
A comparative study for the rejection of Nickel ions from wastewater by PES, fMWCNTs/PES, TiO₂/PES, and TiO₂-fMWCNTs/PES mixed matrix membranes

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ABSTRACT

In this study, the neat polyethersulfone (PES) membrane and the mixed matrix membranes (MMMs) containing 20 wt. % polyethersulfone (PES) and different amounts of functionalized multi-walled carbon nanotubes (fMWCNTs), TiO₂, and TiO₂ coated on fMWCNTs were fabricated by wet phase inversion and conventional casting methods. The nickel ions rejection and permeate flux performance were then investigated and compared by these fabricated membranes. The characteristics of the membranes were performed by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and contact angle (CA) measurement. The operational parameters such as polymer concentration, pressure, pH, time and nickel ion concentration for nickel ions rejection and permeability were firstly optimized on the neat PES membrane. The performance of MMMs containing various amounts of nanoparticles was then evaluated and compared under these optimized conditions. The obtained results indicated that the membrane containing 20 wt. % PES, and operational condition like pressure 15bar, low concentration of nickel, time =30min and various amount of pH was the best conditions to achieve the highest rejection percentage of nickel ions and permeate flux. In such operational conditions, PES/fMWCNTs and PES/TiO₂ membranes have the highest nickel ion rejection and permeate flux, respectively. Totally the prepared mixed matrix membranes showed that they have higher ability to reject nickel ions from wastewater and a higher permeate flux value compared with the neat PES membrane.

Keywords: Nickel; Functionalized Multi-Walled Carbon Nanotubes; TiO₂; Mixed Matrix Membranes; Rejection

I. INTRODUCTION

In the last decades, the major concern in different countries is the degradation of fresh water resources by water contaminates such as heavy metals. Mostly, water pollution happens due to the

growth in industrial activities and directly discharging of their wastewater to the environment without any suitable treatment [1]. Nickel as one of the harmful and common heavy metals is applied

in various industries such as, electroplating, battery, coins, metallic alloys, mineral processing, porcelain, and enameling and paint [2, 3]. Therefore, Nickel ions can be found in wastewater of these industries with different concentrations. On the other hand, ^{63}Ni and ^{59}Ni the two radioisotopes of nickel were found at nuclear power reactors and their environments as a result of neutron activation of stable nickel (^{58}Ni , ^{62}Ni) existing in the structural materials of nuclear power plants such as steel, graphite, concrete, and lead. These radioisotopes can be released into cooling water followed by concentration in various radioactive wastes, especially dry active wastes, mixed cation and anion exchange resins used for purification of the cooling water and other waste streams [4]. Since ^{59}Ni and ^{63}Ni are radionuclides with a long half-life ($t_{1/2}^{63}\text{Ni}=76,000$, and $t_{1/2}^{59}\text{Ni}=100$ years,) and X-ray and beta emitters, respectively, these radionuclides represent a hazard for biological systems [5]. When nickel ion even in low concentration enters into the living being through various sources (air, water, and food), it readily accumulates in various tissues and causes damage. Thus, it has the potential to produce a variety of pathological effects like lung fibrosis, cardiovascular and kidney diseases, contact dermatitis and even cancer [6]. According to World Health Organization (WHO), to protect human beings, the tolerance limit of nickel in drinking water should be kept at about 0.02 mg/L^{-1} [7]. Hence, to meet the water quality standards, the removal of even trace amount of nickel ions from wastewater by a proper treatment method is very worthwhile.

Considering the hazardous nature of this ion, several chemical and physical techniques including ion-exchange, solvent extraction, precipitation, ultrafiltration, nanofiltration, adsorption, reverse osmosis, ion flotation and electrodeionization [8-15] have been employed for nickel ion removal from liquid solution. Among these methods,

nanofiltration process which can be described as “low-pressure reverse osmosis membranes” benefits from low energy consumption, high efficiency of multivalent ions removal, ease of operation and reliability [16]. However, appropriate material selection with high flux and high rejection rate plays the main role to success of nanofiltration process in the removal and rejection of any pollutants from water. At the present time, Polymeric membranes with a great capability in the field of wastewater treatment were extensively used for the fabrication of asymmetric nanofiltration membranes. The commonly used polymers which have been widely reported in the literature are aromatic polyamides (PA), acetate cellulose (AC), polysulfone (PSU), polyethersulfone (PES), polyvinylidene fluoride (PVDF), and polypropylene (PP) [17-19]. Among these diverse polymers, PES is one of the most commonly used polymers in fabrication of commercial and research nanofiltration membranes. And that is due to its thermal and chemical stability, outstanding mechanical strength, favorable selectivity, film formation property, and good compatibility with hydrophilic filler [20]. However, because of its hydrophobic nature and inevitable problem of its fouling, this polymer should be modified [21]. In order to overcome these disadvantages and increase the performance of this membrane, the mixed matrix membranes have been used to take advantage of the properties of polymeric and inorganic materials [22, 23]. In this regard, incorporation of nanomaterials such as titanium oxide [24], zirconium oxide [25], ferrous oxide [26], cerium oxide [27], graphene oxide [28], magnesium oxide [29], aluminum oxide [30], tin oxide [31], functionalized multiwalled carbon nanotubes (fMWCNTs) [32], and... as modifiers have been explored by many researchers and it seems to be efficient on the heavy metal removal. Also, the use of this material on the structure of polymer

membranes can help increase the rejection of metal ions as a result of adsorption of them on these adsorbents. Among these nanomaterials, TiO_2 and functionalized multiwalled carbon nanotubes have received most attention because of their unique properties such as their high hydrophilicity, good chemical stability, innocuity, and high surface [33, 34].

Recently, only few studies have been done to reject some heavy metals by incorporation of nanoparticles into PES membranes. To the best of our knowledge and based on the detailed review, the literature is silent on the preparation of mixed matrix membranes such as PES/ TiO_2 , PES/fMWCNTs, and PES/ TiO_2 -fMWCNTs for the removal of nickel ions from wastewater. Therefore, the aim of this research work was the preparation of mixed matrix membranes including PES/ TiO_2 , PES/fMWCNTs, and PES/ TiO_2 -fMWCNTs to evaluate nickel ion removal from wastewater by nanofiltration process. In this regard, the operation parameters such as PES concentration, initial concentration of nickel in feed solution, time, operating pressure, and pH were firstly optimized on neat PES membrane. Finally, the performance of nickel ion rejection on these mixed matrix membranes was investigated and compared under the optimized condition.

II. EXPERIMENTAL

A. Materials

All chemicals and reagents used were of the analytical grade obtained from E. Merck or Fluka companies. Polyethersulfone (PES) was purchased from BASF SE, Germany. MWCNTs (purity=95%, outer diam Zeter =10-20 nm, length = 5-15 μm) used in this work were supplied by Chengdu Organic Chemical Co. Ltd., China. A stock solution of nickel (1000 mg/L^{-1}) was prepared by dissolving specific amount of nickel nitrate in demineralized water (DMW). To prepare the solutions with desired concentrations, this stock

solution was further diluted with demineralized water. Also, a negligible amount of nitric acid and sodium hydroxide solutions with the concentration of 0.1 mol/L^{-1} used to adjust the pH value of the solution.

III. PURIFICATION AND FUNCTIONALIZATION OF OF MWCNTs

Purification and functionalization of MWCNTs were performed according to literature method described elsewhere [35]. In this procedure, 1 gram of MWCNTs was immersed in a 100 mL concentrated nitric acid and refluxed for 2h at 140°C . After separation of MWCNTs through a polytetrafluoroethylene (PTFE) filter membrane ($0.45 \mu\text{m}$ pore size), functionalized MWCNTs were washed repeatedly using demineralized water until the solution pH value reached 6.5. Finally, the samples were dried in an oven at 80°C for 24h.

IV. SYNTHESIS OF AMORPHOUS TiO_2

Nanosized TiO_2 was prepared by sol-gel method using TiCl_4 as a precursor. In the first stage, a certain amount of TiCl_4 was dissolved in 50 mL of cooled demineralized water into 250 mL conical flask while the container was placed in an ice water bath. The concentration of titanium was adjusted to 0.3 M and after that pH of this aqueous solution reached 7 by addition of negligible amount of 2.5 M NH_3 solution. The prepared precipitate is filtered and repeatedly washed with demineralized water. Finally, to remove the remaining ammonium and chloride ions, the prepared particles were washed repeatedly by demineralized water and the residue was dried over night at 30°C .

V. SYNTHESIS OF FMWCNT/ TiO_2

To prepare fMWCNTs/ TiO_2 hybrid material, it was performed according to literature method described elsewhere [36]. To this end, an appropriate amount of TiCl_4 was added to HCl solution until the 3M titanium solution in 0.5 M HCl was achieved. Then, 5 mL of 3 M titanium was added to 295 mL of demineralized water. In the next step, 1.5 mL of

50 ppm polyethyleneimine (PEI) solution was added while the solution was stirred. After that, the container was covered by aluminum foil and put in an oven for 3 hours at 70 °C. Subsequently, 0.1 g fMWCNTs were added to this mixture and put in an ultrasonic for 10 minutes. Ultimately, the mixture was refluxed at 70 °C for 2 hours and the synthesized hybrid was separated by filtration, washed frequently with demineralized water and dried in an ambient temperature for 24 h.

VI. MEMBRANE FABRICATION

Wet phase inversion and conventional casting methods were used to fabricate flat sheet nanofiltration membranes including pure PES, PES/MWCNTs, PES/TiO₂, PES/MWCNTs-TiO₂. For this purpose, at first the specific amount of pure PES was added to N-methyl pyrrolidone (NMP) as a solvent. Then, 0.25% polyvinylpyrrolidone (PVP) was added to the mixture, sonicated for 30 minutes and stirred for 24 h to distribute entirely the particle in the solvent. Also, to prepare the MMMs, the various amounts of prepared fMWCNTs, TiO₂ and MWCNTs-TiO₂ were added to the solution after the complete dissolution of PVP and PES in NMP. The air bubbles into the polymeric solutions were omitted using ultra sonic bath for 30 min and allowed to settle overnight. To fabricate flat sheet membranes, the mixtures were casted on a glass plate by a casting knife with thickness of 110 μm and immediately they were immersed in DMW bath. To complete the separation phase and the removal of the remaining solvent from membrane, the obtained polymeric films were kept in distilled water for 24 h. Finally, the prepared flat sheet membranes were dried at an ambient temperature for one day [37].

VII. EQUIPMENT

Micrograph of prepared hybrid (TiO₂ coated on fMWCNTs) was obtained with a transmission electron microscope (TEM) using the acceleration voltage of 200 kV (model: CM30, Phillips). Morphology of fabricated membranes was also characterized using field emission scanning

electron microscopy (FESEM) model S-4160, Hitachi, Japan. The static contact angle was measured by the sessile drop method using a contact angle measurement instrument (OCA15EC, Data physics, Germany). The amount of nickel ions in the feed and permeate solutions was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) technique.

To evaluate the performance of the fabricated PES and the mixed matrix membranes for nickel ions rejection, the permeation tests including the measurement of the permeate flux and rejection percentage were used. At first, the operating condition for rejection of nickel ions was optimized on pure PES membrane and then the rejection of nickel ions by others membrane in the optimized conditions was investigated and compared.

Fig. 1 shows a cross-flow stainless steel nanofiltration (NF) setup which was selected to perform these experiments. As shown in Fig. 1, the NF setup is outfitted with a membrane cell with an effective area of 33 cm²[38]. To monitor the operating pressure of both sides of the cell, two pressure gauges (Wika, Korea) were used. In addition, a high-pressure dosing pump (Jesco, Germany) was used to transfer the feed solution into the membrane cell. Other main constituents which used on the NF setup were two flow-meters on permeate and retentate streams, one pressure control valve and one pressure safety valve.

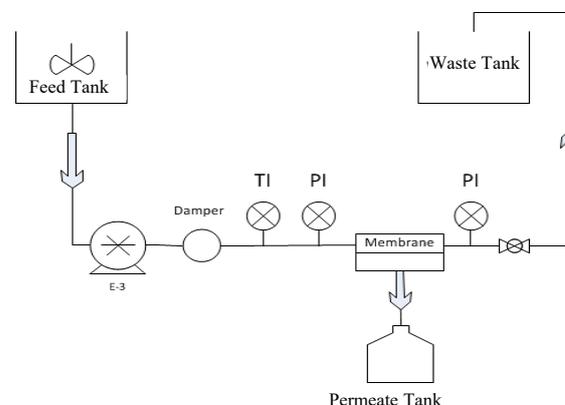


Fig. 1. Schematic depiction of nanofiltration setup

VIII. RESULT AND DISCUSSION

A. Characterization

To investigate the morphology of prepared fMWCNTs-TiO₂ hybrid, transmission electron microscopy technique was used. TEM image of this hybrid material has been shown in Fig. 2. As can be seen, the attachment of TiO₂ nanoparticles on the external surface of functionalized MWCNTs as defects with an average size of 10 nm was done successfully.

FESEM analyzer was used to study the structure and morphology of the fabricated flat sheet membranes. Fig.3a-3d show the FESEM pictures of cross sectional of these membranes. As can be seen in the all images, the structure of these flat sheet membranes was well-designed finger-like sub-layer with dense top-layer. These photographs show that with increasing all the nonmaterials (fMWCNTs, TiO₂ and fMWCNTs-TiO₂) in the structure of PES(Fig. 3B, C and D), the thickness of skin layer decreases compared to the structure of neat PES membrane. Also, we can see that by addition of TiO₂ the size of macrovoids was diminished and the lengths of them were elongated(Fig. 3C) while FESEM images of membranes containing fMWCNTs and fMWCNTs-TiO₂(Fig. 3B and 3D) show that the size of macrovoids was expanded and the lengths of them were shortened. Therefore, we can conclude that the mechanism of the in MMMs rejection alters by the addition these nanomaterials. Nevertheless, the finger-like structure of all the fabricated membranes was not influenced by nanomaterials. Some papers have been reported similar results with our work [39].

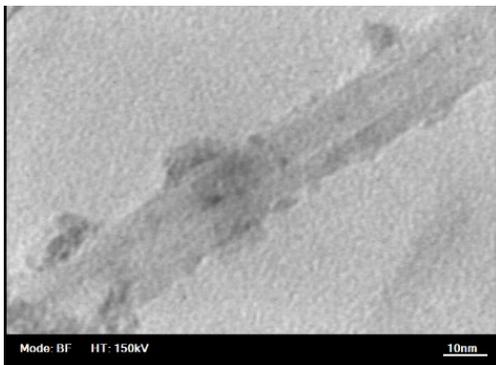


Fig. 2. TEM image of TiO₂ coated on fMWCNTs

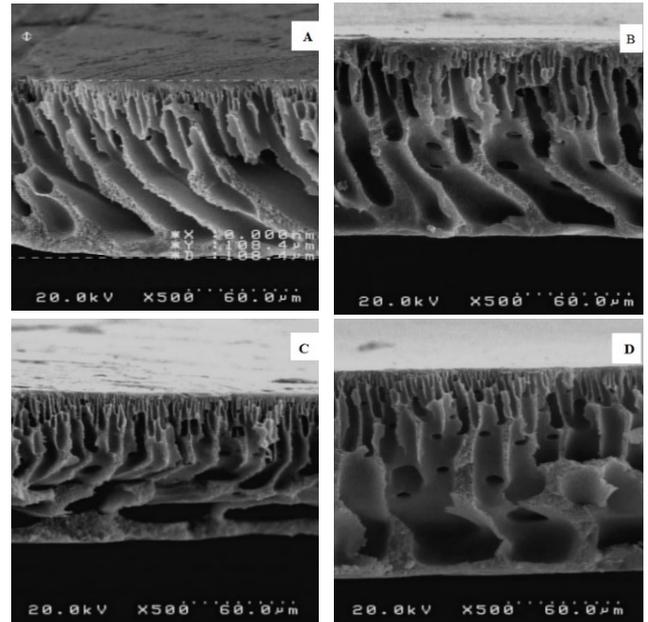


Fig. 3. The cross-section FESEM images of membranes (A) pure PES, (B) MWCNT (C)TiO₂ (D)TiO₂-MWCNT

One of the important properties of membranes, which can affect the flux and anti-fouling ability of membrane are the surface hydrophilicity. Membrane hydrophilicity property was evaluated by measuring the contact angle that was formed between the membrane surface and water as the probe liquid. These measurements were performed at three random locations for all of the fabricated membranes to minimize the experimental error. The obtained results of water contact angle have been presented in table 1. As can be seen in the table, the addition of nanomaterials can reduce the contact angle and consequently enhance the hydrophilicity properties of these membranes. According to the data, the pure PES and PES/TiO₂ membranes have the highest and lowest water contact angle, respectively ($72.5 \pm 1.9^\circ$, $50.75 \pm 1.4^\circ$). Due to the presence of hydrophilic functional groups on the surface of fMWCNTs, the increasing of them to PES can cause the increasing its hydrophilic properties. As shown in table 1, by embedding TiO₂ coated on fMWCNTs into the structure of PES, the hydrophilicity of the prepared mixed matrix membranes was higher than non-coated fMWCNTs membranes. However, the fabricated membrane containing TiO₂

nanoparticles caused to more decreasing of contact angle and enhanced hydrophilic properties of PES membrane. And this is due to the presence of TiO₂ nanoparticles which contain a great deal of hydroxyl groups, responsible for the hydrophilicity increase [21].

B. Permeation test results

To evaluate the effect of polymer concentration on the maximum nickel rejection and flux, four solutions containing 15, 18, 20 and 22 wt. % PES were prepared and the membrane was fabricated by wet phase inversion and conventional casting methods. The result of permeate flux and nickel ions rejection percentage by these membranes have been shown in Fig. 4. As shown, the rejection percentage of nickel ions increases with a raise in polymer concentration while the permeate flux decreases. As a result of the use of high concentration of polymer, the thickness of polymer active layer and the size of porosity will be increased and decreased, respectively [40]. Therefore, this influences on the amount of solvent passing from membrane (reduce the amount of flux) and increase the rejection of nickel ions. The highest rejection percentage would be advantageous for the membrane performance, but disadvantageous for the permeate flux. Based on the obtained results, the optimal concentrations of polyethersulfone were determined as 20% PES. The membranes made of these concentrations will be studied in the rest of the article and will be referred as neat PES.

Table 1
Water Contact Angels of the Fabricated Membrane

Sample	Contact angel
PES (20% wt.)	72.85 ± 1.9°
PES/fMWCNTs (PES, 20%wt. / MWCNTs, 0.7% wt.)	60.75 ± 1.6°
PES/TiO ₂ (PES, 20%wt. / fMWCNTs, 0.7% wt.)	50.75 ± 1.4°
PES/fMWCNTs -TiO ₂ (PES, 20%wt. / fMWCNTs, 0.7% wt.)	55.05 ± 1.7°

The effect of feed pressure on the nickel ion rejection percentage and the permeate flux was demonstrated in Fig. 5. The results revealed that an enhancement of pressure has a favorable effect on the raise of the permeate flux. However, the amount of nickel ions rejection percentage was firstly enhanced linearly and then kept constant with increasing the pressure value. At low pressure, high diffusive transport of nickel ions through the membrane compared to convective transport is the reason for low rejection [41]. As convective transport becomes more important with a raise in pressure value, the rejection of ions will also increase. It is important to note that the increasing of concentration polarization as a result of the increase of pressure will be also led to the decrease in rejection of ions (due to the decrease of Donnan effect). The counteracting contributions of increased convective transport and increased concentration polarization will be resulted in a constant rejection value of ions as it can be seen in Fig. 5 for nickel ions rejection.

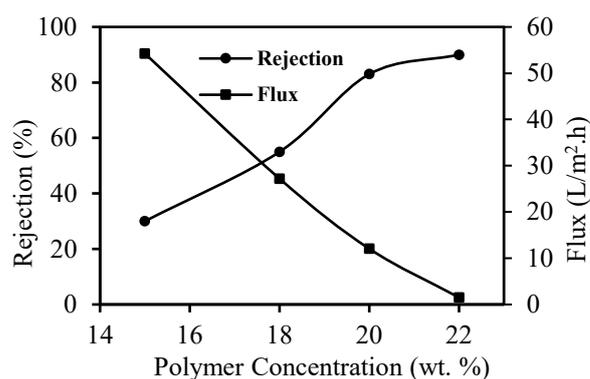


Fig. 4. Permeate flux and nickel ion rejection percentage by the neat PES membranes versus the polymer concentration (wt.%) (12 bar, 35 L/h, 20 ppm Ni²⁺, pH=6 ± 0.1, 30 min)

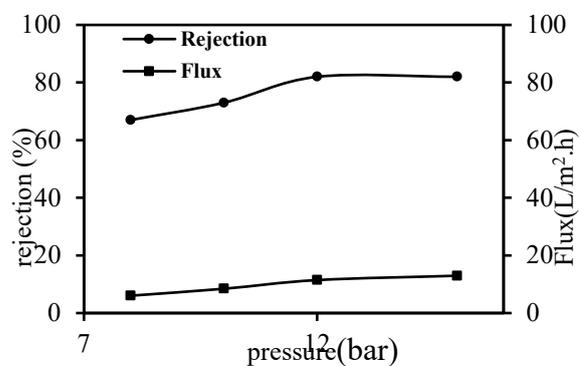


Fig. 5. Permeate flux and nickel ions rejection percentage by the neat PES membranes versus the pressure (PES 20 wt.%, 35 L/h, 20 ppm Ni²⁺, pH=6 ± 0.1, 30 min)

The effect of the feed solution pH on the rejection of nickel ions and permeate flux was studied and the result was depicted in Fig. 6. According to the solubility product of Ni(OH)_2 ($\text{pK}_{\text{sp}}=15.69$), it is clear that the most dominant species of nickel at pH values above 6 was found to be as Ni(OH)_2 , and other species such as Ni^{2+} and Ni(OH)^+ is negligible. In other word, the fouling of the membrane by Ni(OH)_2 particles at higher pH is challenge to investigate the scrutiny of nickel ions rejection. Therefore, the effect of pH was studied up to 6. As shown in Fig. 6, there is very negligible change in the rejection percentage of nickel ions with changing in the feed solution pH. Also, this figure shows that the permeate flux reduced with increase in feed solution pH which it can be due to the shrinking of the active layer as a result of the hydration differences of ionized groups on the membrane [42].

The effect of nickel ion concentration on its rejection percentage and permeate flux was studied and the results have been shown in Fig. 7. As shown, an enhancement of nickel ion concentration from 5 to 30 ppm decreases the rejection rate from 88% to 71%. This phenomenon can be due to the increase in osmotic pressure when increasing feed concentration; this osmotic effect subsequently leads to a permeate flux decline and thus the rejection is also decreasing as less solvent is passing through the membrane as shown in Fig. 7 [43].

The effect of time on the rejection percentage of nickel ions and the permeate flux at seven different times of 5, 15, 30, 45, 60, 120 and 180 minutes was studied and the obtained results have been shown in Fig. 8. As it can be seen, the rejection percentage of nickel ions and the amount of flux decrease considerably with increasing the experimental time. The drastically decreases of the permeation flux with operation time may be due to the concentration polarization, gel layer formation and plugging of the pores. All these factors induced additional resistances on the feed side for the transport across the membrane. The decreasing trend of nickel ions rejection during the experiment can be attributed to the formation of nitrate ions concentration polarization in the higher time. This means that the rejection of anions by negatively charged polyethersulfone membrane surface increases the co-ion (nitrate) and counter-ion (nickel) concentration in the vicinity of the

membrane surface. This phenomenon can cause the decrement of the nickel ions rejection percentage due to the reduction of the membrane fixed negative charge [42].

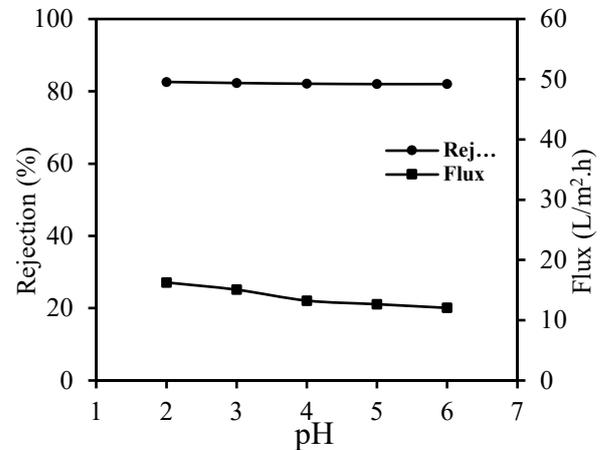


Fig. 6. Permeate flux and nickel ion rejection percentage by the neat PES membranes versus the pH (12 bar, PES 20 wt. %, 35 L/h, 20 ppm Ni^{2+} , 30 min)

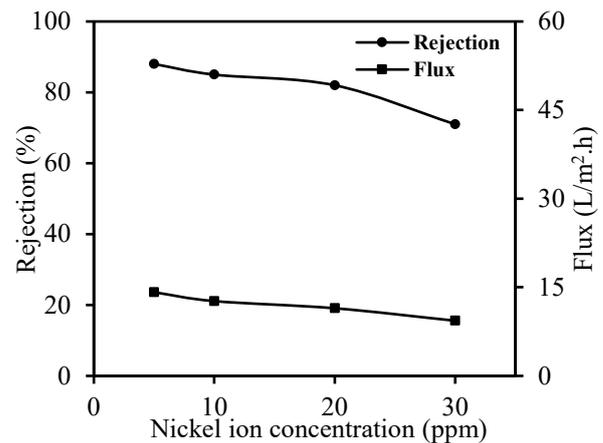


Fig. 7. Permeate flux and nickel ion rejection percentage by the neat PES membranes versus nickel ion concentration (12 bar, PES 20 wt.%, 35 L/h, pH=6 ± 0.1, 30 min)

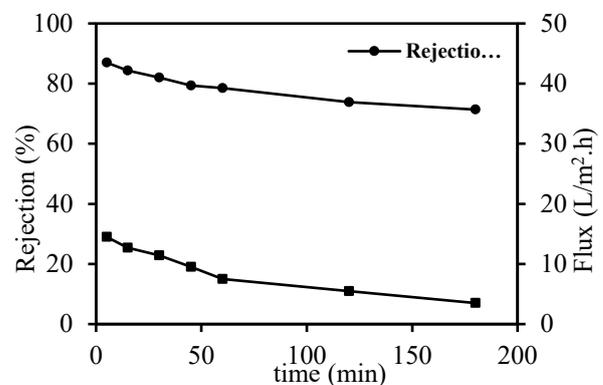


Fig. 8. Permeate flux and nickel ion rejection percentage by the neat PES membranes versus time (12 bar, PES 20 wt.%, 20 ppm Ni^{2+} , 35 L/h, pH=6 ± 0.1)

Fig. 9 shows the rejection behavior of various amount of fMWCNTs in the structure of PES membrane (20 wt.%) for nickel ions rejection from aqueous solution along with the permeate flux under the condition of optimized parameters in neat PES. As shown, the rejection capability of the membrane was gradually increased by adding of fMWCNTs concentration. Oxidation of MWCNTs by nitric acid introduces a large number of functional groups such as ketone, phenol, and carboxylic acid on the external surfaces of MWCNTs [36]. As a result of dissociation of these groups in an aqueous solution, membranes become a negatively charged membrane which can absorb nickel ions from the solution and cause electrostatic repulsion of the similarly charged solutes. By increasing the functional groups because of the raise of fMWCNTs concentration in the structure of membrane, the adsorption of nickel ions increases which results in the higher rejection of this ion. Therefore, the fMWCNTs blended membranes could be classified as Donnan exclusion mechanism [44].

As it can be seen in fig. 9, the permeate flux of membrane containing fMWCNTs increase gradually by increasing fMWCNTs concentration up to 0.2 wt.% and then decrease by 0.7 wt.% of fMWCNTs. The initial increase of flux can be explained by hydrophilic property of fMWCNTs in the prepared polymeric solution which consequently causes fast exchange between solvent and non-solvent during phase inversion. This phenomenon creates more pores and increase of the pore size of top layer of the membrane surface. On the other hand, when the fMWCNTs amount exceeds 0.2 wt%, the high density of MWCNTs in the casting solution leads to an increase in the viscosity of the solution. This will hinder the exchange between solvent and non-solvent during the phase inversion and slow down the precipitation of the membrane which leads to aggregation and reducing the effective surface and hydrophilicity properties of membrane [32].

The influence of TiO_2 content in the structure of PES onto the rejection percentage of nickel ions and permeate flux was investigated and the results have been shown in Fig. 10. The results show that the permeate flux and the rejection percentage of nickel ions were enhanced with increasing TiO_2 concentration. According to the table 1, the contact

angle is reduced by the addition of TiO_2 which confirms the increase of hydrophilic properties of prepared membrane and consequently the enhancement of the permeate flux. This can be explained by the homogeny distribution of the TiO_2 nanoparticles which contain a great deal of hydroxyl groups and cause the raise in membrane mean pore size and the hydrophilic properties of membrane. As shown in Fig. 10, the increase of nickel ions rejection percentage enhanced gradually with a raise of TiO_2 concentration. And that is due to nickel ion adsorption on TiO_2 nanoparticles.

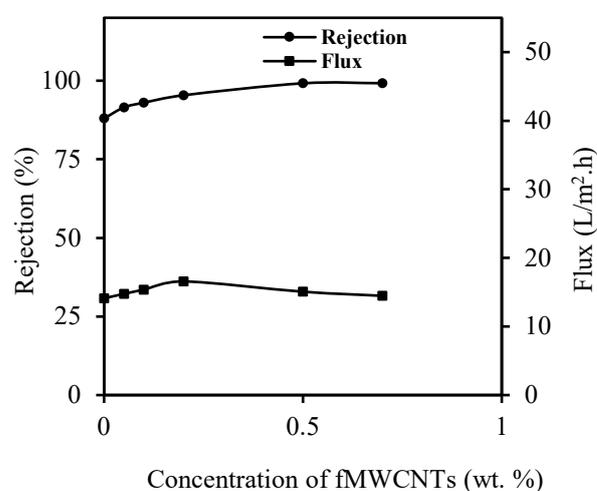


Fig. 9. Permeate flux and rejection percentage of nickel ions by the MMM containing 20 wt. % PES and various amount of fMWCNTs (12 bar, 20 ppm Ni^{2+} , 35 L/h, $\text{pH}=6 \pm 0.1, 30$ min)

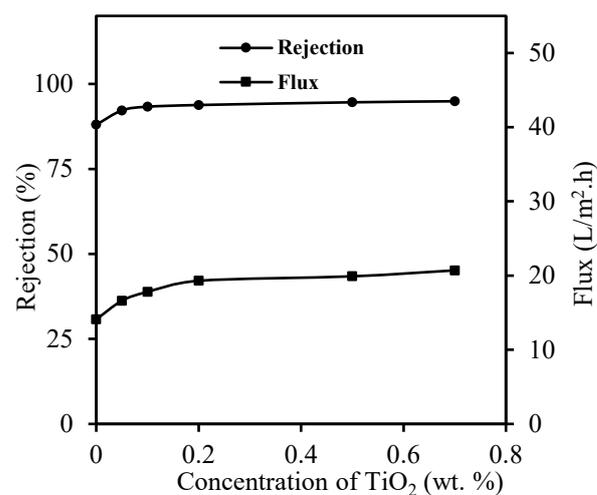


Fig. 10. Permeate flux and rejection percentage of nickel ions by the MMM containing 20 wt. % PES and various amount of TiO_2 (12 bar, 20 ppm Ni^{2+} , 35 L/h, $\text{pH}=6 \pm 0.1, 30$ min)

Fig. 11 shows nickel ions rejection percentage and the permeate flux of MMMs containing PES (20wt. %) and TiO₂-fMWCNTs as a function of various amount of this hybrid in the structure of PES. As it can be seen in this figure, with increasing the amount of TiO₂-fMWCNTs in the polymer matrix, the fabricated membrane shows a higher permeate flux than the neat PES membrane. This improvement in the flux value can be ascribed to the rise in hydrophilic properties of the membrane as confirmed by measuring the contact angle in table 1. By attracting water molecules inside the membrane matrix, the movement of them through the membrane is facilitated. Moreover, the polymer chain may be disrupted by the addition of these nanoparticles to the polymer casting solution and the interaction among them. Therefore, the introduction of more voids and increasing porosity improve the water permeability of membranes [34].

Also, based on the obtained results, the rejection percentage of nickel ions increased firstly by adding TiO₂/fMWCNTs to PES and then removing. The initial vigorous increase can be due to the increase in the adsorption capability of these nanoparticles onto the structure of the MMM. In the second stage, the decrease in nickel ions rejection percentage can be due to the increase of concentration polymerization as a result of gathering adsorbed counter-ions (ions with the opposite membrane charge) at the interface of membrane and solution which can increase Donnan effect and decrease the rejection of nickel ions. On the other hand, this phenomenon can be because of the disruption of the polymer chain packing as a result of the enhancement of nanoparticles concentration in the polymer matrix and the formation of more and large voids in the membrane structure which lead to higher flux, too [45].

Nickel ions rejection percentage of fabricated mixed matrix membranes containing PES, PES/fMWCNTs, PES/TiO₂, and PES/fMWCNTs-TiO₂ has been graphed in fig. 12. As it can be seen in this figure, with the exception of the low concentration of TiO₂-fMWCNTs onto the structure of PES/fMWCNTs-TiO₂, the rejection performance of nickel ions by the prepared entire membranes was improved compared to the neat PES membranes. The physical adherence and

electrostatic interactions between the ions in the feed aqueous solution and the membrane's matrix are two main mechanisms to eliminate metal ions by membrane processes. Therefore, the highest rejection percentage of nickel ions by PES/fMWCNTs can be as a result of the high adsorption ability of nickel ions by functional groups of MWCNTs on their structure.

The observed trend in the rejection of nickel ions by these mixed matrix membranes in the lower and higher concentration of nanoparticles was as follow:

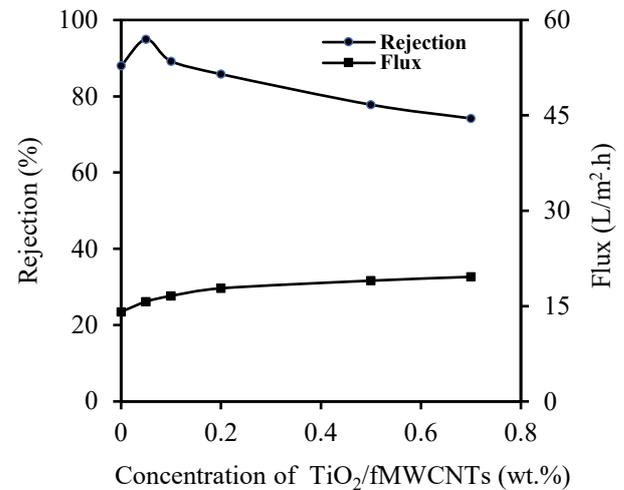


Fig. 11. Permeate flux and rejection percentage of nickel ions by the MMM containing 20 wt. % PES and various amount of TiO₂-fMWCNTs (12 bar, 20 ppm Ni²⁺, 35 L/h, pH=6 ± 0.1, 30 min)

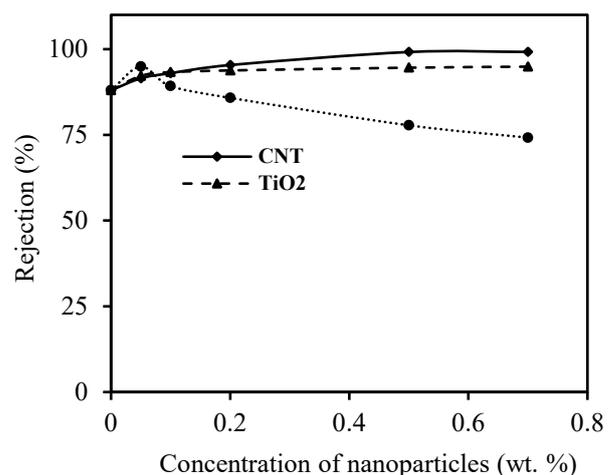


Fig. 12. Nickel ion rejection percentage of fabricated mixed matrix membranes containing PES, PES/fMWCNTs, PES/TiO₂ and PES/fMWCNTs-TiO₂ (12 bar, 20 ppm Ni²⁺, 35 L/h, pH=6 ± 0.1, 30 min)

PES/fMWCNTs>PES/TiO₂>PES/fMWCNTs-TiO₂>PES (lower concentration of nanoparticles)
 PES/fMWCNTs-TiO₂>PES/fMWCNTs>PES/TiO₂>PES (Higher concentration of nanoparticles)

Fig. 13 has been depicted to compare the permeability of all the prepared membranes. Due to the nanoparticles' hydrophilicity properties, these materials tend to move on the membrane surface during the phase inversion process and easily deprotonated or adsorbed water molecules which increase the hydrophilic properties of the fabricated membrane and permeate flux. As shown, the fabricated membrane containing TiO₂ has the highest permeate flux which is as a result of its ability on adsorption of hydroxyl groups of water molecules and its more hydrophilicity properties.

IX. CONCLUSION

The flat sheet nanofiltration membranes of neat PES and MMMs were prepared by wet phase inversion and conventional casting methods. To improve the hydrophilicity properties of neat PES and to enhance the rejection performance of nickel ions and permeate flux, nanomaterials such as fMWCNTs, TiO₂, and fMWCNTs-TiO₂ were added. The obtained results showed that the best performance of neat PES was achieved at 20 wt. % PES, pressure 15 bar, lower concentration of nickel ions, time=15 minutes, and different amounts of pH. The use of nanomaterials in the structure of PES showed that under similar operational conditions, the performances of the membranes such as the permeate flux and rejection of nickel ions have significantly improved. In another point of view, the rejection percentage of nickel ions and permeate flux and the best performances are related to the PES containing TiO₂ and fMWCNTs nanomaterials, respectively.

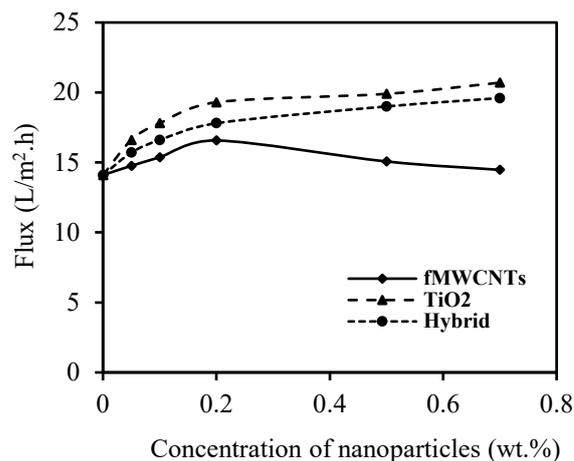


Fig. 13. Permeate flux of fabricated mixed matrix membranes containing PES, PES/fMWCNTs, PES/TiO₂ and PES/fMWCNTs-TiO₂ (12 bar, 20 ppm Ni²⁺, 35 L/h, pH=6 ± 0.1, 30 min)

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