at 70 °C for 24 h to dry completely.

2.5. MWCNTs and TiO_2 Characterization

A transmission electron microscope (TEM, CM30, Philips, Netherlands) was used to examine the internal structure of the MWCNTs. A certain amount of MWCNTs was added to water, into which an agar copper grid was immersed to be coated with a thin layer of the suspension. Finally, imaging was performed by installing the grid inside the device and passing electrons through the specimens. The specific surface area, porosity, and total pore volume of TiO_2 were determined by BET (NOVA 2000e, Quantachrome, Germany). There are five types of possible adsorption isotherms, as shown in Figure 3 [73, 74].

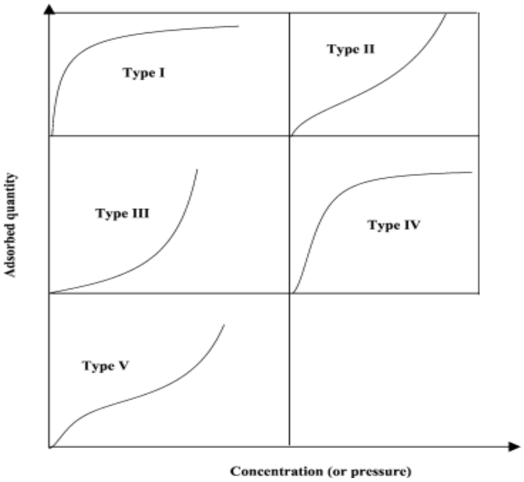

Figure 3. *Five types of BET adsorption isotherms* [72]

2.6. Membrane Preparation

The membrane was fabricated by the phase inversion technique. The polymer solution containing 20 wt.% PES, 0.25 wt.% PVP, and various percentages of functionalized MWCNTs, TiO_2, and TiO_2-functionalized MWCNTs in NMP were cast on a glass plate, immersed into a coagulation bath (water), and kept there for 24 h, followed by drying in an ambient atmosphere for 24 h. The membrane thickness of the cast film was 80 μm. **Error! Reference source not found.** shows the mixed matrix membrane fabrication procedure.

2.7. Membrane Characterization

Gas Permeation System is used to determine the average diameter of the pores on the membrane using nitrogen gas. The gas was passed through the membrane at a certain pressure and the volumetric flow rate (Q) of the permeated gas was measured using a bubble flow meter (as shown in Figure 4). Using measured Q, one can calculate gas permeance (P/l) by Eq. 1 in which A is membrane surface area and l is membrane thickness.

$$\frac{P}{l} = \frac{Q}{A \times \Delta p} \tag{1}$$

Assuming that the surface pores of the synthesized membranes are straight and cylindrical, and that gas diffusion follows Poiseuille and Knudsen flow regimes, Equation 2 can be used to calculate the permeability. Therefore, we have:

$$P = P_p + P_k = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5} \frac{r_{pm}}{RT}\frac{\varepsilon}{L_p} + \frac{1}{8\mu}\frac{r_{pm}^2}{RT}\frac{\varepsilon}{L_p}\bar{p} \tag{2}$$

$$P = A + B\bar{p} \tag{3}$$

In equation 2, P is the total gas permeability (mol/m^2.Pa.s), P_p is the gas permeability in the Poiseuille regime (mol/m^2.Pa.s), P_k is the gas permeability in the Knudsen regime (mol/m^2.Pa.s), R=8.314, M is the molecular mass of the gas, T is the absolute temperature (K), r_{pm} is the average pore radius (m), μ is the gas viscosity (Pa.s), ε is the surface porosity, L_p is the effective pore length (m), and $\bar{p}$ is the average pressure. It is obvious that if the permeability (P) is plotted in terms of the average pressure ($\bar{p}$), using the width from the origin (A) and the slope of the line (B) in the P vs. $\bar{p}$ graph, the average pore size and effective porosity can be obtained using Equation 4 [75].

$$r_{pm} = \frac{16}{3}\frac{B}{A}\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \tag{4}$$

The contact angle of water droplets on the membrane surface was measured by the sessile drop method using a goniometer (OCA 15plus, Data physics, Germany). It is necessary to note that this experiment was repeated 4 times and the average of results was reported.

SEM was used to observe the cross-sectional image of the membrane. The membrane sample was broken in liquid nitrogen, followed by a coating with a thin layer of gold. The sample was then fixed on a brass plate and set inside the SEM equipment (ZEISS, Germany). Finally, a cross-sectional image of the membrane was generated using an electric field [76].

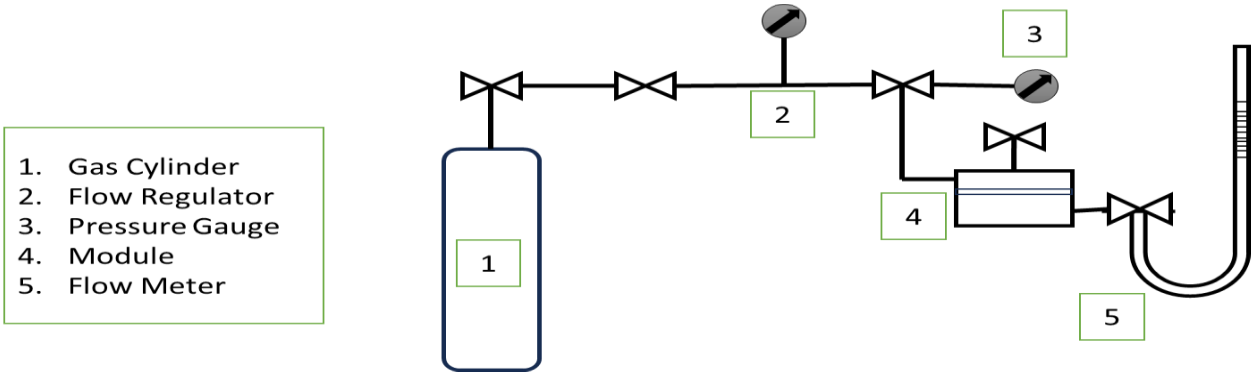

Figure 4. *A simple schematic of the Gas Permeation System*

2.8. Filtration Experiments

To investigate the membrane filtration performance, a permeation system shown in Figure 5 was used at an operating pressure of 10 bar and feed (2 ppm manganese) flow rate of 40 Lh-1. The flux J ($Lm^{-2}h^{-1}$) was calculated by equation 5, where V is the permeate volume (L), t is the duration of the test (h), and A is the effective membrane area (0.00332 m^2) [76].

$$J = \frac{V}{A\ t} \tag{5}$$

The solute rejection R % was determined by equation (6).

$$\%R = \frac{C_f - C_p}{C_f} \times 100 \tag{6}$$

Where C_f and C_p are the manganese concentration of the feed and permeate, respectively [77]. The manganese concentration was measured by the UV-Vis spectrophotometer (Model 4802, UNICO, USA) via complex formation with formaldexime [78].

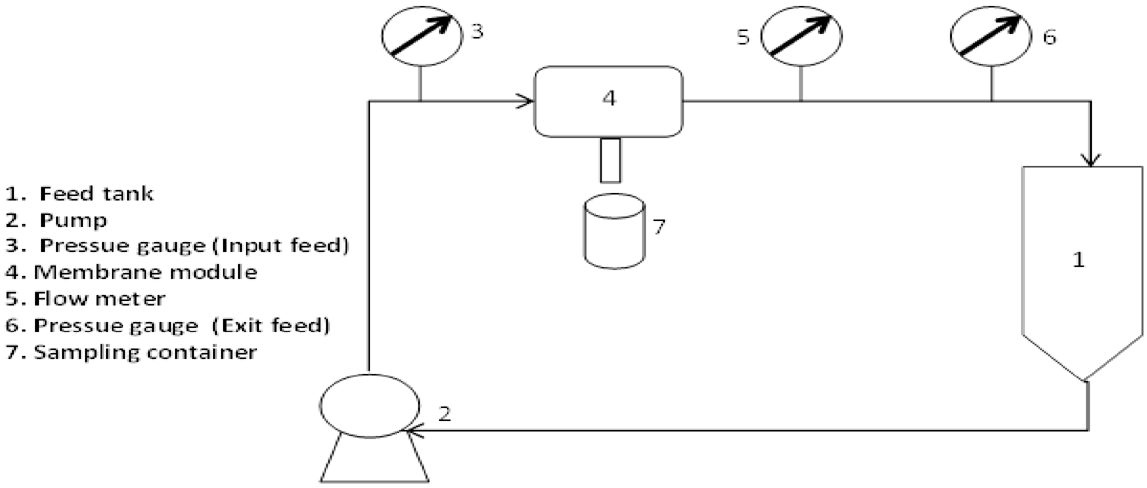

Figure 5. *A simple schematic of the permeation system used*

3. RESULTS

3.1. Morphology Investigation of MWCNTS and TiO_2-Functionalized MWCNTs Nanocomposite by TEM

Figure 6 shows the TEM images of MWCNTs before and after purification and functionalization by concentrated nitric acid. The dark spots of the MWCNTs before purification and functionalization (Figure 6-A), due to the accumulation of MWCNTs and the impurities on their surfaces, decreased significantly after purification and functionalization (Figure 6-B), and the length of MWCNTs was shortened.

In the TEM image of the TiO_2-functionalized MWCNTs nanocomposite (Figure 6-C), the TiO_2 nanoparticles attached to the wall of the MWCNTs can be observed. During the acid treatment of MWCNTs, hydroxyl, and carboxyl groups are formed at the surface of the nanotubes, which allows the uniform dispersion of titanium dioxide nanoparticles on the MWCNTs surface, enabling stable attachment in the polar solutions [72].

3.2. Characterization of TiO_2 by BET

TiO_2 nanoparticles were subjected to the BET analysis in the relative pressure range of 0.20 to 0.99. The results shown in Figure 7 correspond to the type III isotherm of Figure 3. Deviating significantly from the Langmuir theory, it shows multilayer formation due to the adsorbate-adsorbed layer interaction which is more significant than the adsorbate-adsorbent surface interaction. It seems the first monolayer was not fully formed, because the horizontal part was not visible in the isotherm [73, 79–81]. Also, BJH analysis showed that TiO_2 nanoparticles had a surface area of 16.87 m^2/g, pore volume of 0.028 cc/g, and pore diameter of 2.743 nm.

3.3. Average Pore Size of Membrane Surface

Nitrogen gas permeability test was used to calculate the average pore size of the of the fabricated membranes and also to determine the nanofiltration range based on the polymer concentration. The results indicate that the average pore size on the surface of the polymer membrane, containing 20% PES and 0.25% PVP with a thickness of 80 μm, was approximately 2.5 nm. The test confirmed that the pore size of the produced membranes was within the nanofiltration range.

3.4. Contact Angle of the Membranes

Figure 8 shows the contact angle results of PES membranes fabricated from the casting solutions containing different amounts of functionalized MWCNTs (Figure 8-A), TiO_2 nanoparticles (Figure 8-B), and TiO_2-functionalized MWCNTs nanocomposites (Figure 8-C).

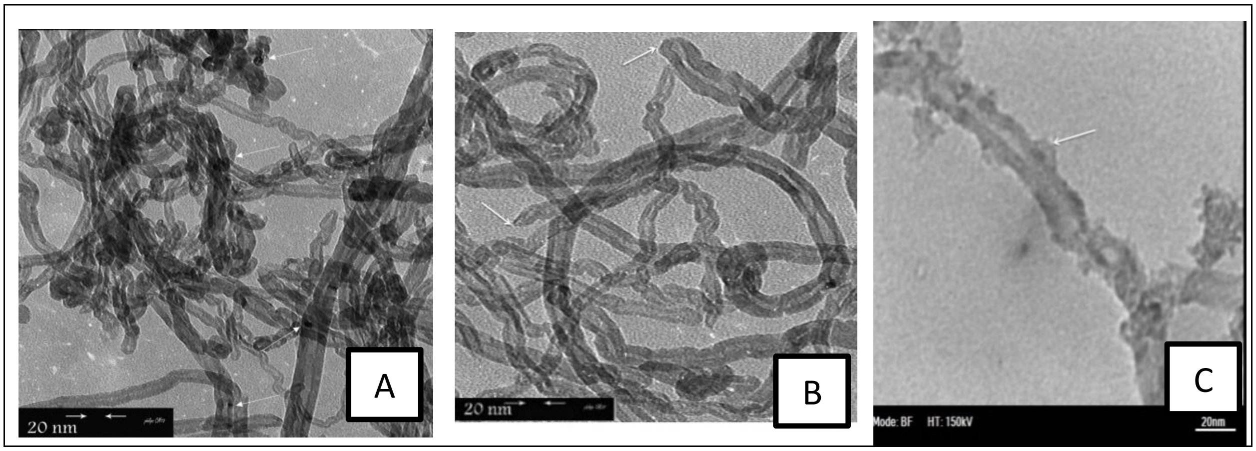

Figure 6. *TEM images of MWCNTs* ***A)*** *before purification and functionalization* ***B)*** *after purification and functionalization C) TiO_2-functionalized MWCNTs nanocomposite*

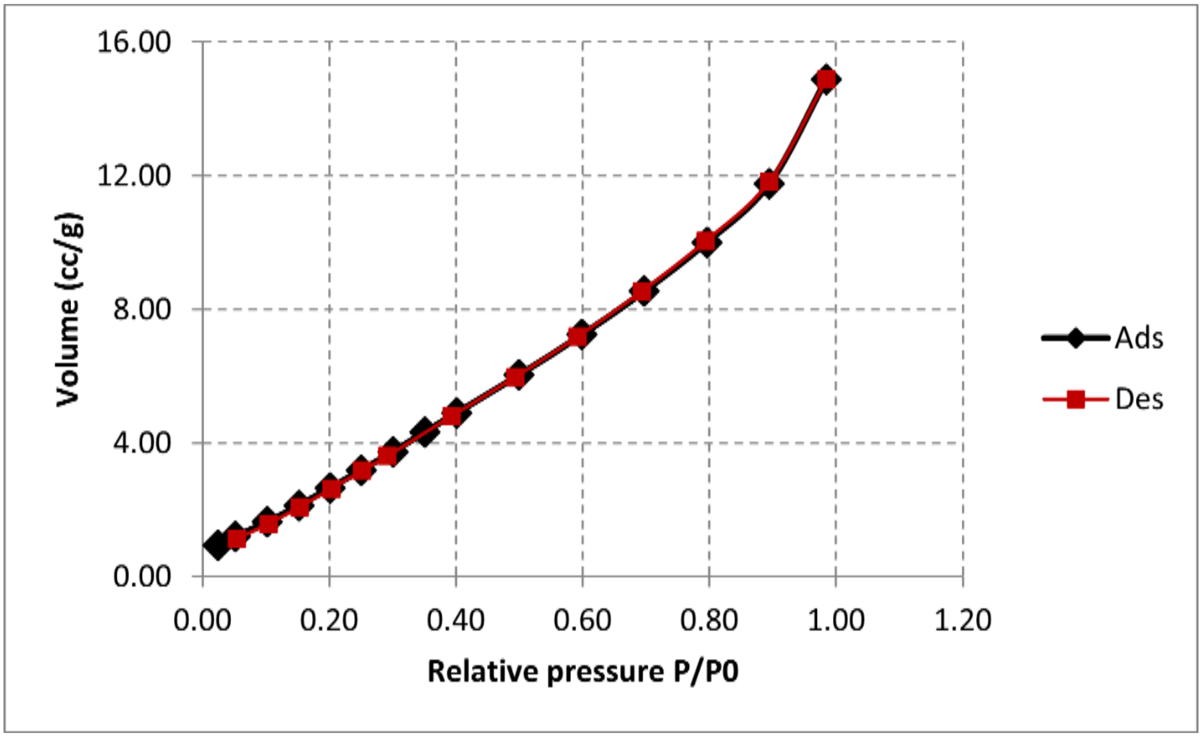

Figure 7: *Nitrogen adsorption and desorption isotherms for* TiO_2

As shown in Figure 8-A, the contact angle decreased upon the addition of functionalized MWCNTs, which is attributed to the presence of –OH and –COOH functional groups in the functionalized MWCNTs. It seems hydrophilic functionalized MWCNTs spontaneously migrated to the interface between the membrane and the non-solvent water during the coagulation process, evidenced by the darker top surface than the bottom surface by visual inspection [47]. Further increase in functionalized MWCNTs slightly increased the contact angle, possibly due to the reduced active surface area of the functionalized MWCNTs by their coagulation [23, 40, 41, 47, 82].

Similarly, increasing the TiO_2 content in the casting solution (0–0.5 wt.%) progressively decreased the contact angle, owing to the intrinsic hydrophilicity of TiO_2 nanoparticles (Figure 9-B). A comparable trend was observed for the TiO_2-functionalized MWCNTs nanocomposite (Figure 9-C) [52, 61].

The addition of TiO_2-functionalized MWCNTs nanocomposite also reduced the contact angle progressively as the amount of the filler increased (Figure 8-C). Comparing the 0.5% addition of functionalized MWCNTs and TiO_2-functionalized MWCNTs nanocomposite, the latter showed a lower contact angle, as expected. It is also likely that the spontaneous migration of TiO_2-functionalized MWCNTs nano-composite fillers took place during the phase inversion process, which caused the contact angle to decrease [82].

3.5. Membrane Morphology

As can be seen in Figure 9, Figure 10, **Error! Reference source not found.** all the m embranes were asymmetric with a denser active layer on top of the porous sublayer. The formation of finger-like macropores were also observed in all the samples [83].

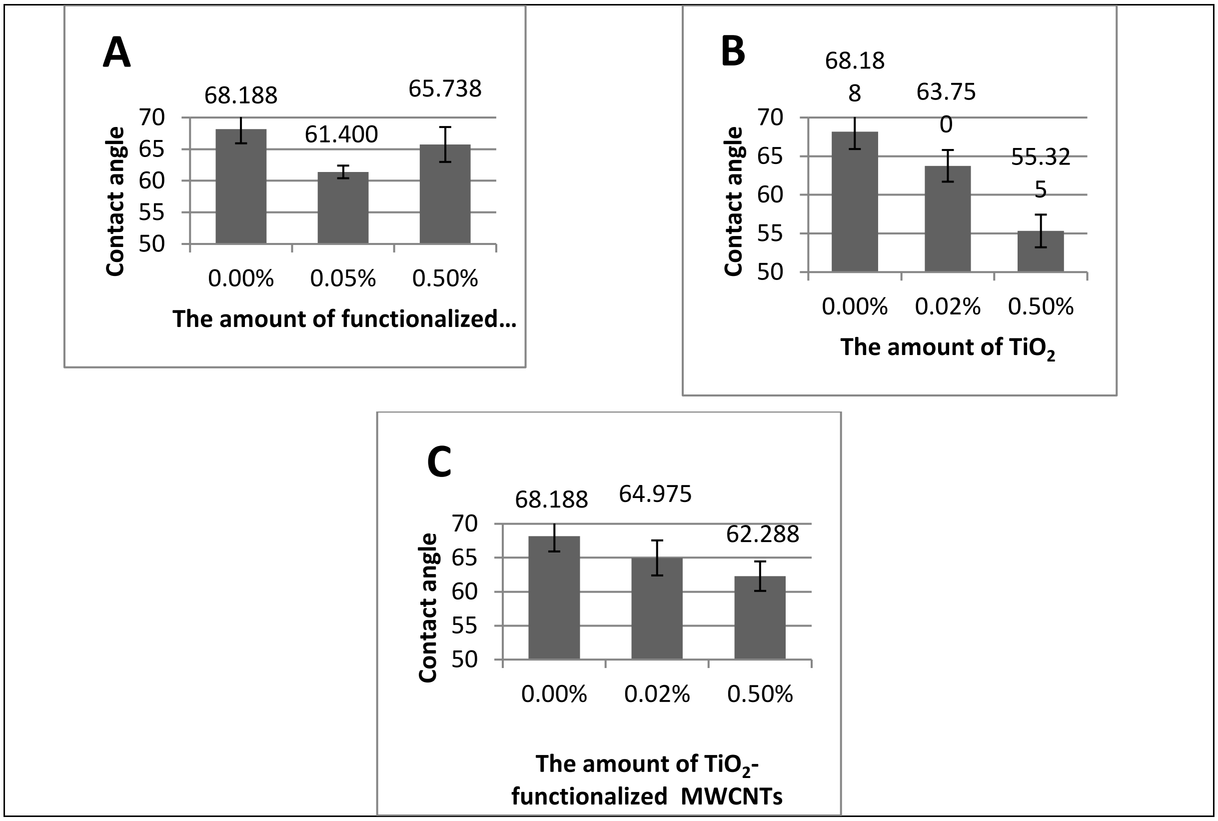

***Figure 8**. Contact angle test results of **A)** PES membrane fabricated from the casting solution containing different amounts of functionalized MWCNTs **B)** different amounts of TiO_2 **C)** different amounts of TiO_2-functionalized MWCNTs nanocomposite*

Figure 9 shows the SEM images of the membranes cast from the solutions containing different percentages of functionalized MWCNTs. These images show that, as the amount of functionalized decreased, which is ascribed to the interplay of the effect of the hydrophilic property of functionalized MWCNTs, which facilitates the solvent-nonsolvent exchange during the phase inversion process, and the increase in viscosity which slows down the solvent-nonsolvent exchange, as already stated [23, 46, 47, 84].

Figure 10 shows the SEM images of the membranes cast from the solutions containing different percentages of TiO_2 nanoparticles. As in Figure 6, finger-like pores are developed, but unlike Figure 6, the pore size did not change noticeably. Probably the amount of TiO_2 nanoparticles was too small to observe the impact of the viscosity increase [83].

Figure 10 shows the cross-sectional SEM images of the PES membranes cast from the solutions containing different percentages of TiO_2-functionalized MWCNTs nano-composite fillers. The figures show the extension of the finger-like pores toward the bottom with a slight increase of the pore size as the fillers increase, which may be due to the increase in the solvent/nonsolvent exchange rate [80].

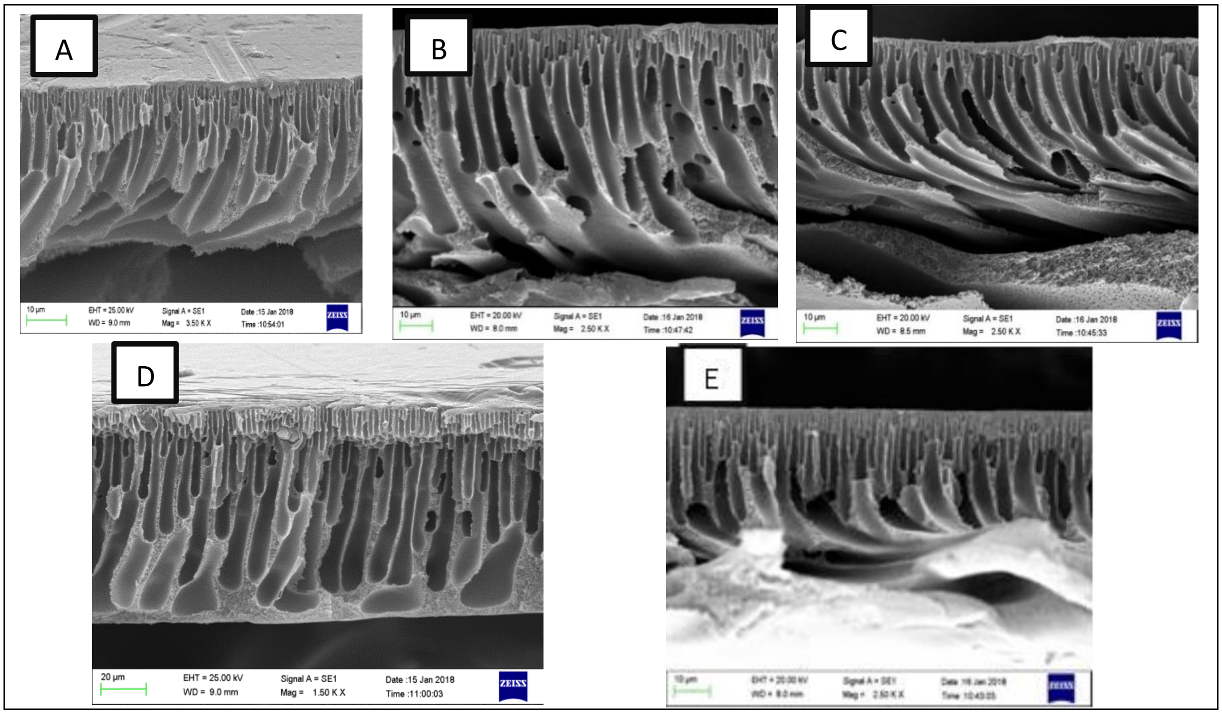

Figure 9. *Cross-sectional images of PES membranes with different amounts of functionalized MWCNTs of* ***A)*** *without functionalized MWCNTs* ***B)*** *0.05 wt.%,* ***C)*** *0.1 wt.%* ***D)*** *0.2 wt.%* ***E)*** *0.5 wt.%*

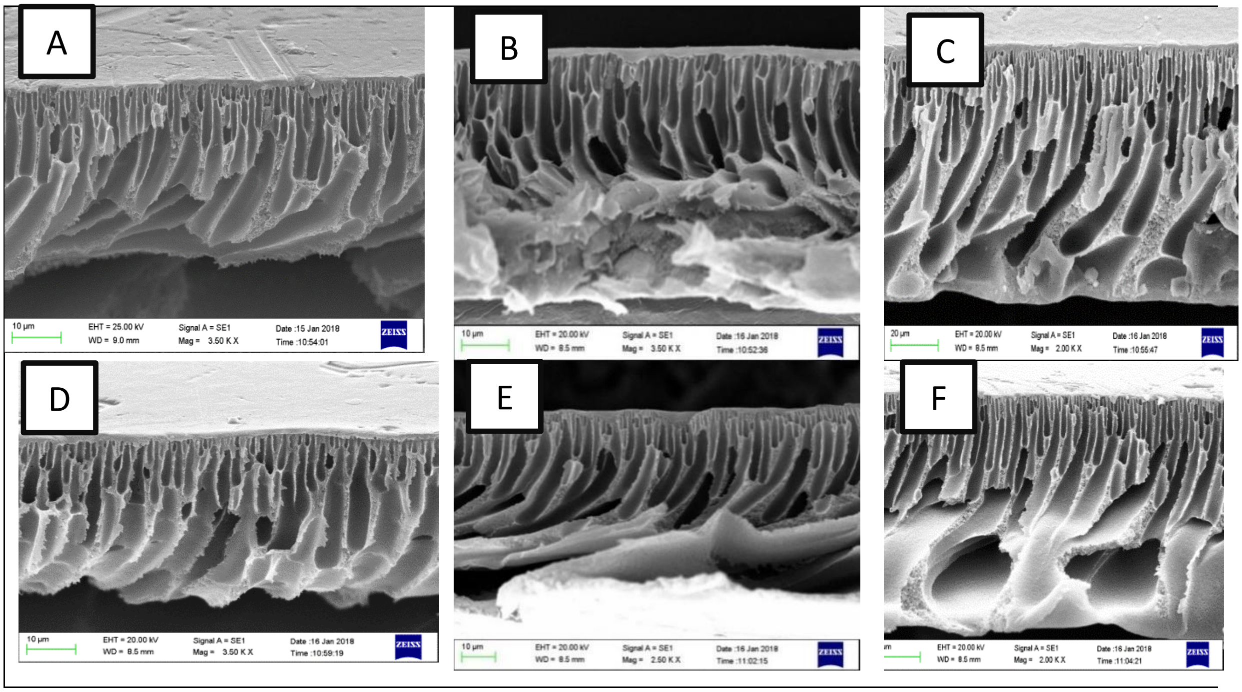

Figure 10. *Cross-sectional SEM images of the PES membranes cast from the solutions containing different percentages of* TiO_2 ***A)*** *without* TiO_2 ***B)*** *0.02 wt.%* ***C)*** *0.05 wt.%* ***D)*** *0.1 wt.%* ***E)*** *0.2 wt.%* ***F)*** *0.5 wt.%*

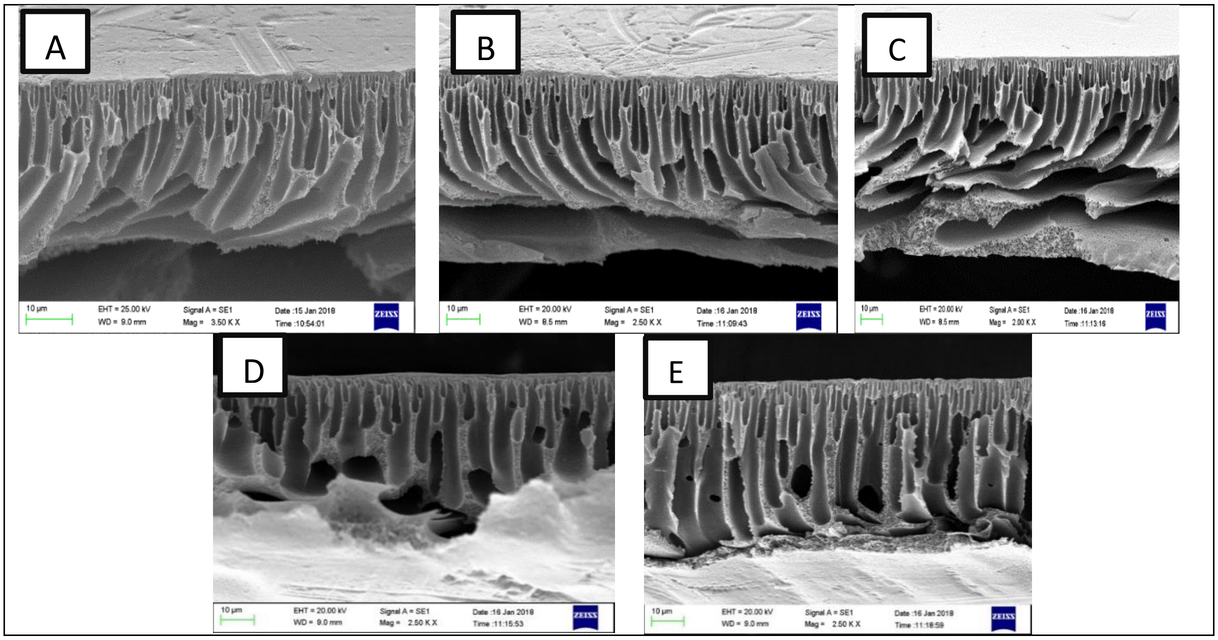

Figure 11*: Cross-sectional SEM images of PES membranes cast from the solutions containing different percentages of* TiO_2*-functionalized MWCNTs* ***A)*** *without* TiO_2*-functionalized MWCNTs* ***B)*** *0.05 wt.%* ***C)*** *0.1 wt.%* ***D)*** *0.2 wt.%* ***E)*** *0.5 wt.%*

3.6 Water Flux and Manganese Ion Rejection Percentage

Figure 12 shows the average results of 3 repetitions of experiments to obtain the water flux and manganese ion rejection percentage. Figure 12-A shows how adding functionalized MWCNTs to the polymeric casting solution affects the flux and manganese ion rejection percentage. Upon the addition of 0.1 wt.% functionalized MWCNTs, both flux and the manganese ion rejection increased. The increase in membrane flux can be attributed to the increase in hydrophilicity by the addition of functionalized MWCNTs (Figure 8-A). The filler functionalized MWCNTs also acted as the pores, providing additional channels for water transport and increasing membrane flux. Also, functionalized MWCNTs, which have -COOH functional groups on their inside and outside surfaces, prevented co-ion (Cl^-) passage due to their negative charge (Donnan effect) and electro-neutrality, leading to an increase in manganese ion rejection percentage [41, 86] When more than 0.1 wt.% of functionalized MWCNTs were added, both flux and separation decreased progressively with an increase of functionalized MWCNTs addition. The flux decrease is likely due to the densification of the membrane, observed as the decrease in the size of the finger-like pores [23, 47] (Figure 9) Aggregation and inappropriate dispersion of functionalized MWCNTs also occurred, thereby increasing the space between functionalized MWCNTs and polymer matrix, and thus reducing manganese ion rejection percentage. The results of the study of the effect of adding TiO_2 nanoparticles to the polymer solution on the water flux of membrane and manganese ion rejection percentage are shown in Figure 12-B. Due to the hydrophilic property of TiO_2, the water influx into the cast film increases during the phase inversion, which is supposed to increase the flux of the membrane. However, the experimental data showed an opposite trend. This was probably due to the closure of the membrane surface pores by the nanoparticles during the phase

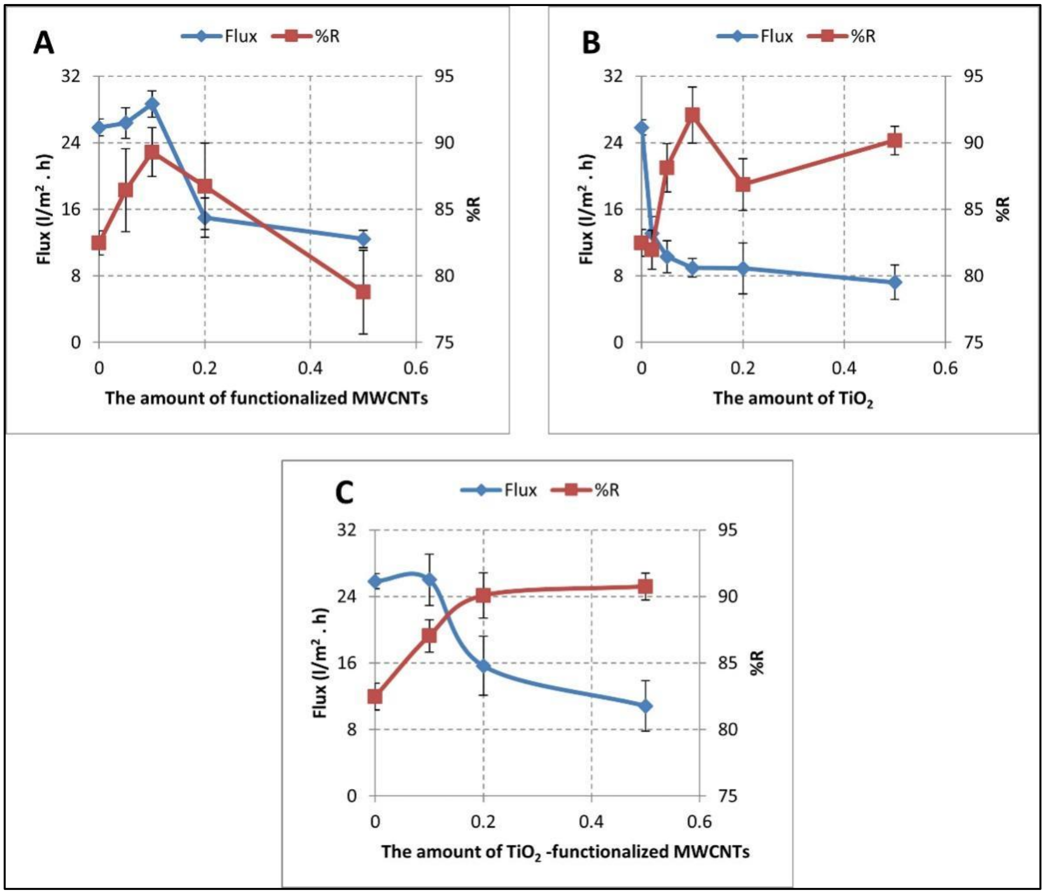

Figure 12. *Effect of the filler addition on the flux and manganese ion rejection percentage A) effect of functionalized MWCNTs B) effect of TiO_2 C) effect of TiO_2-functionalized MWCNTs nanocomposite*

inversion process, working against the hydrophilic effect [57, 87]. This also explains the increase in the manganese ion rejection percentage by adding TiO_2 [57].

Figure 12-C shows the performance of membranes containing different amounts of TiO_2-functionalized MWCNTs nanocomposite. It can be seen that upon adding 0.1 wt.% of TiO_2- functionalized MWCNTs nanocomposite the flux slightly increases and thereafter decreases, while the manganese ion rejection percentage keeps increasing with the increase of TiO_2-functionalized MWCNTs. This is the result of the complicated interplay of hydrophilicity increase (Figure 8-C), acting of functionalized MWCNTs as the additional channels for water transport, prevention of manganese ions from passing those channels due to Donnan effect and electro-neutrality, and the blocking of pores by TiO_2 nanoparticles [47, 82, 86].

4. CONCLUSION

In this study, the removal of manganese ions from aqueous residues of the chemical industries was attempted using neat and mixed matrix polyethersulfone (PES) membranes. Functionalized multi-walled carbon nanotubes (MWCNTs), titanium dioxide nanoparticles (TiO_2), and the nanocomposite of the functionalized multi-walled carbon nanotubes/titanium dioxide nanoparticle (TiO_2-functionalized MWCNTs nanocomposite) were used as the fillers in the mixed matrix membranes. The following important conclusions can be drawn from the experimental data:

1. TEM images show that MWCNTs were purified and functionalized well by nitric acid and TiO_2 nanoparticles were attached to functionalized MWCNTs surfaces.
2. The SEM images showed that the addition of functionalized MWCNTs to the polymer solution caused the formation of finger-like pores and the reduction of the size of the pores. Also, the addition of TiO2-functionalized MWCNTs nanocomposite resulted in a slight increase in the membrane's pore did not change the membrane's morphology drastically.
3. Contact angle test proved that the addition of functionalized MWCNTs and TiO2-functionalized MWCNTs nanocomposite decreased the contact angle and thus increased the membrane's hydrophilicity.
4. Permeation test showed that the addition of functionalized MWCNTs and TiO_2-functionalized MWCNTs nanocomposite increased the membrane flux and manganese ion rejection percentage. However, by the addition of TiO_2 nanoparticles, membrane flux was nearly constant while the manganese ion rejection percentage was increased.

Since no study has been done on the separation of manganese ions from wastewater by mixed matrix nanofiltration membranes containing functionalized MWCNTs, TiO_2, and TiO_2-functionalized MWCNTs nanocomposite, in this study, we showed that the addition of these nanoparticles can positively affect the membrane's performance in removing manganese ions from wastewater.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest associated with this publication. The author has read and agreed to the publication of the manuscript.

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