Membrane Water Treatment, *Vol. 9, No. 6 (2018) 481-487*
DOI: https://doi.org/10.12989/mwt.2018.9.6.481

Improving hydrophilic and antimicrobial properties of membrane by adding nanoparticles of titanium dioxide and copper oxide

Susan Khosroyar* and Ali Arastehnodeh

Department of chemical engineering, Quchan branch, Islamic Azad University, Quchan, Iran

(Received September 23, 2017, Revised July 23, 2018, Accepted September 18, 2018)

Abstract. Membrane clogging or fouling of the membrane caused by organic, inorganic, and biological on the surface is one of the main obstacles to achieve high flux over a long period of the membrane filtration process. So researchers have been many attempts to reduce membrane fouling and found that there is a close relationship between membrane surface hydrophilicity and membrane fouling, such that the same conditions, a greater hydrophilicity were less prone to fouling. Nanotechnology in the past decade is provided numerous opportunities to examine the effects of metal nanoparticles on the both hydrophilic and antibacterial properties of the membrane. In the present study the improvement of hydrophilic and antimicrobial properties of the membrane was evaluated by adding nanoparticles of titanium dioxide and copper oxide.

For this purpose, 4% copper oxide and titanium dioxide nanoparticles with a ratio of 0, 30, 50, and 70% of copper oxide added to the polymeric membrane and compare to the pure polymeric membrane. Comparison experiments were performed on E. coli PTCC1998 in two ways disc and tube and also to evaluate membrane hydrophilic by measuring the contact angle and diameter of pores and analysis point SEM has been made. The results show that the membrane-containing nanoparticle has antibacterial properties and its impact by increasing the percentage of copper oxide nanoparticles increases.

Keywords: membrane process, hydrophilic, antibacterial properties, nanoparticles, titanium dioxide, copper oxide

1. Introduction

Membrane as the material is introduced which some particles more easily than other particles can pass through it, and is the basis of some separation processes. Solvent pass through the pores of the membrane called permeate and materials that do not pass through the membrane, called retentive or residue. Regardless of the significant advantages that the application of this technology compared to other separation methods, often membrane processes faced with the limitations and problems that industrial use them in some cases limit. Membrane clogging or fouling of the membrane as a result of organic, inorganic, and biological membrane is created on the surface (Dong *et al*. 2015). Membrane fouling is one of the main obstacles to achieve high flux over a long period of membrane filtration process (Zhou *et al.* 2010, Khulbe *et al.* 2010). Thus whit over time, significantly reducing leakage of fluid from the membrane is shown. The permeate flux is heavily influenced by the behavior of hydrophilic or Hydrophobic of the membrane and the material absorbed on the surface. So researchers have been many attempts to reduce membrane fouling and found that there is a close relationship between membrane surface hydrophilicity and membrane fouling, such that the same conditions, a greater hydrophilicity were less prone to fouling. Because many of the contaminating materials on the membrane surface and the eclipse are hydrophobic. On the other hand, if the possibility of creating antibacterial properties of the membrane in addition to health issues, also fouling potential reduced. By increasing the concentration of nanoparticles due to the increase of the membrane hydrophilic, the amount of clotting is reduced and has a positive effect on the Permeability flux. But from one place onwards, the flux decreases with increasing nanoparticle concentration due to their clumping into the membrane structure and the possibility of clogging of some of the membrane cavities (Lee *et al*. 2008). According to past studies, it was found that nanoparticles of metal such as aluminum (Al_2O_3) (Wang *et al.* 2011, Saleh *et al.* 2012), zinc oxide (ZnO) (Hong and He 2014, Liang *et al.* 2014), silicon dioxide (SiO_2) (Balta *et al.* 2012, Wu and Mansouri 2013), titanium dioxide (TiO_2) (Kwak *et al*. 2001, Lee *et al*. 2008, Tavakolmoghadam *et al.* 2016) and zeolite (Junaidi *et al.* 2013) can increase the hydrophilicity of the membrane (Leo *et al*. 2013). In addition, these materials may have the ability to produce bio-membrane with anti-fouling properties (Kim *et al.* 2010). Among the mineral nanoparticles mainly titanium dioxide nanoparticles due to good performance such as high hydrophilic, good chemical stability, catalytic effect and antibacterial properties, etc., has its own interest (Rahimpour *et al.* 2011). Antibacterial effects of titanium dioxide nanoparticles to the small size and large surface for interaction with biological membranes have been attributed (Dizge *et al.* 2017). Cell wall on the outside of the cell membrane of bacteria, and it is essential for the survival of the bacteria. Nanoparticle surface is placed directly in contact with the outer membrane of

∗Corresponding author, Assistant Professor
E-mail: susankhosroyar@yahoo.com

http://www.techno-press.org/?journal=mwt&subpage=7 ISSN: 2005-8624 (Print), 2092-7037 (Online)

bacteria and rupture the cell wall and thus destroy the bacteria (Ravishankar and Jamuna 2011). The researchers recommend the use of copper and silver ions as the best disinfectants in hospitals wastewater containing infectious microorganisms. All the research suggests that copper plays a very important role as an antibacterial agent, but other nanoparticles such as platinum, gold, iron oxide, silicon and its oxides and nickel, are not shown antibacterial effects on Escherichia coli (Dong *et al.* 2015). Copper and its alloys (brasses, bronzes, copper-nickel, copper-nickel-zinc) are natural antimicrobial materials that have intrinsic properties to eliminate the range of microorganisms.

Antibacterial effect of copper nanoparticles has been attributed as small size and large surface for interaction with biological membranes. The researchers showed that nanoparticles of titanium dioxide increases the antibacterial properties of sulfated hybrid nano-composite of comparison of *polyvinylidene fluoride* and *polyether sulfone*membranes (Rahimpour *et al.* 2011) as well as the composition of CuO and TiO_2 on the bacterial species Klebsialla pneumoniae (Yousef *et al.* 2012) and Propylene on Staphylococcus aureus and Escherichia coli has antimicrobial properties (Valipoor *et al.* 2012). Given the importance of industrial waste water treatment, as well as the increasing use of membrane processes in water treatment and wastewater treatment, many attempts is done by various researchers to provide improved methods for the purification and also improve the properties of the membrane. In this paper, the effect of nanoparticles on the antimicrobial properties of membrane and output flux of a typical waste water of dairy industries has been investigated.

2. Materials and methods

2.1 Preparation of membranes

To investigate the effects of nanoparticles on the antibacterial properties of membranes, pure polymeric membrane and nanocomposites membrane containing 4 wt% copper oxide and titanium dioxide nanoparticles with a ratios of 0%, 30%, 50%, 70% were compared.

To prepare ultra membranes first the solution contains a certain ratio of NMP, DMF solvents and copper oxide and titanium dioxide nanoparticles and Performer were stirred were stirred by a magnetic stirrer for10 min at 5,000 rpm. Homogenization was carried out using an Ultra-Turex stirrer for 5 hours at 12000 rpm at 30°C to be created suspension with dispersed particles and sustained. Then, about 10% of the total weight of polyether sulfone was added to the dispersed solution and the solution was stirred at a temperature of 50°C to completely dissolve the polymer. After forming a thin layer of polymer on the surface of the nanoparticle, the remains of polyether sulfone was added. After complete dissolution of polymer, a homogeneous solution was produced polyaniline was added and stirred for 18 hours without heating. The prepared homogeneous solution was set aside for 12 hours to remove bubbles. For the purpose of casting solution, the samples were dumped on clean and dry glass surface along a straight line, after ensuring dry stretch film machine, stretch film set on µm 200, then at a steady pace without pause and stop was moved on the casting solution. Finally, the glass was removed from its place and was immersed in the bath containing distilled for 30 minutes.

The prepared membrane samples at this stage were used to examine the antibacterial property in microbiological tests and the best percentage composition of the nanoparticle membrane was used to evaluate hydrophilic properties.

2.2 Microbial testing

Using a sterilized culture loop, bacteria from the mother culture, transferred into the liquid medium that has been pre-sterilized and to the ambient temperature and was cultured**,** then after 24 hours of incubation was used for testing.

Evaluation of antibacterial properties of produced nanocomposites in this study was done in two ways PTCC 1998 for Escherichia coli.

Disk diffusion method: is a test of the antibiotic sensitivity of bacteria (Khosravi *et al.* 2010, Basri *et al.* 2012). The sterile plates containing Mueller-Hinton agar culture medium was prepared. The bacterial suspension of Escherichia coli that equivalent 0.5 McFarland=1.5×10^8 bacteria, as 1.5×10^7 $\frac{cfu}{ml}$ dilution, was prepared. From the control polymer without nanoparticle made discs with 0.5 cm diameter and was sterilized in autoclave for 15 minutes at 121°C. Then a sterile swab plunged into the bacterial suspension (it was prepared equivalent $1.5\times10^7 \frac{cfu}{ml}$) and the plate was cultured in Mueller Hinton agar on cultivating grass. After a short time (about 2 minutes) of bacteria inoculating into the culture medium, by sterile forceps and next to the flame, nanocomposite components and control polymer were placed on plates containing culture medium. Incubated the plates at 37 degrees C for 24 hours. After incubation, the colonies were counted by standard plate count method. This test repeat for 3 times and the number of colonies was averaged.

Tube method: Control polymer and nanocomposites cut into 1 cm pieces and was sterilized in autoclave for 15 minutes at 121°C. Then each piece of the control polymer and nanocomposites without antibacterial material were placed in a test tube separately. Then from any bacteria a bacterial suspension equivalent 0.5 McFarland was prepared (1-5×10^8 $\frac{cells}{ml}$) and the suspension was diluted to 10^8 $\frac{cells}{ml}$. 2 ml of the suspension was poured into a test tube so that parts of polymer control and nanocomposites were immersed in the bacterial suspension (Haji Mirza Baba *et al.* 2010).

The test tubes containing Nano-composite components and solutions of bacteria were incubated at 37°C for 18-24 hours. After 24 hours of incubation, 0.1 CC of samples were cultured by the surface inoculation method (standard Plate Count Agar). To count colonies on plates the plates were placed on a colony counter and were counted the number of bacterial colonies.

2.3 Scanning Electron Microscopy analyses

To investigate the structure and pore diameter, scanning electron microscope (LEO, model VP 1450, Germany) was used.

The Scanning Electron Microscope (SEM) produce a variety of signals at the solid samples surface by using a focused beam of high-energy electrons. The signals which are obtained from the interaction of electrons and solid sample determine information such as morphology, chemical composition and crystalline structure and orientation of the solid sample (Siddiqui and Field 2016).

2.4 Contact Angle measurement

Contact Angle is a measurement used to determine surfaces hydrophilic or hydrophobic properties. The ability of a liquid to spread over a surface without forming individual droplets determines its wettability or hydrophilic characteristics.

Measuring the contact angle was performed merely with drop of water (volume 4 ml) by a system equipped with a CCD camera capable of photographing and filming of drops and software to measure droplet contact angle (OCA 15 plus models Data physics Co.)

3. Results and discussion

3.1 The results of disk diffusion method

The plates containing the test results of bacteria, bacterial colonies had grown very well around of samples without nanoparticle, but bacterial colonies were not developed around the membranes containing copper oxide and titanium dioxide nanoparticles.

It should be noted that the halation was not observed surrounding the membrane that contains titanium dioxide nanoparticles. But by increasing the percentage of copper nanoparticles in the sample, the halation around the membrane was bigger. By measuring the halo of around the samples and compare them, the strength of antibacterial sample be realized.

3.2 Results of tube method

The results of this method were investigated after 24 hours of incubation of cultured plates by the method of counting colonies with colony counter device. Rate of antibacterial property was calculated from Eq. (1):

$$\%R = \frac{B - C}{B} \times 100 \qquad (1)$$

A: rate of antibacterial properties
B: The number of control polymer colonies
C: The number of sample colonies

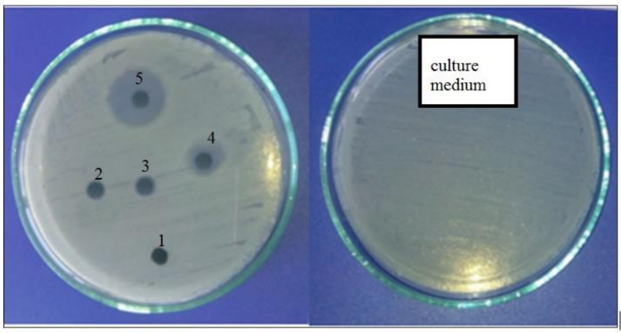

Fig. 1 Result of disk diffusion method

Table 1 The number of colonies grown on each sample

NO	Composition of nanoparticles	The number of grown colonies
1	Without nanoparticles	5230
2	100% of titanium dioxide	3540
3	30% of copper oxide and 70% titanium dioxide	2200
4	50% of copper oxide and 50% titanium dioxide	250
5	70% of copper oxide and 30% titanium dioxide	100

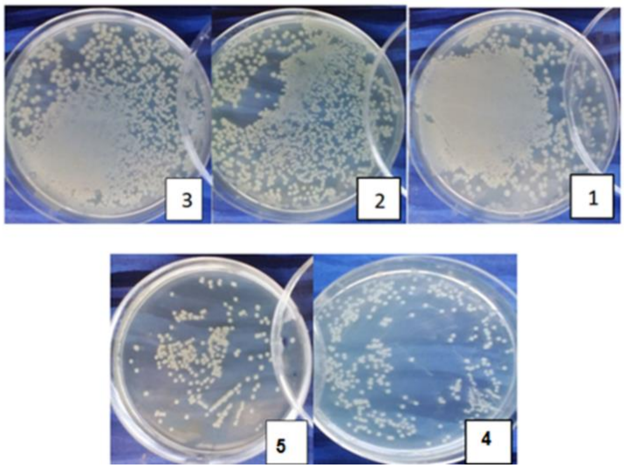

Fig. 2 The number of colonies grown in tube method

1. No polymer nanoparticles
2. Polymer with 100% TiO_2
3. Polymer with 30% CuO, 70% TiO_2
4. Polymer with 50% CuO, 50% TiO_2
5. Polymer with 70% CuO, 30% TiO_2

According to previous research (Rahimpour *et al*. 2011, Rai and Bai 2011, Dong *et al.* 2015) because of having high surface area to volume ratio, which increases contact area with target organisms nanoparticle improve antimicrobial properties. Here, Both nanoparticles have antimicrobial properties, but this property increase by adding CuO nanoparticle.

3.3 The results of the contact angle test

Drop contact angle with horizontal plane simultaneous influenced by hydrophilic and the size of the pores in the porous surface (Fig. 3). By adding nanoparticles to the membrane surface, increases roughness then reduces the contact angle. This indicates that the hydrophilic membrane increases with increasing nanoparticle to the membrane and thereby reduces the amount of congestion. The clogging of such membrane in an exposure with a water food like dairy waste is less because even after the initial connection of solute particles on the membrane surface, hydrophilic membrane causes the water molecules quickly at the junction of soluble particles, penetrate and as a result, their link be weaken. In this state, the probability of detachment of soluble components from the membrane surface increases by scrubbing with a stream that passes from their

Table 2 Rate of antibacterial activity against E. coli

Composition of nanoparticles	Rate of antibacterial activity
100% of titanium dioxide	32.31
30% of copper oxide and 70% titanium dioxide	93.57
50% of copper oxide and 50% titanium dioxide	95.21
70% of copper oxide and 30% titanium dioxide	98.08

Table 3 The results of the contact angle test for sample 5

sample Number	Wt% of nanoparticles	contact angle
1	0	1.0±75.16
2	0.1	1.7±67.78
3	0.5	2.1±64.99
4	1	2.8±64.76
5	2	1.9±63.91
6	4	1.5±63.73
7	6	1.3±59.19

vicinity, which in turn means a reduction in the amount of fouling.

Best composition of Nano-particle (No. 5) was added to membrane according to Table 3. The results show in the membrane having the highest percentage of nanoparticle, having the least amount of congestion.

3.4 SEM images

To investigate of membrane morphology, polyether sulfone / titanium / copper dioxide nanocomposite were prepared for cross-sectional images of samples 1, 3, 5, 6 and 7 to test SEM. Fig. 4 shows cross-sectional images of nanocomposite membranes with different percentages of nanoparticles in both 1000 and 5000 magnification. As you can see, all synthetic membranes with asymmetrical structure are including the porous top layer and substrate. The finger holes in the membrane structure can be related to the rapid exchange of solvent and anti-solvent (water) was in the coagulation bath, which causes immediate phase separation during submergence nanocomposite film in the coagulation bath (Soroko and Livingston 2009). The solvent is NMP solvent DMF cause pores finger and cause the foam pores in the membrane structure. The presence of NMP solvent causes the formation of cavities finger and the presence of DMF solvent causes the formation of sponge pores in the membrane structure. Since the optimum solvent ratio of polyether sulfone polymers to polyaniline for the preparation of membranes equal to 27.20 percent, so a combination of both solvent with above ratio was used for the production of polymeric solution. Sponge / finger membrane structure in Fig. 4 can be for this reason. On the other hand, PVP additive to the amount of 2 wt% as maker hole and achieve to more fluxes flow of membrane permeate was used in making the samples. Images obtained in 1000 magnification of membrane structure shows that by adding nanoparticles to a polymeric network from 0 to

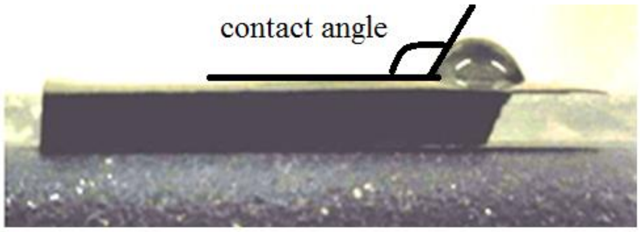

Fig. 3 Contact angle test image

6wt%, reduced thickness of the upper finger layer. In other words, finger pores dragged to the closer distances of surface membrane. Also, with increasing the percentage of nanoparticle, pore structure has changed and finger mode change to spongy mode. Two different phenomena may cause changes in the thickness of the top layer of the membrane, that be discussed below. When nanoparticles as solid phase placed in compound of casting solution, creates a less stable polymeric solution and the time required for phase separation is reduced. Therefore, it is expected that the polymeric film submergence stage in the coagulation bath, phase separation occurs instantaneously. On the other hand in a nanocomposites solution with constant polymer percent, increasing percentage of nanoparticles causes to obstruct the interchange of solvent and non-solvent and tends to delayed phase separation (Mulder 1996, Balta *et al.* 2012). Since the accumulated nanoparticles over the nanoparticles that distributed uniformly in the polymeric network, have a smaller specific surface, then this will impact less on the decrease of interchange rate of the solvent and non-solvent (Ma *et al.* 2012). So when the nanoparticles accumulate, their effect on the thermodynamic instability of the solution is the dominant factor in the separation phase. In Fig. 4, according to the cross-sectional images of the membrane (Fig. 6), it seems, the nanoparticles are well distributed in the polymeric network that can be the result of covalent bonds between polymeric chains and nanoparticles. The top layer thickness of the sample membrane 6 to the membrane sample 1 declined. In fact addition of 4% wt of the composition of the nanoparticles to the polymeric solution reduces thermodynamic stability. The distributed nanoparticles by creating prevention against exchange of non-solvent and solvent, to some extent reduce the effect of the particles in instability of the polymeric solution. That's why a reduction in the thickness of the upper layer of the sample membrane 6 compared to samples 1, 3 and 5 is less. For sample membrane 7 accumulations of nanoparticles in some parts of the membrane is shown that the inhibitory effect of solvent and non-solvent exchange decreases by nanoparticles. With increasing concentrations of nanoparticles due to increasing accumulation of nanoparticle, density of mineral phase increased in the polymeric solution and led to the replacement of this phase to the lower segments of the membrane. Furthermore duo to increasing the viscosity of the polymeric solution this hydrophilic nanoparticle will not be able to climb to the surface of the membrane. So the concentration preventive factor decreased against exchange of solvent and non-solvent on the upper surface of membrane and finger holes

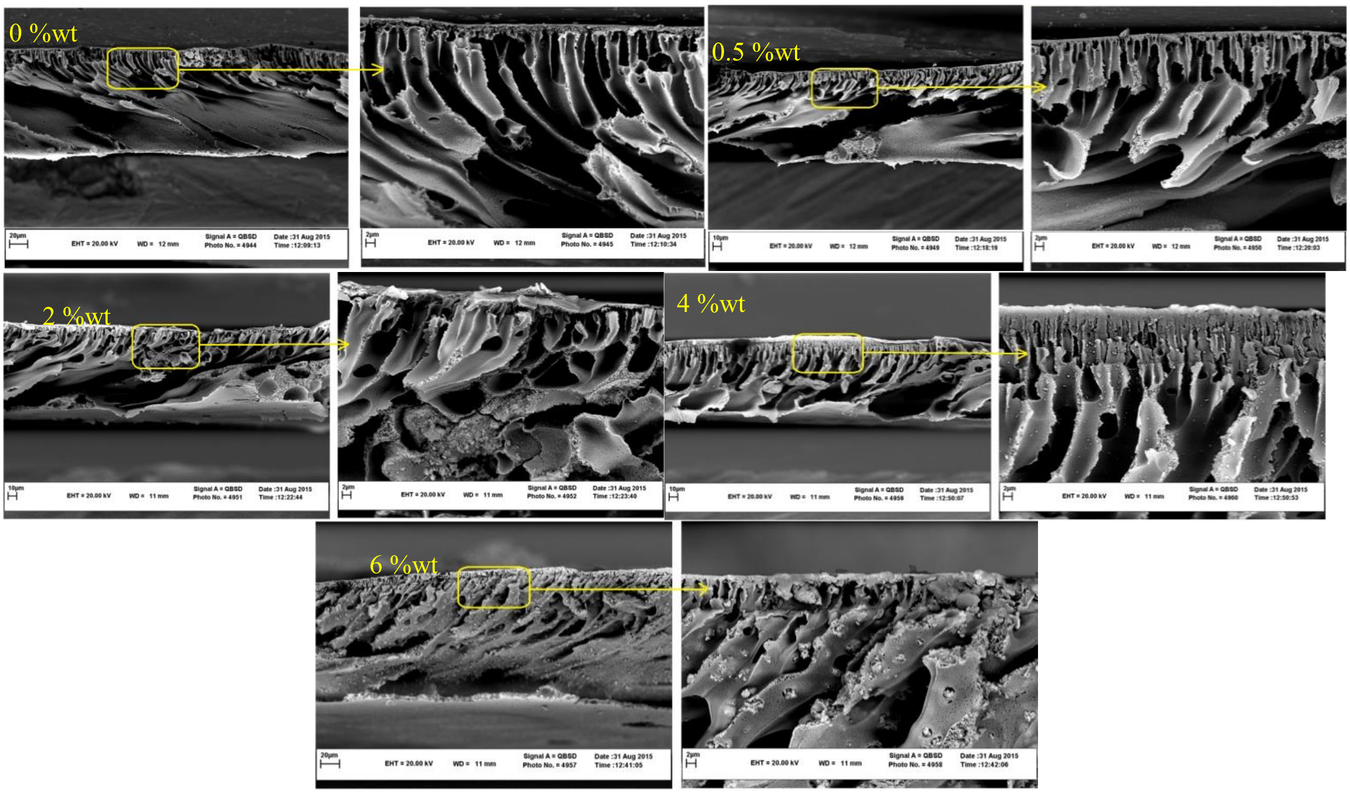

Fig. 4 SEM images of the cross-sectional morphologies of the nanocomposite membrane polyethersulfone / titanium / copper dioxide with different percentages of nanoparticles

Table 4 Results of pure water flux passed of membranes in 3 bar pressure

sample membrane number	1	2	3	4	5	6	7
Permeate flux (LMH)	45.1	46.2	50.7	58.4	53.6	51.3	47.2

Table 5 The results of analysis of elements in sample 7

Spectrum +	C	O	Ti	Cu	Total
Spectrum 1	38.52	25.22	13.57	22.70	100.00

be closer to the membrane surface. SEM image analysis in both 1000 and 5000 magnification confirmed that increasing the percentage of nanoparticles, nanoparticles aggregates and placed in the lower segments of membrane. The results of pure water flux testing in 3 bar pressure of the membranes are given in Table 4. According to the flux results can be found in the concentration 18 wt% of the polymeric mixture PES / Pani, the resultant membranes are containing pores size in the range of ultrafiltration membrane. Also, according to the performed interpretations on the SEM images and observing the pure water flux of membranes can be concluded that the most pure water flux of the membrane containing the 2 %wt nanoparticles. At higher concentrations of nanoparticles due to their agglomeration in the membrane structure and the possibility of clogging some of pores, pure water flux decreases (Soroko and Livingstone 2009). On the other hand, in nanoparticles concentrations about 1% by weight due to the hydrophilic properties of the membrane, pure water flux passed of membranes containing nanoparticle is more of pure membrane. At higher concentrations of nanoparticles due to their agglomeration in the membrane structure and the possibility of clogging some of pores, pure water flux decreases. On the other hand, in nanoparticles concentrations about 1% (sample 4) by weight due to the hydrophilic properties of the membrane, pure water flux passed of membranes containing nanoparticle is more of pure membrane.

3.4 EDX images

EDX analysis is a method for determining the elemental composition of a sample or a portion of a sample that have been brought in order to prove the presence of titanium dioxide and copper oxide nanoparticles here. Fig. 4 Shows SEM images at 20,000 Magnification and EDX of the cross structure of sample membranes 5, 6 and 7. As are clear from the images, carbon and oxygen peaks are related to polymeric membrane layers and Ti and Cu peaks are reason for the presence of titanium dioxide and copper oxide nanoparticles in polyether sulfone membrane structure that improve the performance of the membrane. (Gold peak was related to the coating sample for analyzed). Also according to the explanations already be given, the percentage of copper oxide nanoparticles (due to increased antimicrobial properties) was higher in made samples from the percentage of titanium dioxide nanoparticles. The results of measuring of percentage of the elements in the samples on the bottom also confirm this. For example, for sample 7, these values have been brought in Table 5.

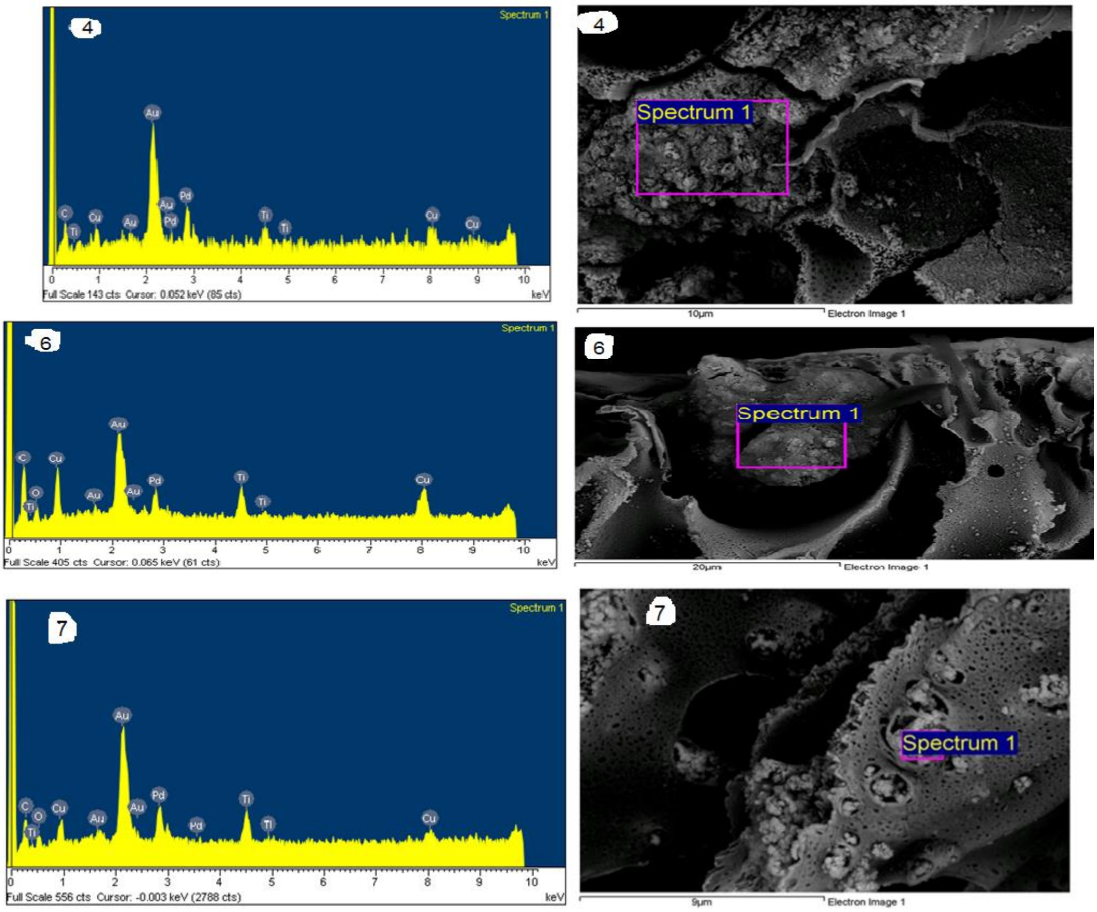

Fig. 5 EDX and SEM images at 10,000 Magnification of the membrane cross-sectional of samples 4, 6, 7

4. Conclusions

In this article were evaluated the manufacture, modification and testing of nanocomposite membrane polyethersulfone / titanium / copper dioxide to enhance hydrophilic and increase antibacterial properties of these membranes. To evaluate the performance of made membranes, experiments were done under various conditions. Initially membranes were prepared with different composition of titanium dioxide and copper oxide and to study the effects of the concentration of nanoparticles on the antibacterial performance of membrane on the E. coli bacteria, bacteriological tests were assessed and the best combination of nanoparticles was determined in the membrane. The making of polyethersulfone/titanium/copper dioxide nanocomposite was done with different composition of constant percentage of nanoparticles and overall percentage of nanoparticles.

1. Investigation of the combination effect of titanium dioxide and copper oxide nanoparticles concentration with the ratios of copper oxide to titanium dioxide as 0%, 30%, 50%, 70%, on species E. coli was found that most anti-bacterial property is achieved at the combination of 70%.

2. According to the SEM images can be claimed to combination of the polymer with nanoparticles are well done and the results of EDX was confirmed the presence of nanoparticles in the membrane.

3. According to the SEM images of the cross section of membranes that prepared by deposition-immersion and direct combination of the nanoparticle with casting solution as expected, nanoparticles of titanium dioxide and copper oxide do not have a significant impact on the membrane pore structure and pore structure remains to finger mode.

References

Balta, S., Sotto, A., Luis, P., Benea, L., Van der Bruggen, B. and Kim, J. (2012), “A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO”, *J. Membr. Sci.*, **389**, 155-161.

Basri, H., Iamail, A.F., Aziz, M., Nagai, K., Matsuura, T., Abdullah, M.S. and Ng, B.C. (2010), “Silver filled polyether sulfone membranes for antibacterial application−Effect of PVP and TAP addition on silver dispersion”, *Desalination*, **261**(3), 264-271.

Dizge, N., Ozay, Y., Simsek, B., Gulsen, E., Akarsu, C., Turabik, M., Unyayar, A. and Ocakoglu, K. (2017), “Preparation, characterization and comparison of antibacterial property of polyethersulfone composite membrane containing zero valent iron or magnetite nanoparticles”, **8**(1), 51-71.

Dong, L.X., Yang, H.W., Liu, S., Wang, X.M. and Xi, Y.F. (2015), “Fabrication and anti-biofouling properties of alumina and zeolite nanoparticle embedded ultrafiltration membranes”, *Desalination*, **365**, 70-78.

Haji Mirza Baba, H., Montazer, H. and Rahimi, M. (2010), "Antimicrobial effects of Nano-silver on nylon carpets", *J. Islamic Azad U.*, **2**(21), 101-107**.**

Hong, J. and He, Y. (2014), "Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning", *Desalination*, **332**, 67-75.

Junaidi, M.U., Leo, C.P., Kamal, S.N. and Ahmad, A.L. (2013), "Foulingmitigation in humic acid ultrafiltration using polysulfone/SAPO-34 mixed matrix membrane", *Water Sci. Technol*., **67**(9), 2102-2109.

Khosravi, R., Akhavan Sepahi, R. and Khanafari, A. (2010), "Effects of antimicrobial silver and copper nanoparticles and compared with vegetative cells and spores with sodium hypochlorite on Bacillus subtilis and Bacillus cereus", *J. Microbial Biotechnol. Islamic Azad University*, **2**(7), 44-37.

Khulbe, K.C., Feng, C. and Matsuura, T. (2010), "The art of surface modification of synthetic polymeric Membranes", *J. Appl. Polym. Sci.*, **115**(2), 855-895.

Kim, J. and Van der Bruggen, B. (2010), "The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment", *Environ. Pollut.*, **158**(7), 2335-2349.

Kwak, S.Y., Kim, S.H. and Kim, S.S. (2001), "Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal antifouling. 1. Preparation and characterization of TiO2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane", *Environ. Sci. Technol.*, **35**, 2388-2394.

Lee, H.S., Im, S.J., Kim, J.H., Kim, H.J., Kim, J.P. and Min, B.R. (2008), "Polyamide thin-film nanofiltration membranes containing TiO_2 nanoparticles", *Desalination*, **219**, 48-56.

Leo, C.P., Ahmad Kamil, N.H., Junaidi, M.U.M., Kamal, S.N.M. and Ahmad, A.L. (2013), "The potential of SAPO-44 zeolite filler in fouling mitigation of polysulfone ultrafiltration membrane", *Sep. Purif. Technol*., **103**, 84-91.

Liang, S., Qi, G., Xiao, K., Sun, J., Giannelis, E.P., Huang, X. and Elimelech, M. (2014), "Organic fouling behavior of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes functionalized with surface-tailored nanoparticles: implications for organic fouling in membrane bioreactors", *J. Membr. Sci.*, **463**, 94-101.

Ma, Y., Shi, F., Zhao, W., Wu, M., Zhang, J., Ma, J. and Gao, C. (2012), "Preparation and characterization of PSf/clay nanocomposite membranes with LiCl as a pore forming additive", *Desalination*, **303**, 39-47.

Mulder, M. (1996), "Basic principles of membrane technology", Kluwer Academic Publishers, Dordrecht, the Netherlands.

Rahimpour, A., Jahanshahi, M., Rajaeian and B., Rahimnejad, M. (2011), "TiO_2 entrapped Nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties", *Desalination*, **278**, 343-353.

Ravishankar Rai, V. and Jamuna Bai, A. (2011), "Nanoparticles and their potential application as antimicrobials", *Science against Microbial Pathogens: Communicating Current Research and Technological Advances*, **3**(1), 197-209.

Saleh, T.A. and Gupta, V.K. (2012), "Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance", *Sep. Purif. Technol*., **89**, 245-251.

Siddiqui, F.A. and Field, R.W. (2016), "Fouling and cleaning of a tubular ultrafiltration ceramic membrane", *Membr. Water Treat.*, ***7***(5), 433-449.

Soroko, I. and Livingston, A. (2009), "Impact of TiO_2 nanoparticles on morphology and performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes", *J. Membr. Sci.*, **343**, 189-198.

Tavakolmoghadam, M., Mohammadi, T., and Hemmati, M. (2016), "Preparation and characterization of PVDF/TiO_2 composite ultrafiltration membranes using mixed solvents", *Membr. Water Treat*., **7**(5), 377-384.

Valipoor, P., Sidi, L., Taqi. M. and Moussavian, H. (2012), "Preparation and investigation of properties of polypropylene antibacterial using Nano-coating containing Nano-particles of zinc oxide and titanium dioxide", *J. Textile Sci. Technol.*, **2**(1), 63-59.

Yousef, A., Barakat, N.A.M., Amra, T., Deyab, S., Hassan, M.S., Hay, A. and Kim, H.Y. (2012), "Inactivation of pathogenic kelebsiella pneumonia by CuO-TiO_2 nano fibers: A multifunctional nanomaterial via on-step electrospinning", *Ceramics Int.*, **38**(6), 4525-4532.

Wang, X.M., Li, X.Y. and Shih, K., (2011), "In situ embedment and growth of anhydrous and hydrated aluminum oxide particles on polyvinylidene fluoride (PVDF) membranes", *J. Membr. Sci.*, **368**, 134-143.

Wu, H. and Mansouri, J.V. (2013), "Chen Silica nanoparticles as carriers of antifouling ligands for PVDF ultrafiltration membranes", *J. Membr. Sci.*, **433**, 135-151.

Zhou, J., Li, W., Gu, J.S. and Yu, H.Y. (2010), "Surface modification of polypropylene membrane to improve antifouling characteristics in a submerged membrane-bioreactor: Ar plasma treatment", *Membr. Water Treat.*, **1**(1), 83-92.

CC