

# Fabrication and Characterization of Polycarbonate/Titanium Oxide Nanotubes Mixed Matrix Membranes for Efficient Removal of Cadmium and Copper from Aqueous Solution

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## ABSTRACT

*In this study, novel polycarbonate-titanium oxide nanotubes (PC-TNT) ultrafiltration mixed matrix membranes (MMMs) were fabricated for decontamination of  $Cd^{2+}$  and  $Cu^{2+}$  metal ions from aqueous solution. The weight percentage of TNTs in the polycarbonate membrane matrix was changed from 0 to 15. The synthesized neat PC membrane and PC-TNTs MMMs were characterized with respect to structural morphology and hydrophilicity using scanning electron microscopy (SEM) and water contact angle, respectively. The effects of TNTs loadings on the pure water flux, mean pore size, porosity and water contact angle of fabricated membranes and  $Cd^{2+}$  and  $Cu^{2+}$  heavy metal ion rejection were also studied. By increasing the loading of TNTs nanoparticles in the membrane matrix, the membrane mean pore size tended to increase, while the porosity decreased. Also, the increase in TNTs loading resulted in an increase in membrane water flux which was mainly attributable to the enhancement in mean pore size and partly caused by the decreased contact angle value (more hydrophilic). Of all the membranes studied, it was found by UF experiments that PC-TNT MMM was the most efficient material in heavy metal ions removal due to the superior adsorption capacity of TNTs material. The generic results revealed that TNTs material can be favorite candidates for MMMs preparation in order to be conveniently used in the  $Cd^{2+}$  and  $Cu^{2+}$  heavy metal ions decontamination from polluted water resources.*

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## 1. Introduction

Nowadays, many researches are focused on heavy metals removal, as the major contaminants in water resources. These pollutants are not biodegradable and tend to

accumulate in the living organisms, causing various diseases and disorders. Therefore, because of environmental, health and safety aspects, it is necessary to remove dangerous

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species from water [1-3]. Hence, in recent years, drinking water regulations reduced the allowable maximum contaminant level (MCL) for heavy metals.

According to the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) regulations, the typical heavy metals such as  $Cd^{2+}$  and  $Cu^{2+}$  in aqueous solutions are more toxic even at trace levels and have caused adverse health impacts on human beings. Owing to the stringent environmental regulations, great demands exist to improve the efficiency of the techniques for heavy metal removal from contaminated water resources.

A wide range of processes has been applied for the treatment of heavy metals ions from aqueous solution including chemical precipitation, ion exchange and biological treatment [4,5] which suffer some drawbacks such as low metal removal efficiency, high loss of reagents, uneconomical energy consumption and imposed post-treatment operations due to the secondary waste production. Application of membrane-based filtration is another technique for the removal of heavy metals ions. Even though nanofiltration (NF) and reverse osmosis (RO) membranes have been proposed for this purpose, the high operating pressure has limited the commercial utilization of these two types of membranes [6-8]. On the other hand, microfiltration (MF) and ultrafiltration (UF) membranes, which operate at lower pressures, are not effective processes for the removal of heavy metals ions due to their intrinsic porous structure [9,10].

Adsorption, one of the most widely used processes, is the other technique to decontaminate toxic heavy metals ions from polluted water, because it has been found to

be very effective, economical, versatile and simple [11-13]. Traditional adsorbents for the removal of toxic metals include activated carbon, zeolites, ion exchange resins, as well as many low cost materials such as agricultural wastes, natural zeolite and fly ash. Unfortunately, these adsorbents cannot trap the toxic substances to meet the new stringent regulations. Thus, it necessitates the development of new specific adsorbents for efficient removal of toxic heavy metals from aqueous solution. Among the available adsorbents, metal oxides nanoparticles such as ferric oxide and aluminum oxide were reported as efficient materials for cleaning the environmental contaminants due to their high surface area and unique structural characteristics [14-17]. In the meantime, some semiconductor metal oxides including titanium oxide and zirconium oxide showed a remarkable potential towards photocatalytic degradation of contaminants and heavy metal ions removal [18-21]. Following the discovery of carbon nanotubes, many studies have been concentrated on the preparation of various nanotubular materials [22,23]. Among these nanostructured materials, the nanotubular titanium dioxide has received a great deal of attention due to its good chemical and thermal stability, strong oxidizing power, high surface area, nontoxic character, high photocatalytic activity and inexpensive production process [24-26]. Nevertheless, there is a lack of knowledge about the application of titanium oxide nanotubes for water purification, particularly decontamination of heavy metal ions such as  $Cd^{2+}$  and  $Cu^{2+}$ .

Even though metal oxide nanoparticles are known as strong materials for the adsorption of heavy metal ions, it is not possible to use them directly in chemical processes; that is

related to the small size of metal oxides which result in high pressure drops. Another problem is the requirement of additional post-treatment process for the separation of these very fine particles from water. Therefore, many researchers investigated the impregnation of metal oxide nanoparticles into porous media such as zeolite [27], cellulose [28] and polymer [29,30] to eliminate the disadvantages of very fine nanoparticles and to develop their application in heavy metals removal.

Thus, by creating a relationship between adsorption and membrane based separation processes, a novel technique known as mixed matrix membranes (MMMs) has been improved which takes advantage of both systems and overcomes the aforementioned problems [31-34]. Among the various polymeric materials used in preparation of membranes, polycarbonate (PC) can be considered as a good candidate for the membrane fabrication due to its excellent physical properties, good toughness, high heat and chemical resistance and low cost.

In order to represent an efficient and applicable treatment process for  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  decontamination, the main objective of this work is to develop novel UF mixed matrix membranes (MMMs) by impregnating inorganic titania nanotubes into porous membranes made of polycarbonate (PC) material. In this study, MMMs were prepared from the casting solutions consisted of different weight percent of in-house made TNTs (synthesized via hydrothermal process). The  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  removal performance of fabricated PC-TNT MMMs was evaluated and compared.

## **2. Experimental**

### **2.1. Materials**

Polycarbonate (grade: 0710) was purchased from Khuzestan Petrochemical Company (Iran) and was used as the base polymer for membrane fabrication. N-methyl-2-pyrrolidone (NMP) was used as the solvent and cellulose acetate (CA) and glycerol were used as the nonsolvent additives to the casting solution. Commercial  $\text{TiO}_2$  nanoparticle (with the purity of 99.98 %, 78.8 % anatase phase and 21.2 % rutile phase and average particle size of 18 nm) and NaOH were supplied from Tecnan Navarrean Nanoproducts Technology (Iran) and Merck, respectively and were used for synthesis of titanate nanotubes via the hydrothermal process. In addition, Hydrochloric acid (HCl) from Merck and deionized water were used for washing the synthesized TNTs. HCl was purchased from Merck and was used for the regeneration of saturated PC-TNT MMMs. To prepare aqueous feed solutions containing specific concentrations of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were purchased from Merck, respectively. The determination of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  concentrations was carried out using a UV-visible spectrophotometer [35]. For this purpose ammonium pyrrolidine dithiocarbamate (APDC), Tween 80 and  $\text{KH}_2\text{PO}_4$  were purchased from Merck for the preparation of standard solutions described in that method. All the chemicals used in this study were of analytical grade and used without further purification.

### **2.2. Synthesis of titania nanotubes**

Using the hydrothermal synthesis method [36], titanate nanotubes were prepared by treating 5 gr of  $\text{TiO}_2$  nanoparticles with 10 M aqueous NaOH solution in a Teflon-lined stainless steel autoclave. Prior to transferring the solution to the autoclave, the solution was

stirred by the magnetic stirrer for one hour at room temperature and then sonicated in the ultrasonic bath for another one hour. The stainless steel autoclave containing the solution was heated at 160 °C in an oven for 72 hours. The obtained white precipitates were filtered using the vacuum pump and then were washed with deionized water and HCl solution to decrease the pH of the product to 7. As the final step, the synthesized titanate nanotubes were dried in an oven at 80 °C for 12 hours.

### 2.3. Fabrication of PC-TNT mixed matrix membranes

Phase inversion method was used for the fabrication of all membranes. The casting solutions consisted of polycarbonate (PC), glycerol, cellulose acetate (CA) and TNTs were prepared by dissolving the components in NMP. Four membranes including three mixed matrix membranes and one neat PC membrane were prepared in this study where the compositions of casting solutions, used for the fabrication of each membrane, are illustrated in Table 1.

**Table 1**

Compositions of the casting solutions for the preparation of membranes (wt %).

Membrane ID	PC (wt %)	CA (wt %)	Glycerol (wt %)	TNTs (wt %)	NMP (wt %)
PC	10	3	0.89	0	86.14
PC-TNT-5	10	3	0.89	5	81.11
PC-TNT-10	10	3	0.89	10	76.11
PC-TNT-15	10	3	0.89	15	71.11

The first step of mixed matrix membrane fabrication process is the preparation of a homogeneous dispersion of solid particles in the polymer solution. For better distribution of inorganic nanoparticles and avoiding their agglomeration, the following procedure was used for the preparation of casting solution [37].

At first, polycarbonate (PC), cellulose acetate (CA) and TNTs were dried in the oven at 100 °C overnight. Then, the predetermined amount of TNTs inorganic nanoparticles was dispersed in NMP and was stirred for 6 hours at 50 °C. The prepared suspension was then sonicated for 90 min to produce a suspension with well-dispersed nanoparticles. Another solution was prepared by dissolving predetermined amount of polycarbonate, cellulose acetate and glycerol in NMP which

was then stirred for 24 h at 50 °C. The casting solution preparation was followed by adding the latter solution gradually to the nanoparticle suspension. The final resulting solution was stirred for 24 h by mechanical stirrer at 50 °C to obtain a uniform solution. After cooling to room temperature, the casting solution was cast onto a smooth and clean glass plate to form a film of 600 micrometer thickness and subsequently, was immersed into water coagulation bath at room temperature. Once the membrane was formed and peeled off from the glass plate, it was transferred to fresh distilled water bath for 48 h to guarantee the complete phase inversion. Water was changed daily to remove the residual NMP and glycerol from the membrane. Lastly, the membrane was dried at ambient conditions for 24 h. Referring to

Table 1, the as prepared membranes are coded based on the TNTs loadings.

#### 2.4. Characterization tests

The morphology of the as prepared titania nanotubes, PC-TNT mixed matrix membranes and neat PC membrane was characterized using scanning electron microscope. The membrane samples were cut into small pieces and then coated with a thin film of gold layer by a DC sputtering system to make them conductive before the SEM examination. For the cross section scanning, all membranes were fractured in liquid nitrogen.

The hydrophilic property of the fabricated neat PC membrane and PC-TNT MMMs were determined based on the water contact angle using an automated contact angle goniometer (Dataphysics OCA 15, Germany) to apply the sessile drop method. A total of 4  $\mu\text{L}$  of a single water droplet was located on the dry membrane surface using a microsyringe. The reported contact angles were obtained by repeating the measurement three times and the average of those values were calculated.

Membrane porosity plays an important role on the performance of membrane. To measure the porosity of the prepared membranes, membrane samples with a surface area of 4  $\text{cm}^2$  were immersed in deionized water for 48 h. The excess water on the surface of the membrane sample was removed by filter paper and then the weight of the wet membrane was measured. After that, the wet membrane was put in an oven at 60  $^\circ\text{C}$  for 24 h to dry completely. Finally, the dry membrane was weighed and the porosity of

the membrane is calculated through Eq. 1 [38]:

$$\varepsilon = \frac{\frac{m_{\text{wet}} - m_{\text{dry}}}{\rho_w}}{\frac{m_{\text{wet}} - m_{\text{dry}}}{\rho_w} + \frac{m_{\text{dry}}}{\rho_p}} \times 100 \quad (1)$$

where  $\varepsilon$  is the membrane porosity,  $m_{\text{wet}}$  and  $m_{\text{dry}}$  are the mass of wet and dry membranes, respectively.  $\rho_p$  is the density of the polymer (1.22  $\text{g cm}^{-3}$  for polycarbonate) and  $\rho_w$  is the density of water (0.998  $\text{g cm}^{-3}$ ). In order to minimize the experimental errors, the porosity of each membrane was calculated three times and the average porosity was reported.

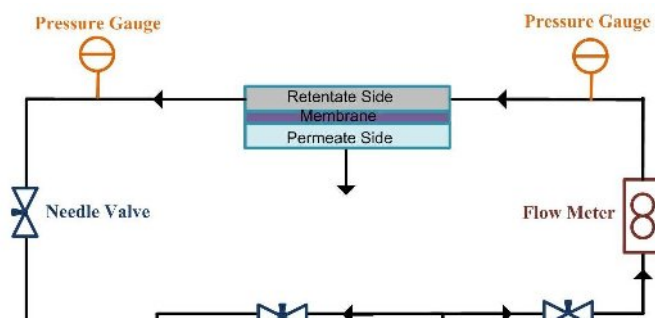
In addition, the pure water flux data was used for the calculation of mean pore size of the membrane ( $r_{\text{ave}}$ ) through Eq. 2 [39]:

$$r_{\text{ave}} = \sqrt{\frac{8\eta l q (2.9 - 1.75\varepsilon)}{\varepsilon A \Delta P}} \quad (2)$$

where  $q$  is the pure water flux ( $\text{m}^3 \text{s}^{-1}$ ),  $\eta$  is the water viscosity ( $8.9 \times 10^{-4} \text{ Pa.s}$ ),  $l$  is the membrane thickness (m),  $A$  is the membrane area ( $\text{m}^2$ ) and  $\Delta P$  is the transmembrane pressure difference ( $10^5 \text{ Pa}$ ).

#### 2.5. Continuous ultrafiltration experiment

In this study, a cross flow ultrafiltration set-up containing a rectangular membrane module was used to evaluate the performance of synthesized PC-TNT MMMs in terms of water permeability and  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  rejection rate. A schematic representation of experimental cross-flow UF system is shown in Fig. 1.



**Figure 1.** Schematic of the system used for cross-flow ultrafiltration tests.

Prior to UF experiment, each membrane sample with an effective surface area of around 32 cm<sup>2</sup> was compacted for 60 min using deionized water at 4 bar pressure. The experiments were followed by replacing pure water with Cd<sup>2+</sup> and Cu<sup>2+</sup> feed solutions where for each experiment, 5 L feed solutions with predetermined concentrations of heavy metal ions were prepared at constant pH and temperature. Water permeability measurements and rejection evaluation in UF tests were performed at the fixed pressure of 1 bar with a feed flow rate of 1 L/min. The flux of the membranes was then calculated through Eq. 3.

$$J = \frac{Q}{A \Delta t} \quad (3)$$

where  $J$  is the permeation flux (L m<sup>-2</sup> h<sup>-1</sup>),  $Q$  is the volume of the collected permeate (liter) and  $\Delta t$  is the sampling time interval (h). The permeation flux was recorded at the steady state condition.

The heavy metal ion rejection ( $R$ ) was calculated by Eq. 4.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where  $C_p$  and  $C_f$  are the heavy metal ion concentrations in the permeate and feed solutions, respectively. At predetermined time intervals, samples were taken from the permeate and the feed solution and their heavy metal ion concentrations were determined using a UV-visible spectrophotometer (ChromTech, CT-2200). It should be mentioned that the maximum light adsorption of Cd<sup>2+</sup> and Cu<sup>2+</sup> occurred at 294 nm (UV region) and 445 nm (visible region) for Cd<sup>2+</sup>, respectively. At the end of each UF experiment, the membrane was immediately subjected to regeneration process where the saturated membrane was washed for 2 hours by 0.01 M HCl solution (pH 2) and then rinsed through deionized water circulation for 1 hour. Thus, the regenerated membrane became ready to be used in the next UF experiments.

### 3. Results and discussion

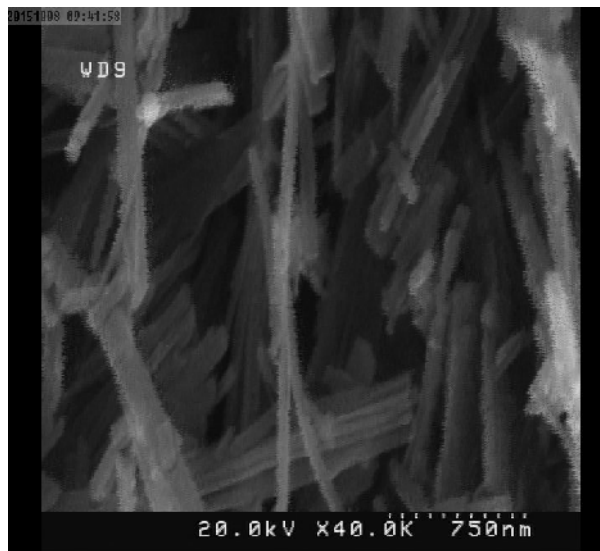
#### 3.1. Characterization test

### 3.1.1. SEM analysis

Figure 2 represents the FESEM micrographs of the as prepared TNTs at different magnifications. According to Fig. 2a and 2b, the spherical particles of  $\text{TiO}_2$  were transformed to tubular structures and grown through the hydrothermal synthesis. The



(a)



(b)

**Figure 2.** FESEM micrographs of synthesized titania nanotubes at different magnifications.

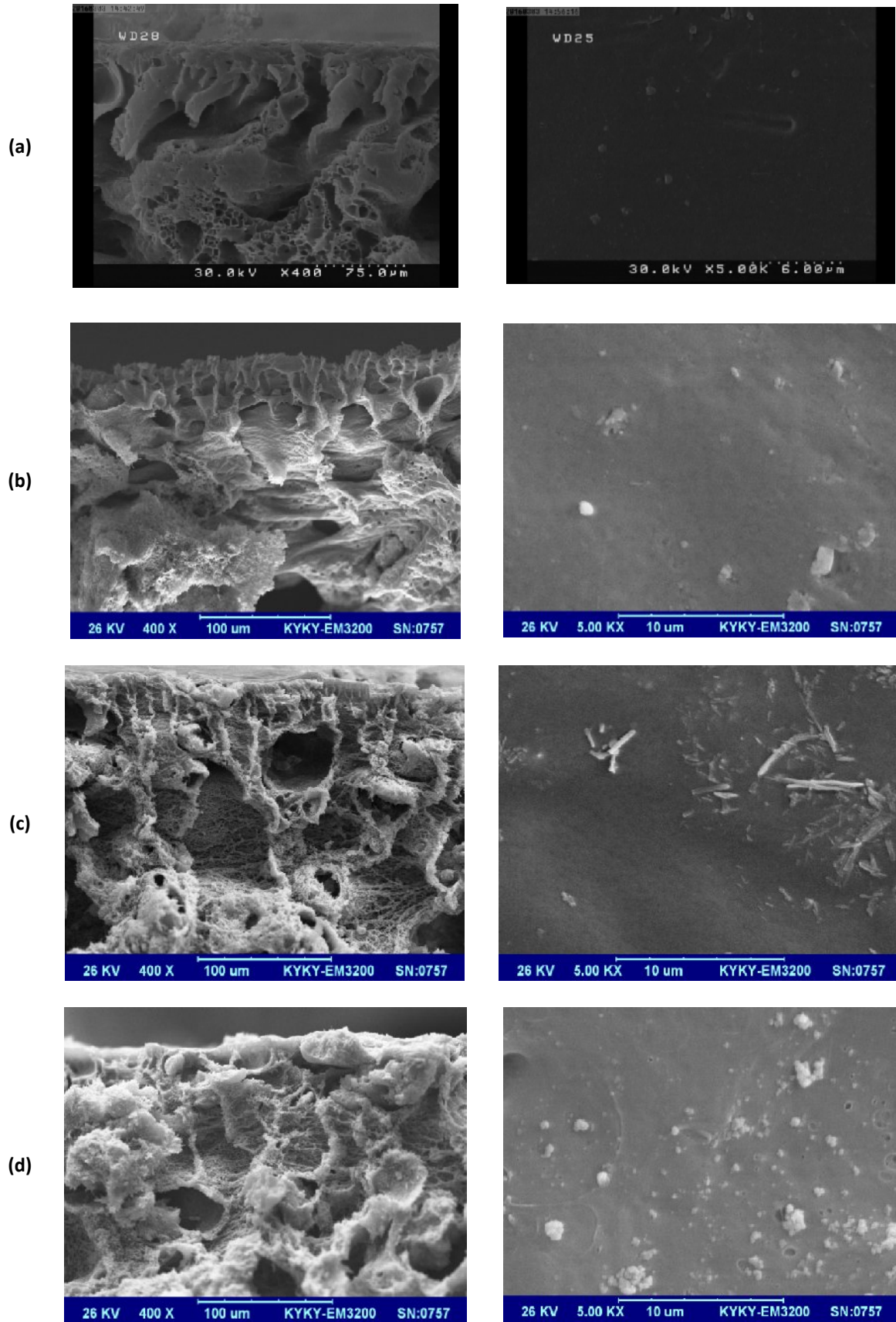
Referring to the SEM micrographs of the membranes' cross section, it is obvious that all fabricated membranes have an asymmetric structure with a porous skin layer supported by a sublayer. It can be clearly seen that the PC-TNT MMMs generally consist of short finger-like pores which are supported by the sponge-like structure. These finger-like pores were gradually hindered by increasing the nanoparticles loading so that an almost fully sponge-like structure can be observed at the higher loadings of nanoparticles. The change in the sublayer structure from finger-like pores to sponge-like structure in MMMs can be ascribed to the increase in the viscosity of the casting solutions due to the addition of nanoparticles [40,41], which reduced the rate

average diameter of the synthesized TNTs was estimated by image analyzer software to be about 33 nm.

In addition, the SEM micrographs of the top surface and cross-section of the neat PC membrane and the fabricated PC-TNT MMMs are demonstrated in Fig. 3.

of intrusion of coagulant to the polymer solution (kinetic effect). Even though the addition of nanoparticles reduced the thermodynamic stability of polymer solution which enhanced the demixing rate, but it seems that the viscosity effect was more prominent which eventually resulted in the sponge-like structure of the membrane. Similar results were found elsewhere [33,42] which reported that both thermodynamic and kinetic factors contributed to the determination of membrane structure. The overall results indicated that the morphology of mixed matrix membranes was altered by the addition of different loading amounts of inorganic nanoparticles.





**Figure 3.** SEM micrographs of the cross section and surface of fabricated membranes; a: neat PC membrane, b: PC-TNT-5, c: PC-TNT-10, d: PC-TNT-15.



In addition, the SEM micrographs of the top surface and cross section of mixed matrix membranes show some agglomeration of TNTs which are more visible at higher loading of nanoparticles. Moreover, the nanoparticles are dispersed throughout the MMMs which confirmed the successful impregnation of TNTs in the membrane matrix. Such aggregates and lumps of nanoparticles in the structure of membrane were reported in other researches [43-45].

### 3.1.2. Mean pore size, porosity and pure water flux

The characterization tests results for the

fabricated neat membrane and MMMs are presented in Table 2 where the mean pore size of neat membrane was calculated as 80.7 nm. Furthermore, as TNTs loading increases from 5 to 15 wt %, the average pore size increased from 85.7 nm to 99.4 nm for the TNT-MMMs. Also, the mean pore size of PC-TNT MMMs was higher than the mean pore size of the neat membrane. This phenomena can be related to how the phase inversion mechanism of each system may be affected by different parameters involved in this process [42] such as solvent-coagulant miscibility [46], viscosity of dope solution [40,41] and type of additives and their concentrations [46,47].

**Table 2**

The characterization test results for the fabricated membranes.

Membrane ID	Pure water flux @ 1 bar ( $L m^{-2} h^{-1}$ )	Overall porosity (%)	Pore size (nm)	Contact angle
PC	440.63	83.98	80.7	73.4
PC-TNT-5	450.00	80.63	85.7	51.2
PC-TNT-10	478.13	76.54	93.8	46.3
PC-TNT-15	496.88	74.37	99.4	34.5

The porosity measurements of the fabricated MMMs revealed that the porosity of mixed matrix membranes decreased as the loading of nanoparticles increased, e.g., as the loading of nanoparticles increased from 5 to 15 wt %, the porosity of membranes varied in the range of 80.63 % - 74.37 % for PC-TNT MMMs.

According to the pure water permeation experiments, it was found that the pure water flux of as prepared PC-TNT MMMs was improved from 440.63  $L m^{-2} h^{-1}$  for the neat PC membrane to 496.88  $L m^{-2} h^{-1}$  for PC-TNT-15 MMM. This can mainly be explained by the trend of variations in mean pore size of PC-TNT MMMs compared to the neat PC

membrane. Furthermore, the pure water flux of all MMMs increased as the nanoparticle loading increased from 5 to 15 wt %. This trend is explained mainly by the increase in the mean pore size of MMMs and partly by the hydrophilic nature of impregnated TNTs material which made the fabricated MMMs more hydrophilic at higher loading amounts. The super hydrophilic nature of titania nanotubes was attributed to the capillary effect of the nanotubes [48]. Furthermore, the hydrophilic characteristics of TNTs could be ascribed to the accumulation of -OH groups on its surface and the great polarity of O-Ti-O bond [49]. In addition, crystalline phase of TNTs plays a fundamental role in its

hydrophilicity, as Munirathinam et al. [50] reported, the hydrophilic behavior of TNTs is mainly due to the presence of mixed crystalline phase (anatase and rutile).

### 3.1.3. Contact angle measurement

The contact angle of water droplet on the surface of the membrane is considered to be an indication of the membrane hydrophilicity even though it further depends on some other characteristics of membrane such as pore size and its distribution and surface roughness. The water contact angles of the neat PC membrane and PC-TNT MMMs are illustrated in Table 2 where PC-TNT-15 MMM and neat PC membrane exhibited the lowest ( $34.5^\circ$ ) and the highest ( $73.4^\circ$ ) contact angle values, respectively. Furthermore, the contact angle decreased from  $51.2^\circ$  to  $34.5^\circ$  as TNTs loading increased from 5 to 15 wt %, which is attributed to the hydrophilic (intrusion) nature of TNTs nanoparticles. The hydrophilic surface of PC-TNT MMMs is obviously due to the presence of a number of substantially hydrophilic hydroxyl groups which has reducing effect on the contact angle of PC membrane.

### 3.2. $\text{Cd}^{2+}$ and $\text{Cu}^{2+}$ rejection

In order to evaluate the performance of fabricated MMMs, the rejection efficiencies of the heavy metal ions ( $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$ ) were investigated using the PC-TNT MMMs at the feed concentration of 120 mg/L. Figure 4 represents the variation of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  rejection efficiency versus time using the fabricated MMMs. As it is clear, the nanoparticle loading amount of 15 wt % exhibited the highest rejection efficiency of metal ions in PC-TNT MMMs. This is attributed to the adsorption characteristics of MMMs which were remarkably enhanced by

increasing the quantity of nanoparticles in the membrane matrix.

According to the ultrafiltration test results, it was obviously revealed that PC-TNT MMMs have a strong ability for heavy metal ions removal which is representative of the high adsorption capacity of titania nanotubes. This can be confirmed by superior rejection efficiency of heavy metal ions obtained by PC-TNT MMMs. However, MMMs fabricated via TNTs materials exhibited a good efficiency for heavy metal ions decontamination. Furthermore, the kinetic investigation of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  removal by fabricated MMMs represented that PC-TNT MMMs approached to the saturation state in a short time interval. This confirmed that the removal process of heavy metal ions using PC-TNT MMMs possess very fast kinetics.

## 4. Conclusions

Titania nanotubes were synthesized via hydrothermal process and were successfully impregnated in polycarbonate matrix to fabricate PC-TNT mixed matrix membranes through the phase inversion technique. In this study different loading amounts of titania nanotubes were impregnated in PC membrane matrix and the performance of the fabricated mixed matrix membrane in the removal efficiency of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  heavy metal ions was investigated using an ultrafiltration system.

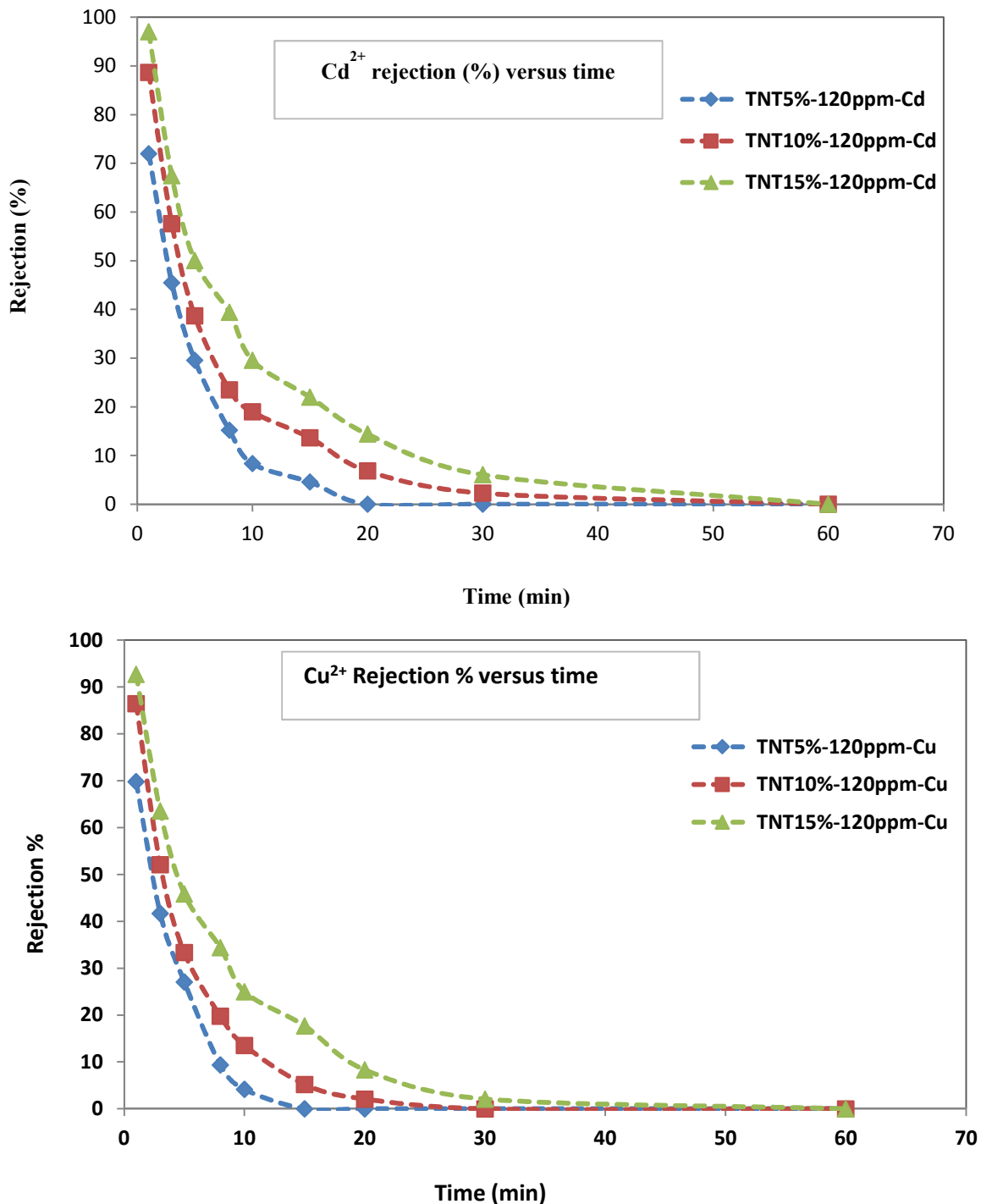
The conclusions are as follows:

- 1- The structural morphology and hydrophilicity of the prepared membranes were characterized by SEM analysis and water contact angle measurement, respectively. The more spongy structure was seen in SEM images of PC MMMs with higher loading amounts of TNTs. Also, the titania nanotubes incorporation in the

membrane matrix remarkably improved the hydrophilic property of polycarbonate membrane.

increase in TNTs loading can be attributed to the increase in mean pore size and membrane hydrophilicity of fabricated MMMs.

2- The pure water flux enhancement with an



**Figure 4.** Plots of rejection efficiency of Cd<sup>2+</sup> and Cu<sup>2+</sup> versus time using PC-TNT MMMs with different nanoparticle loadings.

3- The heavy metal ions removal efficiency was investigated via ultrafiltration experiments using polycarbonate MMMs by different loading amounts of TNTs. The maximum rejection efficiency of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  was achieved by PC-TNT-15 MMMs after 1 minute of contact time, due to the adsorption characteristics of MMMs which was remarkably enhanced by increasing the quantity of nanoparticles in the membrane matrix.

4- The kinetic investigation of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  removal using fabricated MMMs confirmed that the removal process of heavy metal ions using PC-TNT MMMs possess very fast kinetics.

5- According to the experimental results, it can be concluded that TNTs are efficient inorganic materials for incorporation in the polycarbonate mixed matrix membrane. Generic results revealed that the hybrid materials of PC-TNT MMMs offer a promising alternative for decontamination of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  from aqueous solution and deserves further investigation.

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