

Preparation of Novel Thin-Film Composite Nanofiltration Membranes for Separation of Amoxicillin

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Abstract

Several novel composite membranes were prepared to separate and recycle amoxicillin from pharmaceutical wastewater via nanofiltration process. The synthesis of these membranes included three stages: 1- preparation of polysulfone ultrafiltration membranes as a support via phase separation process, 2- modification of its surface by interfacial polymerization as a selective layer (polyamide), and 3- self-assembly of TiO₂ nanoparticles on the selective layer as an anti-fouling agent. The rejection of all nanofiltration membranes was more than 99% and only its flux was changed proportional to different conditions. In the presence and absence of TiO₂ nanoparticles, the pure water flux of polyamide thin-film membrane also obtained 44.4 and 38.4 L/h.m² at 4 bar pressure, respectively. These were equal to 34 L/h.m² for amoxicillin solutions. The results showed that TiO₂ nanoparticles increased hydrophilicity of polyamide selective layer and therefore, nanoparticles decreased the fouling level. SEM images illustrated the excellent establishment of polyamide layer and distribution of TiO₂ nanoparticles on the selective layer. The properties of membrane surface were taken into consideration by using AFM, indicating the increment of surface roughness with interfacial polymerization and TiO₂ nanoparticles self-assembly. The pore size of membranes was in the nanoscale (2.653 and 2.604 nm without and with TiO₂ nanoparticles self-assembly, respectively).

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1. Introduction

An important issue regarding the effects of antibiotics on the environment is the development

of antibiotic resistance which is considered a threat to the usefulness of antibacterial substances [1]. According to Zucker and Levy report, Iran has one of the highest ranks in antibiotic consumption [2]. Because of widespread remedial use of amoxicillin among other antibiotics, this substance naturally enters the environment through various ways [3]. One of the important entrance places is the production place where factories are established. It is obvious that separating of this substance from effluent, in addition to preventing environmental pollution, can play an important role in increasing economic efficiency of the production process and company profit by increasing the production of this substance. This antibiotic substance has been removed or separated via adsorption on chitosan beads [4], activated carbon and bentonite [5], photo-Fenton process [6], ozonation [7], combined chemical oxidation-filtration [8]. But, the membrane filtration processes (especially nanofiltration) can be selected as the best technique.

Nanofiltration (NF) membranes, which exhibit separation characteristics in the intermediate range between reverse osmosis and ultrafiltration membranes, are gaining interest worldwide because of advantages such as low operation pressure, high permeate flux and high retention of multivalent ion salts [9-11]. NF process has been used in many applications such as wastewater reclamation [12-13], industrial water production, water softening [14-15] and the separation of compounds having different molecular weights [16-17]. Most NF membranes developed to date have a thin-film composite (TFC) structure due to key advantages compared to asymmetric membranes [18-21]. In a TFC membrane, the support layer provides an appropriate mechanical strength with low resistance to permeate flow and

each layer can be optimized for the desired combination of permeate flux and solute rejection [18, 20]. Among different techniques, interfacial polymerization (IP) is the best one used for the preparation of these membranes [22-23]. This technique does not only change the physical morphology of membrane surface (i.e., roughness, pore size, porosity, etc.), it also significantly affects the chemical properties of membrane surface (i.e. hydrophilicity, surface charge, etc.). Both physical and chemical properties indirectly affect the membrane performance (permeability and rejection) and certain degrees of fouling [22-23].

There are various types of polymeric membranes. Among them, polyamide membranes are those showing suitable performances in separating different types of pharmaceuticals wastewater [24-28]. But, the membrane fouling is an important problem in the nanofiltration membranes as it increases energy consumption, decreases membrane life and makes the preparation performance unpredictable [29]. Also, the fouling decreases the interaction between the membrane surface and the feed of membrane processes. Several researchers have concluded that membrane fouling is directly related to hydrophilicity [30], although the opposite results have been reported [31]. Many studies have been conducted for increasing the membrane resistance to fouling.

One of the important methods in developing non-fouling nanofiltration membranes is binding inorganic particles in nanoscale to membrane [32]. This process incorporates many important properties to polymeric membranes (high performance of desalination, flexibility and ease of construction) with unique advantages of molecular sieve (adjustable hydrophilicity, load density, pore structures, mechanical and thermal stability). To

fabricate nanofiltration membranes, organic/inorganic compounds can be directly deposited on the membrane surface or bound into the membrane structure through interfacial polymerization process [32].

In this research, Titania (TiO₂) nanoparticles were used as anti-fouling agents for the preparation of polyamide thin-film composite membranes. These nanoscale particles were deposited on the selective layer of membranes and their performance was measured in the separation of amoxicillin via nanofiltration process. The characterizations of these membranes were obtained via FT-IR, SEM, AFM, molecular weight cut-off (MWCO) and filtration apparatus. The task of cross-flow mode filtration experiments was used in order to ensure the maximum permeability and rejection efficiency.

2. Experimental procedure

2.1. Materials

Polysulfone pellets were supplied by Sigma-Aldrich (PSf, M_n=35,000 g/mol) and used as the polymer for the preparation of ultrafiltration membrane supports. Polyethylene glycol (PEG, M_w=6,000 g/mol) and N-Methyl-2-pyrrolidone (NMP) were purchased from Merck and used as the pore former and solvent, respectively. 1,3,5-Benzenetricarbonyl trichloride (Trimesoyl chloride, TMC) and Piperazine (PIP) as the monomers of polyamide thin-film, Triethylamine (TEA) as the phase transfer catalyst, n-Hexane as the organic phase, and TiO₂ nanoparticles (diameter=25 nm) as the additive were supplied by Merck. Also, deionized water was used as the non-solvent agent in the coagulation bath. Pure amoxicillin (AMX) powder with the molecular weight of 365.4 g/mol (supplied by Dana pharmaceutical Company, Iran) was used for the

preparation of feed solutions in the amoxicillin rejection experiments. These materials were used as received without further purification.

2.2 Preparation of ultrafiltration membrane support

Casting solution for the preparation of ultrafiltration membrane support was prepared by dissolving 18% wt. of PSf and 11 % wt. PEG in NMP at the temperature of 70°C. The solution was magnetically stirred for at least one day and sonicated (Bandelin DT 255H, Germany) for 2 min to guarantee complete dissolution of polymer. The homogenous solution stayed for 1 h where its bubbles were removed. The bubble significantly influenced the membrane porosity. After that, the prepared homogeneous solution was cast using a film applicator to 200 μm clearance gap on a glass plate substrate. Temperature and relative humidity of casting environment were ~24°C and 23%, respectively. The cast film was immediately (without a gap time) immersed in a deionized water bath to complete the phase separation, where the exchange between solvent (NMP) and non-solvent (water) was induced. After complete coagulation, the membrane was transferred into a pure water bath. The bath was refreshed frequently for at least 24 h. This was done to ensure the complete removal of the residual solvent from the membrane.

2.3 Preparation of polyamide selective layer

In order to perform the interfacial polymerization on the membrane support, two immiscible solutions (aqueous and organic) were made. The composition of aqueous solution was 2 % wt. PIP and 0.4 % wt. TEA and organic solution were also prepared by solving 0.1 %v TMC in n-Hexane. After that, the membrane support was

immersed in the aqueous solution for two minutes in order to be impregnated as well. Then, it was placed on the tissue paper and its surface was slowly rolled by a soft rubber roller. To form polyamide layer in the upper surface, the membrane was clamped between a glass and a Teflon frame that had 1 cm height and the inner cavity of 4 cm×8 cm. The organic solution was poured into the frame and polymerization occurred immediately for 60 s. Finally, the obtained membrane was maintained in the distilled water before use.

2.4 Self-assembly of Titania nanoparticles

Since polyamide layer was formed, many unparticipated acyl chloride (-COCl) groups were on the polyamide layer. They were hydrolyzed in contact with water, forming carboxylic acid (-COOH) groups or carboxylate anions (-COO⁻). Now, Titania nanoparticles could be located and stabilized in empty spaces between chains on the polyamide selective layer by strong dative and hydrogen bonds without changing membrane structure [32]. For this reason, the membrane was previously immersed in 2 % wt. sodium carbonate solution for 30 min to convert carboxylic acid groups to carboxylate anion. Then, it was placed in 1 % wt. TiO₂-water suspension in different relaxation times (5, 15 and 30 min). This suspension was prepared after one hour of sonication. Finally, this membrane was washed with pure water.

2.5 Characterization techniques

Surface and cross-sectional morphology of the dried membrane were examined by scanning electron microscopy (SEM, KYKY-EM3200, China). For cross-section analysis, the membrane sample was freeze-fractured in liquid nitrogen. The

sample was sputter-coated with gold before SEM analysis. Roughness of membrane surface was studied by Atomic force microscopy (AFM, NanoScope E). FT-IR spectroscopy (ABB-Bomem MB100, Canada) was used to determine specific functional groups on the polyamide thin-film membrane surface.

2.6 Membrane performance

MWCO measurement, permeability and rejection experiments were carried out by an ultrafiltration setup (Fig. 1). It offered an effective filtration area of 32 cm², a feed velocity on the membrane surface of 6 L/min, a pressure of 4 bar and an operating temperature of 25±2°C. For the measurement of rejection, the concentration of sodium sulfate and amoxicillin in feed was kept constant at 2000 ppm and 5000 ppm, respectively. The concentration of sodium sulfate was obtained through the measurement of aqueous solution conductivity by the use of a conductometer (WTW inoLab Cond 720, Germany) and amoxicillin concentration was measured by UV-Vis spectrophotometer (GBC, model Cintra 101, Australia) at λ=229 nm [33]. Molecular weight cut-off (MWCO) of polyamide thin-film composite membranes in the presence and absence of Titania nanoparticles was investigated using different molecular weights of PEG polymer (2000, 3000 and 4000 g/mol). The analytical method for determining PEG concentration has been given by Sabde et al. [34]. PEG solutions were analyzed using a spectrophotometer at λ=535 nm. The initial concentration of PEG in the feed was 500 ppm. The membrane mean pore size was determined according to an equation reported by Causserand et al. [35].

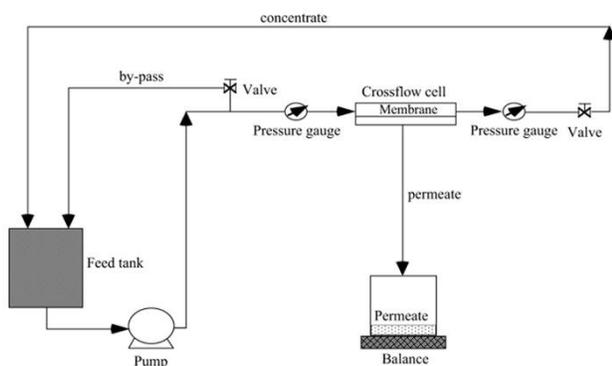


Fig. 1. Used NF setup for measurement of TiO₂ nanoparticles-polyamide TFC membrane performance.

3. Results and discussion

3.1 Physicochemical characteristics of membrane

FT-IR spectra of PSf membrane support and polyamide thin-film composite membrane are presented in Fig. 2. The presence of main peaks was related to polysulfone support (ν_a (C-H, aromatic ring): 3060, 3033, 3000 cm⁻¹, ν_a (C-H, aliphatic chain): 2969, 2923, 2900 cm⁻¹, ν_a (C=C, aromatic): 1585, 1487 cm⁻¹, ν_a (C-SO₂-C): 1323 cm⁻¹, ν_s (C-SO₂-C): 1151 cm⁻¹ and ν_a (C-O-C): 1240 cm⁻¹, 1263 cm⁻¹) and polyamide layer (ν_a (COO-H, =N-H): 3410 cm⁻¹, ν_a (C=O, amide): 1723 cm⁻¹, ν_a (C=O, acid): 1662 cm⁻¹ and ν_a (C=C, aromatic): 1441 cm⁻¹, 1662 cm⁻¹), thereby indicating the successful interfacial polymerization. Besides, it was obvious that there was a negligible amount of PEG in the membrane support (ν_a (O-H): 3402 cm⁻¹, ν_a (C-H, aliphatic chain): 2900, 2923, 2969 cm⁻¹ and ν_a (C-O-C): 1240 cm⁻¹, 1263 cm⁻¹). Here, ν_a and ν_s were the mean frequency of anti-symmetrical and symmetrical stretchings, respectively. Because of the hydrolysis of acid chloride functional groups and their conversion to carboxylic acid, the peak of these functional groups was also observed in the FT-IR spectrum of polyamide selective layer.

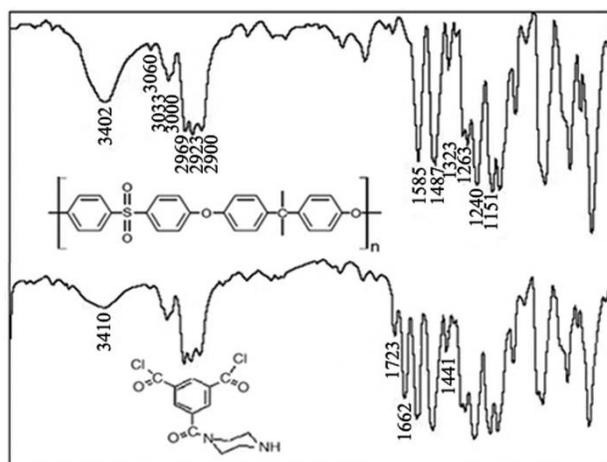


Fig. 2. FT-IR spectra of PSf membrane support and polyamide thin-film composite NF membrane without Titania self-assembly.

Fig. 3 illustrates the surface and cross-section of PSf membrane support and polyamide thin-film composite membrane with and without Titania nanoparticle self-assembly on the surface. It can be observed that the top dense layer and finger-like structure are distinguishable in the cross-section of support before the formation of polyamide selective layer (Fig. 3B and C). This structure was the same as that was formed in the Loeb-Sourirajan or phase separation membranes [36]. Also, the surface morphology of PSf support was smooth and integrated (Fig 3A). In the performance of thin-film composite nanofiltration membranes, the perfect establishment of thin-film selective layer is a very important factor. As shown in Figs. 3E, F, H and I, the polyamide layer was attached completely and correctly to the top surface of support and was separately observed from finger-like layer. When the polyamide thin-film layer was formed, the membrane surface became unsmooth (Fig 3D). Furthermore, the presence of TiO₂ nanoparticles appropriately dispersed on the surface (Fig. 3G) increased the morphological changes of surface, turning it less smoother [35, 37, 38].

Fig. 4 shows AFM images of PSf membrane support surface and polyamide TFC membrane surface with and without TiO₂ nanoparticles over a scan area of 25 μm². By the use of these images, the surface roughness parameters of these membranes were measured and investigated as extracted in terms of mean roughness (S_a), root mean square of Z data (S_q) and also, the mean difference between the highest peaks and the lowest valley (S_z) (Table 1). These parameters were measured via Nanoscope software. As seen, the surface of PSf membrane support appeared to be rougher with the interfacial polymerization of

piperazine and trimesoyl chloride and the formation of polyamide selective layer (Fig. 4A and B). This increment resulted from the ability of these two monomers to form three dimensional cross-linked structures on the surface of PSf support. Furthermore, the outcome of AFM images confirmed that the roughness of polyamide thin-film composite membrane surface was increased with the self-assembly of Titania nanoparticles (Fig. 4C). AFM analysis was in agreement with SEM images and even showed the distribution of TiO₂ nanoparticles on the surface.

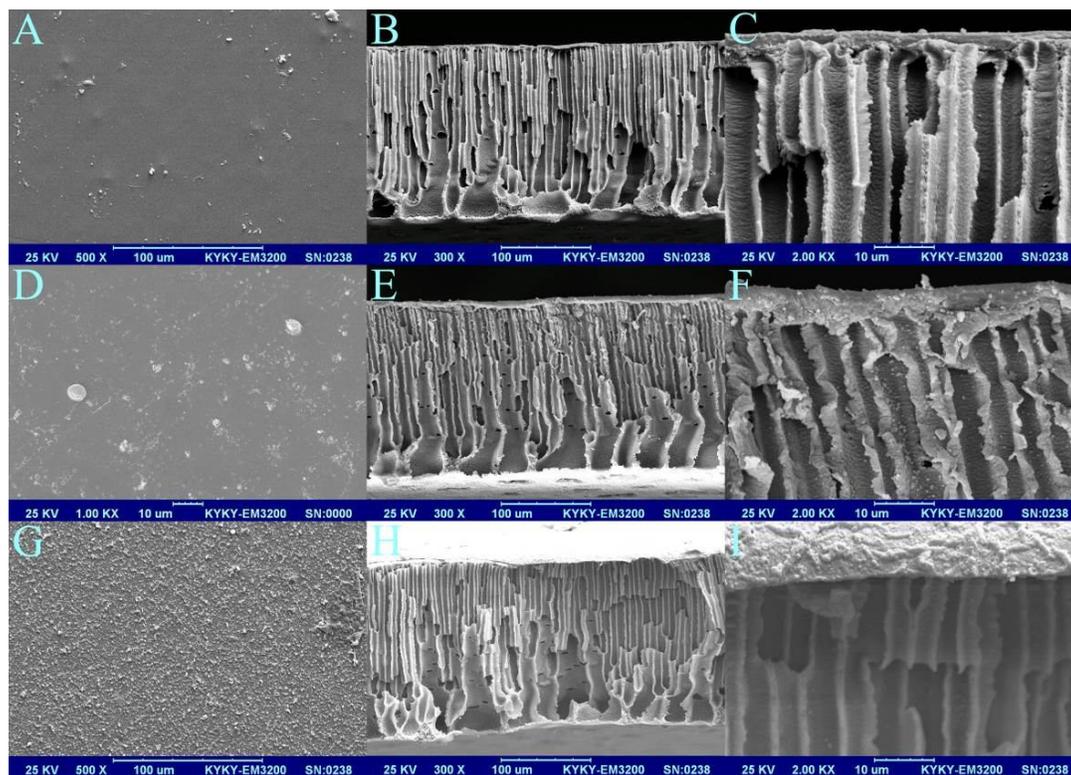


Fig. 3. SEM images of top and cross-section of PSf membrane support (A-C), polyamide TFC nanofiltration membrane without (D-F) and with (G-I) of TiO₂ nanoparticles (relaxation time=15 min).

Based on the MWCO analysis, the molecular weight of PEG for the polyamide thin-film composite membrane without and with TiO₂ nanoparticles (relaxation time=15 min) was 3784.35 and 3660.67 g/mol, respectively; also, their pore size was calculated to be 2.653 and

2.604 nm, respectively [34-35]. This increment in the PEG rejection and decrement in the pore size can be attributed to the presence of Titania nanoparticles. These nanoparticles play the role of filler by being placed in the pores of membrane surface and somewhat increase the rejection time.

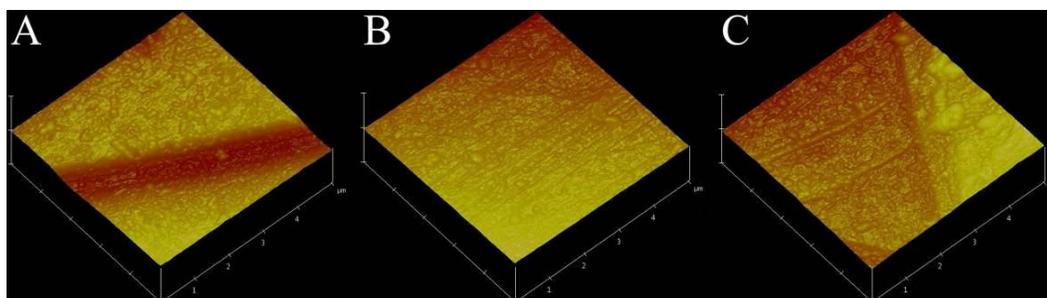


Fig. 4. AFM images of PSf membrane support surface (A), polyamide TFC nanofiltration membrane surface without (B) and with (C) of TiO₂ nanoparticles (relaxation time=15 min).

Table 1. Roughness parameters of PSf membrane support and polyamide TFC membrane in presence and absence of TiO₂ nanoparticles.

Membrane	S _a (nm)	S _z (nm)	S _q (nm)	Surface Area (μm ²)
PSf membrane support	6.113	69.934	8.141	25.3
Polyamide TFC membrane	24.21	191.83	29.944	25.531
TiO ₂ nanoparticles-Polyamide TFC membrane	41.045	349.23	52.586	27.372

3.2 Performance evaluation of membrane

In order to evaluate the performance of TiO₂ nanoparticles-polyamide thin-film composite membrane for the separation of amoxicillin via nanofiltration process, the optimal membrane should be selected. When Titania nanoparticles were self-assembled on the selective layer of thin-film nanofiltration membrane during 5 min relaxation time, the pure water flux was increased from 38.4 to 39.4 L/h.m² and the rejection of Na₂SO₄ was almost constant (96.8 to 96.4%). The cause of this improvement was the increment of hydrophilicity of the membrane surface. This change proved the suitable stabilization of Titania nanoparticles on the selective layer of nanofiltration membrane. With the more increase of relaxation time, the flux was enhanced (44.4 and 50.8 L/h.m² for the relaxation time of 15 and 30 min, respectively), although the rejection was decreased significantly (97 and 87.5%). This considerable decrement can be attributed to the decrease of effective charge on the membrane surface. The more adsorption or accumulation of TiO₂ nanoparticles on the selective layer resulted

in a layer that acted as a barrier and prevented nanofiltration membrane from Donnan repulsion as a main separating mechanism. Therefore, the Na₂SO₄ rejection was declined, though the flux of pure water was increased. Thereafter, the nanofiltration membrane with the relaxation time of 15 min was selected as the optimum membrane for amoxicillin separation and the parameters of nanofiltration process were considered on this membrane.

The outcomes of pressure effects on the composite membrane without and with TiO₂ nanoparticles are presented in Fig. 5. As can be seen, the relationship between pressure and flux was relatively linear in both membranes and flux was increased with pressure and actually, driving force. Since the thickness of precipitation layer was lower in presence of Titania nanoparticles, the pressure driving force was more effective, resulting in the higher flux.

More amounts of flux were gained in higher feed velocity on the nanofiltration membrane, as shown in Fig. 6. It can be stated that a part of amoxicillin precipitation was physically removed

from the membrane surface by enhancing the flow rate and the thickness of precipitation layer was reduced. Also, the quantity of the rejected amoxicillin molecules in the adjacent selective layer or concentration polarization was decreased, causing the increment flux and the slight rejection. Moreover, the flux difference was lower for TFC nanofiltration membranes with TiO_2 nanoparticles (5.2 vs. 6.8 L/h.m^2), indicating the more hydrophilicity of membrane surface.

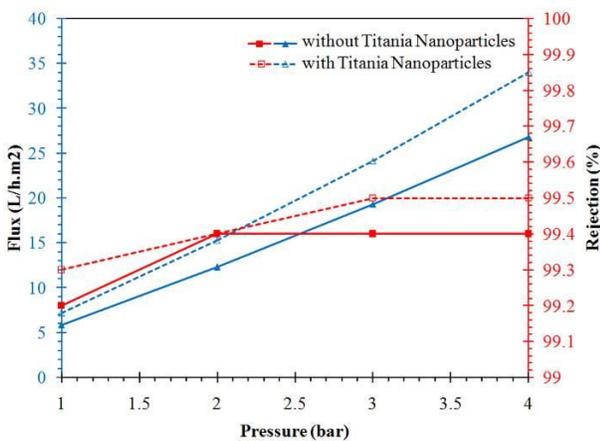


Fig. 5. Influence of pressure on TiO_2 nanoparticles-polyamide thin-film composite membrane.

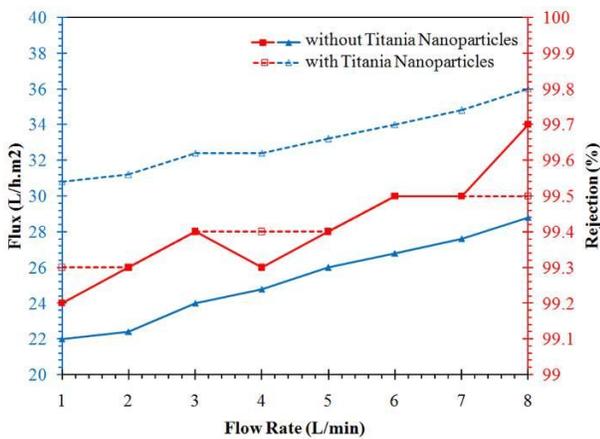


Fig. 6. Influence of flow rate on TiO_2 nanoparticles-polyamide thin-film composite membrane.

The nanofiltration process was also achieved with various feed concentrations (Fig. 7). The rejection of amoxicillin solutions was very high in

both membranes, showing the efficiency of aforementioned membranes in separating this pharmaceutical substance. The noticeable point was the enhancement of polyamide composite membrane flux without Titania nanoparticles in low amoxicillin concentration (especially 100 ppm). The flux of amoxicillin solution with the concentration of 100 ppm was increased to 17%, rather than deionized water. This was due to thin-film deposition of antibiotic on the membrane surface. Antibiotic had high water solubility and or high hydrophilicity (3430 mg/L), because of its structure and the presence of several functional groups such as carboxylic acid, amide, amine and hydroxyl groups.

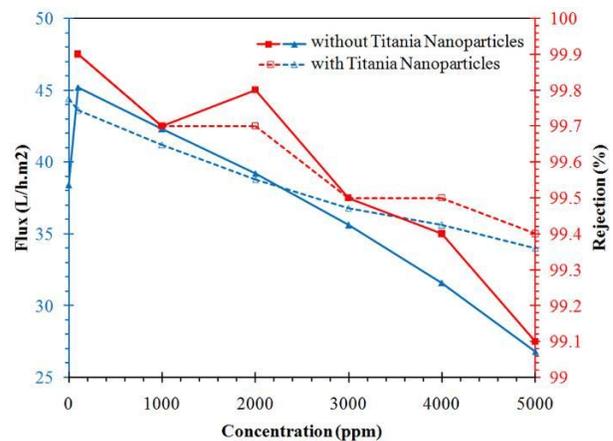


Fig. 7. Influence of amoxicillin concentration on TiO_2 nanoparticles-polyamide thin-film composite membrane.

In the low concentration, a thin layer of this antibiotic was deposited on the entire membrane surface (whole protrusions and grooves), thereby enhancing flux significantly. By increasing antibiotic concentration, the thickness of this layer was improved, leading to long water passage through the membrane and decline flux (fouling). In the presence of TiO_2 nanoparticles, the similar rejection changes were relatively observed, but the behavior of membrane flux was somewhat

different. These membranes were resistant to fouling, thus preventing from antibiotic precipitation in the low concentration and also decreasing its layer thickness in the high concentration. Hence, the water flux was not improved in this concentration (vs. nanofiltration membrane without Titania nanoparticles).

The amoxicillin molecules formed cationic, anionic and di-anionic structures in acidic and basic solutions ($pK_a=2.4, 7.4$ and 9.6) and their aqueous solution had $pH=6.3$ [39]. Also, the surface of TiO_2 nanoparticles-polyamide thin-film composite membranes in this article contained carboxylic acid and third type amine functional groups. Therefore, these charged structures could be used for the separation and removal of this substance by using pH replacement. Fig. 8 illustrates this behavior in various pHs (3.9, 6.3, 8.3 and 11) for two types of membranes.

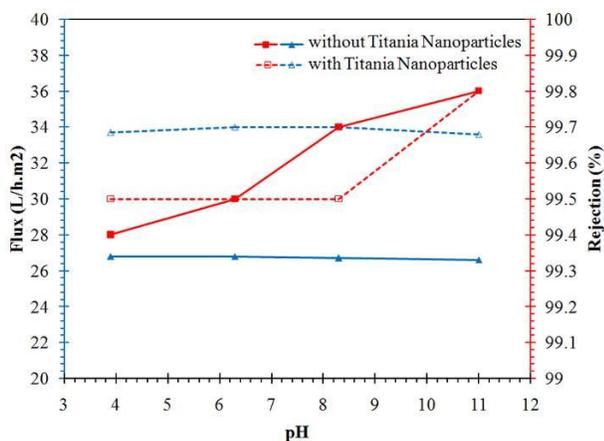


Fig. 8. Influence of pH on TiO_2 nanoparticles-polyamide thin-film composite membrane.

The membrane surface and amoxicillin molecules were similarly charged in both acidic and basic condition and on the basis of Donnan repulsion mechanism, the increment or stability brought about the rejection. Since the polyamide membrane surface was negatively charged, amoxicillin rejection would be increased

significantly in the basic pH due to the change of carboxylic acid groups into carboxylate anion and the formation of di-anionic structure in amoxicillin molecules. Also, all amines contained in the selective layer and amoxicillin molecule could be positively charged in acidic pH and the rejection ratio would be preserved again. However, this rejection was lower in comparison to the basic pH.

In addition, the fouling of membranes was measured in the duration of 15 hours (Fig. 9). By passing every 5 hours, the membrane was rinsed for 1 hour without imposing force and with the flow rate of 8 L/min. The results demonstrated that polyamide membrane with Titania nanoparticles had a higher performance. These membranes showed more resistance to fouling, despite the higher flux. Moreover, the flux of polyamide thin-film composite membranes in the presence of TiO_2 nanoparticles could be relatively returned to their initial flux after the rinsing process ($34 L/h.m^2$) while in the absence of TiO_2 nanoparticles, the initial flux could not be found (26.8 to $25 L/h.m^2$).

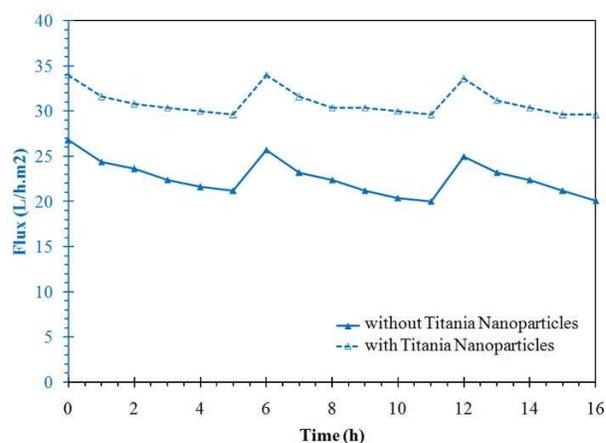


Fig. 9. Influence of fouling on TiO_2 nanoparticles-polyamide thin-film composite membrane.

Namely, the lower loss of water flux could be observed during the nanofiltration process in the presence of TiO_2 nanoparticles. In comparison to industrial nanofiltration membranes, these

membranes showed better performances. NF4040 membrane as an industrial nanofiltration membrane had the pure water flux of 26.4 L/h.m² and the rejection of 97% at the pressure of 4 bar whereas this Titania nanoparticles-polyamide thin-film membrane owned 44.4 L/h.m² and 99%, respectively [28]. Of course, it showed 34 L/h.m² for amoxicillin solution with the concentration of 5000 ppm. Also, Zhang et al. [40] achieved the flux of 23.2 L/h.m² and the rejection of 62% with their own membranes. Derakhsheshpoor et al. [39] performed the flux of 23.2 L/h.m² and the rejection of 80% with acrylic acid-grafted polysulfone membranes. The prepared membrane in this article dominated all these membranes.

4. Conclusion

TiO₂ nanoparticle-polyamide thin-film composite membranes were prepared to separate amoxicillin from the pharmaceutical wastewater via nanofiltration process. In this article, TiO₂ nanoparticles were used in order to increase flux and membrane resistance to fouling. These nanoparticles were deposited on the membrane surface using self-assembly. By means of FT-IR analysis and SEM imaging, the presence of polyamide selective layer on the polysulfone support and the dispersion of Titania nanoparticles were obviously proved. Also, the results of AFM indicated that the roughness of membrane surface was increased with the interfacial polymerization. It was increased with adding the TiO₂ nanoparticles, too. However, the presence of nanoparticles could increase the roughness, but with regard to enhancing the hydrophilicity and diminishing the membrane surface fouling, their presence could totally bring positive results. In the presence of Titania nanoparticles, the size of pores was decreased slightly, probably due to

nanoparticles filling role for membrane pores (2.653 to 2.604 nm). The effect of different pressures, feed flow rates, concentrations, pHs and fouling on the performance of synthesized membrane was investigated too. In all cases, the membrane rejection was preserved up to 99% and only its flux was changed with different operating conditions. The lower loss of water flux could be observed during the nanofiltration process in the presence of TiO₂ nanoparticles. Furthermore, the flux and rejection of these membranes were higher than those of market industrial membranes such as NF4040 membrane (26.4 vs. 44.4 L/h.m² and 97 vs. 99%).

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