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TiO_2 Blended Membranes Used in Wastewater Nanofiltration Systems from Medical Sector

KAMEL EARAR[1], IULIAN CONSTANTIN[1], ANA MAGDALENA BRATU[2]*, MAGDALENA RUSU-NEGRAIA[1], ADRIAN BEZNEA[1]*, NICOLAE SARBU[1], IRINA NICOLETA ZETU[3], CARMEN TIUTIUCA[1], CIPRIAN ADRIAN DINU[1], SIMONA PARVU[2]

[1] Dunarea de Jos University of Galati, Faculty of Medicine and Pharmacy, 47 Domneasca Str., 800008, Galati, Romania
[2] Carol Davila University of Medicine and Pharmacy, 37 Dionisie Lupu Str., 4192910, Bucharest, Romania
[3] Grigore T. Popa University of Medicine and Pharmacy, 16 University Str., 700115, Iasi, Romania

Abstract: *The study aims to investigate the influence of TiO_2 nanoparticles on the permeation and retention properties of polymeric membranes used in wastewater nanofiltration systems from the medical sector. The research is focused on the influence of the TiO_2 nanoparticles concentration on the membrane properties. Additives in general determine enhanced membrane properties like permeation and retention capacity. Hydrophobicityhowever, is decreasing due to the nanoparticles affinity for water and this have an important effect on the permeation properties, at the same time with the decrease in surface roughness, with an important influence on the fouling effect. Membranes with four different concentrations of TiO_2 nanoparticles were studied, from 0 to 2% nanoparticles. Results showed that small percent of nanoparticles have an important impact on the permeation properties of the membranes, finding that at 2% nanoparticles the permeation decreases due to the nanoparticles aggregations which are blocking the pores.*

Keywords: *membranes, TiO_2, wastewater*

1. Introduction

The development of the pharmaceutical industry aggravates the effect of environmental pollution [1-3]. Pollution from the medical sector is known to have a significant impact on natural eco-systems.Wastewater from this sector leads to the alteration of organisms in the aquatic environment and indirectly on the human body.It is known that the concentration of antibiotics in the environment has increased greatly in recent years due to excessive use of such treatments in the livestock industry.There are many methods used to treat wastewater resulted from the medical industry but there is currently no one that is efficient enough to remove the risks to the environment.Many hospitals and clinics have their own biological and chemical treatment plants and the resulting water is discharged into the sewer system.However, in recent years, membrane water treatment systems have been used more and more.In general, depending on the type of pollutants, advanced nanofiltration processes and reverse osmosis are used.The use of nanofiltration for waste water treatment is a good option but the fooling effect and the permeability are aspects which can be improved. The use of nanoparticles as additives [4-7] or surface modification [8-11] has an important impact on the membrane permeability, and retention capacity. Increasing the membrane porosity, the filtration process efficiency is increasing. At the same time additives decrease the surface roughness with an important impact on the fouling effect. Literature is providing some studies on the effect of using TiO_2 nanoparticles in the membrane structure [12-17]. The concentration in the literature of the nanoparticles vary from 0.01 to 10% nanoparticles. At concentration bigger than 2% aggregation occurs and the permeability decreases because many pores are blocked.

**email: anaconstm@gmail.com, adrianbeznea@hotmail.com* *All authors have the same contributions.*

2. Materials and methods

The polymeric membranes used in the study, are manufactured, having a concentration of (0, 0.5, 1 and 2%) TiO_2 nanoparticles. Nanoparticles were first dispersed in solvent for 12h, and then the diverse concentration of polymer was added. The polymeric solution blended with nanoparticles was stirred for 48h at the room temperature. A thin film of the polymer solution with a thickness of 250 μm was cast on a polyester support at the room air humidity and immersed in the coagulation bath (distillate water). For every type of membranes five different solutions were made and from every solution were casted five membranes. The final values were made by analyzing the average results.

All the experiments were made at the room temperatures using a dead end installation with a capacity of 250mL.

To study the influence on the membrane structure a Scanning electron microscopy (SEM)with an accelerating voltage of 20 KeV, was used. For the cross-section the samples were prepared by fracturing the membranes in liquid nitrogen andgold splashed.

To study the hydrophilicity/hydrophobicity (Figure 1) membrane surface was dried. On the top of membranes was placed a 2 µL of distillate water. The contact angle between the membrane surface and the droplet was calculated.

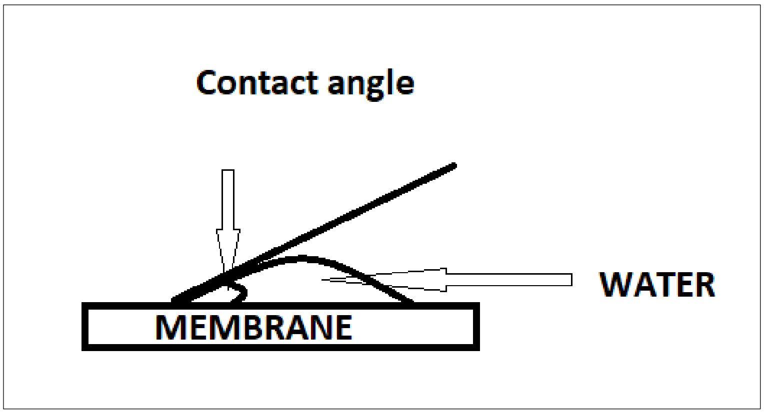


Figure 1. Contact angle measurements

To determine the pure water permeability (*PWP*) was measured the water flux (J_w) at six different pressure (ΔP) from 5 to 20 bar. The *PWP* was calculated by the following equation:

$$PWP = \frac{J_w}{\Delta P} \quad (1)$$

For the rejection performance of the NET and blended membranes, 250 mL of solution was used at 10 bar pressure. After every 20 mL of permeate, a sample of 5 ml was taken.

3. Results and discussions

The obtained membranes were tested at 10 bar pressure to establish the water permeability. In figure 2 is presented the pure water permeability for membranes at 0, 0.5, 1 and 2 % TiO_2 nanoparticles (Figure 2**)**.

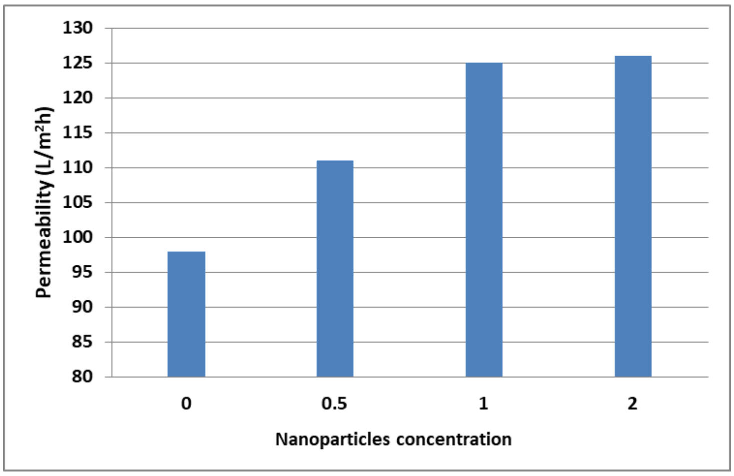


Figure 2. Permeability at different concentration of TiO_2

Adding TiO_2 nanoparticles resulted in increasing membrane permeability from 97 L/m^{2}h for membranes with 0% concentration of nanoparticles to 111 L/m^{2}hfor membranes with 0.5% TiO_2 nanoparticles and 125 L/m^{2}h for membranes with 1 % TiO_2 nanoparticles. At 2% TiO_2 nanoparticles the permeability doesn't show important increasing.

The water flux was determined at four different concentrations from 5 to 20 bars. The dependence of pure water flux on the applied pressure is given in Figure 3.

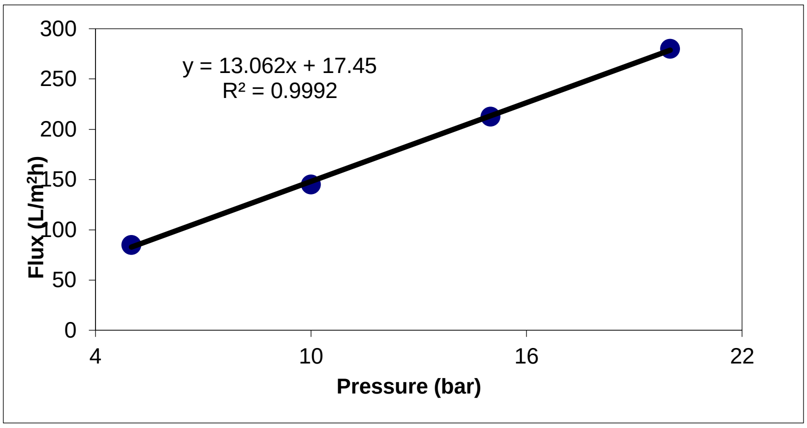


Figure 3. Water flux at 30% polymer

To establish the retention capacity for every membrane type, methylene blue was used as dye. Membranes were tested at a pressure of 10 bars for 250 mL of solution. Table 1 presents the rejection rate in time.

Table1. Methylene blue rejection of membranes with 0.5% nanoparticles

Min.	Sec.	Time(min)	Flowrate (mL/min)	Abs	Con.(ppm)	Rejection (%)	Flux
1	9	1.15	2.61	0.138	0.29	96.65	107.22
1	11	1.18	2.54	0.211	0.63	92.74	104.20
1	11	1.18	2.54	0.310	1.10	**87.37**	104.20
				1.979	8.98		
				1.880	8.51		
					8.74		

Water flux is decreasing due to the fouling effect. Figure 4 presents the influence of the TiO_2 nanoparticles on the rejection capacity of the polymeric membranes.

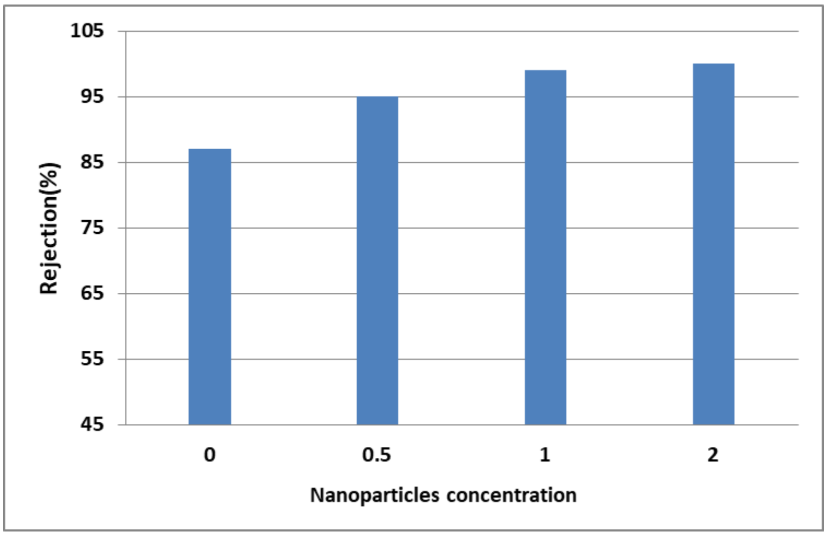


Figure 4. Methylene blue rejection of membranes

TiO_2 nanoparticles have important effect on the rejection capacity, which increases from 86% for membranes without nanoparticles to 95% for membranes with 0.5% TiO_2 nanoparticles and to 97% for membranes with 1 and 2% TiO_2 nanoparticles.

Nanoparticles influence the membranes surface (Figure 5) and the membrane structure, Figure 6 and 7. Figure 5 shows the surface of a membrane with 0.5% of TiO_2 nanoparticles.

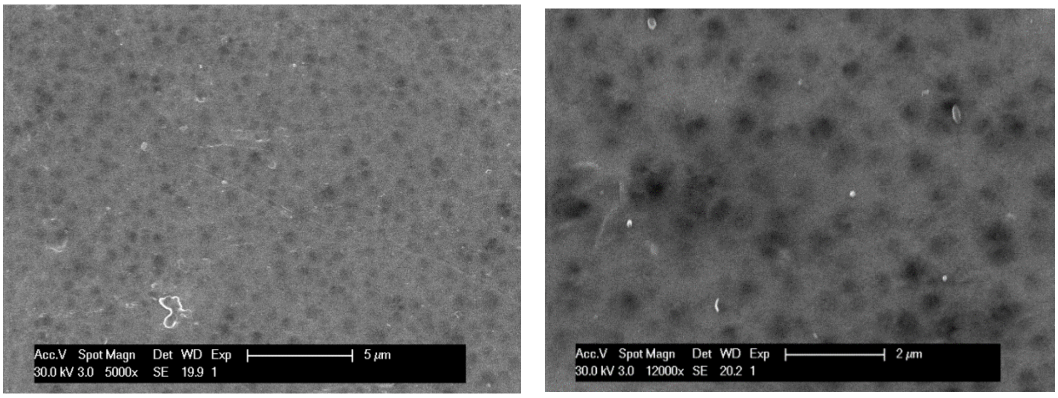


Figure 5. SEM Membrane surface at 0.5% TiO_2

The surface porosity increases due to the effect of the nanoparticles, increasing de membrane permeability and flux. At the same time due to the pore size the rejection increases also.

The effect of 0.5% of TiO_2 nanoparticles on the membrane structure is presented in Figure 6.

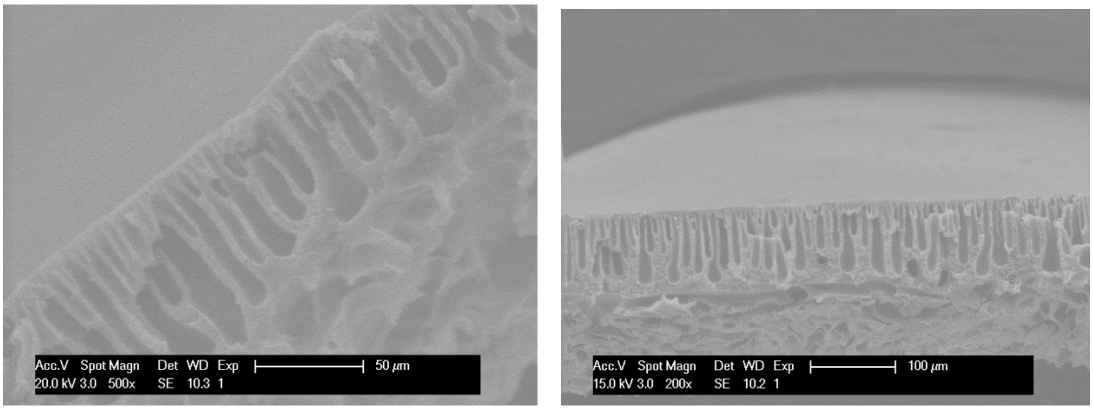
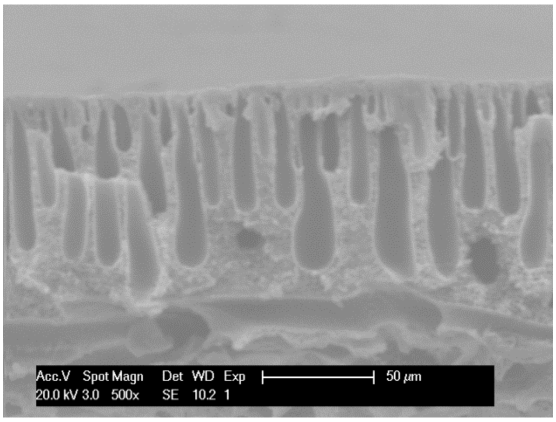


Figure 6. Cross section SEM membranes at 0.5% TiO_2

Adding nanoparticles, all the pores are uniformly distributed and the top layer decreases. This effect explains the permeability performances of the blended membranes. The same efect can be observed for membranes with 1% of TiO_2 nanoparticles, (Figure 7).



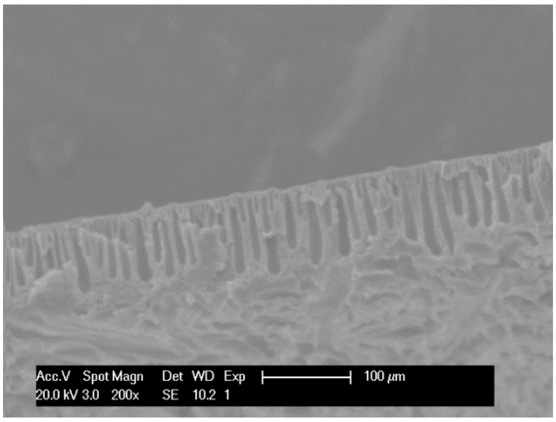


Figure 7. Cross section SEM membranes at 1% TiO_2

To explain the permeation results we determined the membrane hydrophilicity. The water drop on the surface of a membrane with 0.5 % TiO_2 nanoparticles is shown in Figure 8.

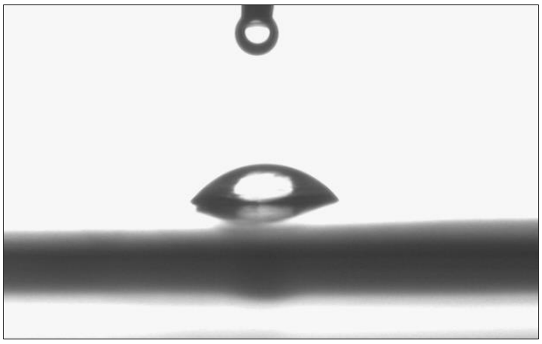


Figure 8. Contact angle formembranes at 0.5% TiO_2

The influence of TiO_2 nanoparticles concentration on the membrane hydrophilicity is presented in Figure 9.

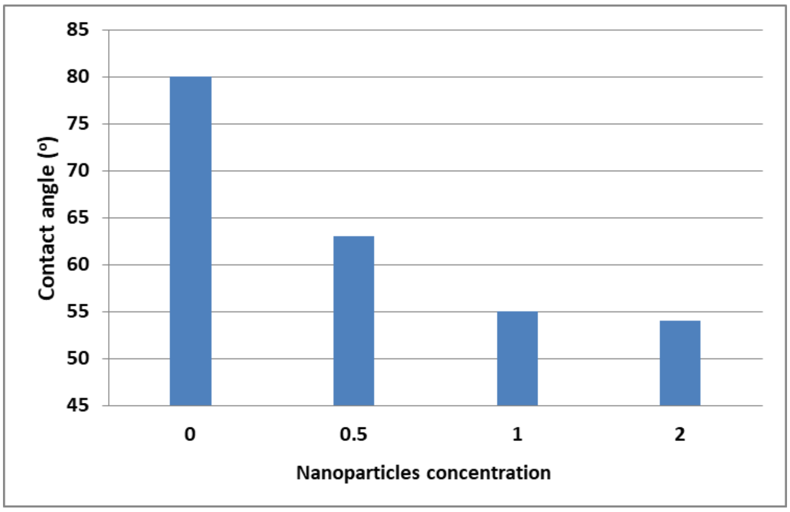


Figure 9. Contact angle

Adding TiO_2 nanoparticles to the membrane structure the contact angle decreases, whereas the hydrophilicity is increasing. Membranes without nanoparticles have a contact angle of 80°. When adding 0.5% nanoparticles, the contact angle decreases to 63° and for 1% nanoparticles, the contact angle decreases to 55^0.

4. Conclusions

The study investigates the influence of different concentration of TiO_2 nanoparticles on the polymeric membrane performance. Adding nanoparticle, results in significant permeability increase, especially for a concentration between 0.5 and 1% TiO_2.The hydrophilicity increase for blended membranes due to the effect on the surface structures. The results show that the TiO_2 nanoparticles concentration is optimal to a maximum of 1%, after which the effect is drastically diminished. The rejection performance is increasing, by adding nanoparticlesat 95% for membranes with 0.5% TiO_2 nanoparticles, and at 97% for membranes with 1 and 2% TiO_2 nanoparticles.

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