Desalination Performance of Antibiofouling Reverse Osmosis Membranes

Andreina García[1*], B. Rodríguez[1], D. Ozturk[1], M. Rosales[1], C. Paredes[2], F. Cuadra[3], and S. Montserrat[1]

1. Advanced Mining Technology Center (AMTC), Universidad de Chile, Chile

2. Faculty of Engineering, Universidad de Carabobo, Venezuela

3. Department of Civil Engineering, Faculty of Physical and Mathematical Sciences, Universidad de Chile, Chile

Abstract: The use of reverse osmosis membranes (RO) is the most used technology for water desalination; however, membrane biofouling is considered a critical issue affecting desalination plants. The incorporation of nanoparticles with antimicrobial properties into RO membranes has been reported as an effective route for enhancing the antibiofouling properties but could diminish the performance of desalination. The aim of this work was to study the performance of antibiofouling of thin film composite (TFC-RO) membrane by incorporating antimicrobial copper-oxide (CuO) nanoparticles. These nanoparticles were incorporated within the structure of the membrane during the interfacial polymerization process. The membranes were characterized by scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscope (EDX) and atomic force microscopy (AFM) in order to observe the morphology and verify the incorporation of nanoparticles within them. Bactericidal tests were performed using Escherichia coli. Anti-adhesion on the membranes was confirmed using epifluorescence microscopy. Membranes performance were evaluated in terms of permeate flux and salt rejection by using a cross flow test cell. FESEM and EDX analyses confirmed the incorporationof nanoparticles into the membrane. These membranes showed significant anti-bacterial and excellent anti-adhesion effect attributed to the copper toxicity. Desalination performance of modified membranes showed an important salt rejection of about 98% with stable water flux about 36 $L.m^{-2}.h^{-1}$ and a recovery of 50%. Measure copper concentrations in the permeate water shows to be negligible, indicating that the copper is not leached. In conclusion, the incorporation of CuO nanoparticles into TFC-RO membranes improves the antibiofouling capacities without impairing the performance of the membrane.

Key words: desalination performance, thin film composite, biofouling, CuO nanoparticles

1. Introduction

Water scarcity has been the driving force for many researchers to focus on the development of suitable methods to obtain freshwater from saltwater and water reuse to sustain future generations. Thereby, the membrane-based processes are considered key components of water treatment and desalination technologies. The reliability of these membrane-based systems has led to their increasing use [1, 2].

The most known polymers membranes for reverse osmosis (RO) with applications in desalination process have been made from aromatic polyamide (PA) groupof polymers known as thin film composite membranes (TFC-RO). These dominates RO membrane field nowadays by their good capacities (water flux and solute rejection) but they are not completely resistant to fouling [1-3]. Membrane fouling is considered as one of the most critical issues affecting seawater desalination plants. It is an inevitable obstacle in the process, and causes a decrease in membrane performance, which consequently increases the operational and maintenance costs [1, 2]. Membrane fouling can be

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Corresponding author: Andreina García, Ph.D., Associate Researcher, research areas/interests: heterogeneous photocatalysis, nanomaterial, adsorbents, membranes. E-mail: andreina.garcia@amtc.cl.

broadly categorized into inorganic fouling, organic fouling, and biofouling [3].

In general, biofouling is caused by the attachment and proliferation of microorganism communities on the membrane surface; these eventually form a biopolymer matrix or complex structure, considered a biofilm, on the membrane surface [3]. Hence, a new generation of membranes with inherent antibiofouling capabilities needs to be developed.

The incorporation of inorganic particles with antimicrobial properties into RO membranes has been reported as an effective route for enhancing the antibiofouling properties of these membranes [1-7]. Several studies have shown that Ag and TiO_2 nanoparticles exhibit good antibiofouling properties and can be used for the development of hybrid organic/inorganic RO membranes [1, 6, 7]. In the same manner, the incorporation of copper particles have been investigated, as these also show antimicrobial properties [8, 9].

The germicidal properties of copper particles make it suitable for incorporation into several antibiofouling polymeric materials [10-12]. In the case of reverses osmosis (RO), ultrafiltration (UF) and nanofiltration (NF) membranes, studies have shown different proposal to improve their antibiofouling properties.

For example, the development of hybrid Cu-containing membrane by modifyinga polyethersulfone (PES) ultrafiltration (UF) membrane by dispersing nanosized Cu particles [12], the modification of commercial RO membranes by having copper hydroxide ($Cu(OH)_2$) particles adsorbed onto them [13], the modification of polysulfone/modified polymer blend coated with copper as protective layer [14], the functionalization of polyamide (PA) with Cu-nanoparticles (Cu-NPs) to cover a pristine TFC membrane by dip-coating [15] and *in situ* surface functionalization with Cu-NPs on the surface of TFC membrane [16].

We have proposal to improve the antibiofouling properties of TFC-RO membranes by incorporating

CuO nanoparticles within. Considering that CuO nanoparticles are also used as antibacterial agents, is cheaper than Ag, can be mixed readily with polymers, and exhibits relatively stable chemical and physical properties [8, 12]. Furthermore, CuO is a highly ionic metal oxide, shows exceptionally good antimicrobial properties, and has been reported to be highly effective against a wide variety of bacteria, fungi, and microalgae [8, 9, 17, 18].

Thus, the incorporation of nanoparticles with antimicrobial properties into RO membranes has been reported as an effective route for enhancing the antibiofouling properties but could diminish the performance of desalination.

The incorporation of hydrophilic nanoparticles in polyamide layer can produce the increase of water flux due to the enhanced hydrophilicity in the membranes [19]. It was shown that CuOhydrophilic nanoparticles have a great potential to improve the performance of the membrane in terms of water flux [20]. However, above a critical concentration of nanoparticles, the reaction interference of nanoparticles in the polyamide polymerization can be significant, thereby leading to a lower degree of polymerization and poor mechanical properties in the membranes [19].

For certain applications, a loss in permeability may be overcome by the benefits of super-hydrophilic or anti-microbial properties of the nanoparticles that significantly reduce membrane fouling, although in general reduced permeability is not a desirable feature [19, 21].

Thus, the aim of this work was to study the desalination performance of antibiofouling RO membranes by incorporating antimicrobial copper-oxide (CuO) nanoparticles.

2. Methodology

2.1 Materials

The polysulfoneUdel P-1700 (in pellet form; Solvay Advanced Polymers), 1-methyl-2-pyrrolidinone (NMP, >9.5%, Sigma Aldrich), and

N,N-dimethylformamide (DMF, > 99%, Sigma Aldrich) were used to fabricate the PSL sample used as the support. Commercial CuO nanoparticles (<50 nm) were obtained from Sigma Aldrich. m-phenylenediamine (MPD) and trimesoyl chloride (TMC), which were used as the monomers for polyamide (PA), were obtained from Sigma Aldrich. Finally, NaOH (>97%) and n-hexane (>95%) were obtained from Sigma Aldrich.

2.2 Preparation of Membranes

2.2.1 Preparation of PSL Supports

The PSL support was fabricated using the phase-inversion method [12]. A casting PSL solution in a DMF/NMP mixture (4:1) was kept agitated for 2 h at 50°C, to allow for complete dissolution. The composition of the PSL/(DMF/NMP) solution was 15/85 (wt%).

The PSL support was prepared by casting the polymer solutions uniformly on glass plate using a casting knife with a knife gap set at 200 μm. Next, the support was recovered from the coagulation bath for 1 min and washed thoroughly with distilled water to remove any residual solvent. The entire casting set up was kept in an air-conditioned room, and the temperature was controlled at 25°C and the relative humidity at 20% during the entire PSL casting process.

2.2.2 Preparation of Unmodified and Modified Membranes

The TFC-RO membranes were synthesized by interfacial polymerization reaction of aqueous phase of MPD and the organic phase of TMC on the porous PSL substrates. The PSL supports were placed for 2 min in a 2 wt% aqueous MPD solution containing 0.05 wt% sodium hydroxide (NaOH). The excess MPD solution remaining on their surfaces was removed with Kimwipes wipers. Next, the membranes were immersed in a 0.2 wt% TMC solution in hexane for 1 min to allow interfacial polymerization. This resulted in the formation of a thin film of PA on the surfaces of the PSL supports. The resulting membranes were subsequently cured in an air-circulation oven at 75°C for 8 min. Finally, the membranes were washed with distilled water and dried at room temperature for 24 h.

The modified membranes were prepared as follows. CuO nanoparticles (0.25 and 1.0 wt%) were homogeneously dispersed in an MPD solution using ultrasonic vibration to prepare nanoparticles-entrapping PA layers on the porous PSL supports; referred to as (PA-CuO)/PSL.

2.3 Characterization of Membranes

The morphologies of the membranes (cross-sectional and surface) were studied using scanning electron microscopy (SEM) (INSPECT F-50, FEI Co.). The membranes were then sputter-coated with a thin film of carbon to make them conductive. The membranes were snapped under liquid nitrogen to give a generally consistent and clean cut. Subsequently, they were investigated using atomic force microscopy (AFM) (AFM/STM Omicron Nanotechnology model SPM1) in contact mode. Elemental analyses were performed using energy-dispersive X-ray spectroscopy (EDS) (Model APOLLO-X, EDAX, software Genesis V6.33), in order to further confirm the presence of the CuO nanoparticles within the membranes.

2.4 Antibiofouling Tests

2.4.1 Bactericidal Test

The bactericidal properties of the unmodified and modified membranes were evaluated by colony forming unit method using *Escherichia coli (E. coli)* as model gram-negative bacteria. Bacteria were first cultured in Tryptone Soya Broth (TSB) solution (30 g/L) and incubated in a shaking incubator in 200 rpm at 30°C overnight. Then the bacteria solution was centrifuged at 3000 rpm for 10 minutes to remove the nutrients and washed in phosphate buffered saline (PBS). This procedure was repeated three times to ensure all nutrients were removed. The prepared bacteria were diluted 100 times in PBS to obtain a bacterial concentration about 1×10^7 cell/mL. The

membrane samples which were cut into the squares of 2×2 cm^2 and sterilized by ultraviolet radiation for 30 min, immersed separately into the 10 mL prepared bacteria solution. Bacteria suspensions with membranes were incubated in the shaking incubator at 30°C for 4 h. At the same time, 10 mL bacteria solution without membrane incubated as a control. After that, the treated solutions were serially diluted with PBS. From the highest dilution, 50 µL of the solution was pipetted into LB agar plates and then spread over the entire surface. The agar plates were incubated at 35°C overnight and were observed for colonies developed to estimate the number of viable E. coli remained in the suspensions.

2.4.2 Anti-adhesion Test

The degrees of attachment of bacteria to the membrane surfaces were assessed with *E.coli* as well. The bacteria were prepared in the same manner as the bactericidal tests. Three pieces of each type of membrane (unmodified and modified membranes) with an area of 2 cm^2 were incubated in the bacterial suspension at 30°C while being shaken at 200 RPM. After being incubated for 4 h, the membranes were removed from the suspension and gently rinsed with a 0.85 wt% NaCl solution in water. For staining cells on the membranes, they were stained with 1 µg/ml 4',6-diamidina-2-phenylidole. Dyes were added to the top surface of the membrane and incubated for 15 min in the dark. After incubation, the stained cells were observed under the epifluorescence microscope (Zeiss, AxioLab A1, Germany) with a 100× objective and were counted to estimate the number of cells adhered on the top surface of the membrane.

2.5 Desalination Performance Test

Membranes performance were evaluated in terms of the permeate flux and salt rejection by using a cross flow test cell with an effective area of 33 cm^2 and a feed solution of 1000 ppm NaCl at 300 psi.

The permeate flux test of membranes during 60min was calculated by the following equation [22]:

$$J = \frac{V}{A.\Delta t} \tag{1}$$

where J (L.m^{-2}.h^{-1}) is the membrane flux, V(L) is the volume of permeated water, A (m^2) is the membrane area and Δt (h) is the permeation time. The experiments were carried out at 25±1°C.

Additionally, solute rejection was measured from the feed and permeate solution concentrations using the following equation [19]:

$$rejection(\%) = \frac{C_f - C_p}{C_f} x100 \tag{2}$$

where C_f and C_p are the concentrations of the feed solution and permeate solution, respectively. The conductivity of these two solutions were measured to obtain their respective concentration values.

2.6 Copper Leaching Crossflow Studies

The copper leaching studies were conducted using cross-flow experiments. A collection bottle to collect the permeate solution, which has passed over the copper charged membrane, was used. Samples were collected at different time of permeate flow. Copper concentration was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, 7300V).

3. Results and Discussion

3.1 Analysis of Surfaces and Morphologies of Membranes

Fig. 1 shows an FESEM image of the surface of the (PA-CuO 1%)/PSL membrane which reveals a tightly packed globular structure and protuberances. The protuberances are so prominent as to produce the strands of polymer forming the ridge and valley structure which is featuresof TFC membrane [23, 24].

The result of EDX analysis of the modified membrane surface is shown in Fig. 2. Results of semi-quantitative analyses(tables inset) showed C, N, O, and Cu as the main elements on the membrane

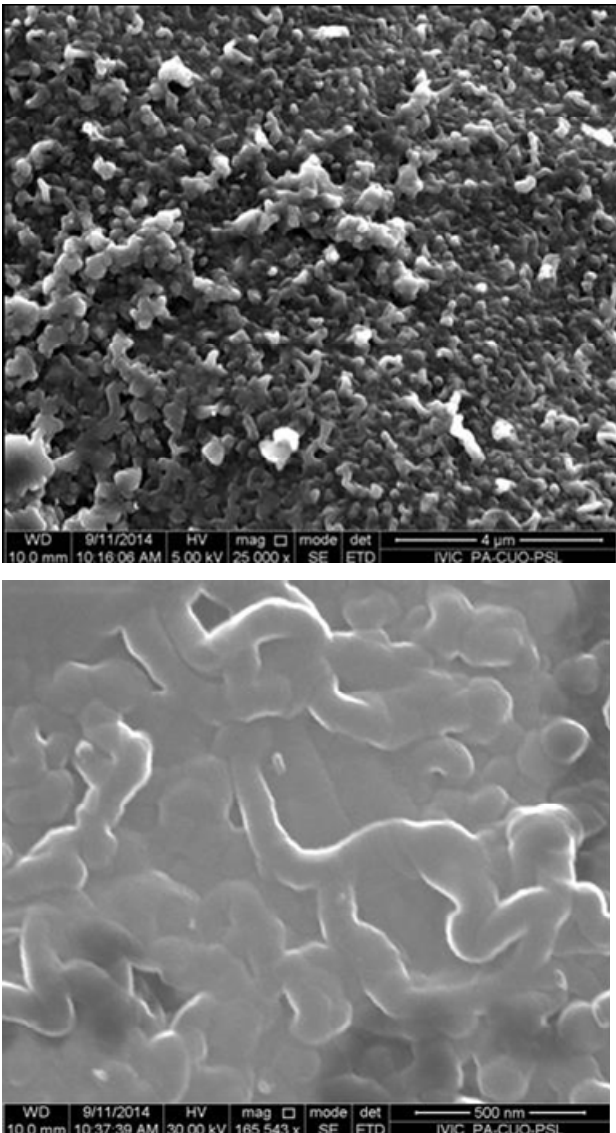surfaces confirming the presence of CuO nanoparticles into PA layerin the membranes.

Fig. 1 Filed emission microscope image (FE-SEM) on surface of (PA-CuO 1%)/PSL membrane.
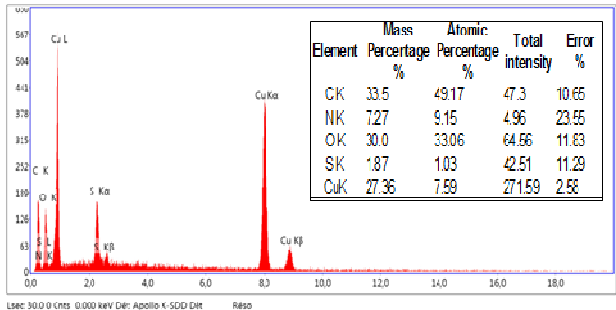

Element	Mass Percentage %	Atomic Percentage %	Total intensity	Error %
C K	33.5	49.17	47.3	10.65
N K	7.27	9.15	4.96	23.55
O K	30.0	33.06	64.66	11.83
S K	1.87	1.03	42.51	11.29
Cu K	27.36	7.59	271.59	2.58

Fig. 2 EDX analysis on surface of (PA-CuO 1%)/PSL membrane.

Fig. 3 shows SEM image of the cross-sections of the (PA-CuO 1%)/PSL membrane. Ultrathin layer of polyamide (PA) over PSL support was observed. Thus, the formation of thin film composite (TFC) structure was confirmed. Moreover, CuO nanoparticles as bright spots into the dense PA layer can be observed, confirming their incorporation into the membrane structure.

On the other hand, it is noted that PSL support contain long finger like voids that extended from the top to the bottom of the substrate. It is a characteristic of polysulfone membrane synthesized by the phase inversion method [25].

AFM imaging (Fig. 4) was realized in order to compare the surface morphologies of the modified membrane (PA-CuO)/PSL and the pristine membrane PA/PSL. The images showed that the top surfaces of the membranes exhibited characteristics consistent with those of interfacially polymerized PA membranes, which consist of ridges and valleys [23, 24]. Moreover, globular structure underneath the ridge-and-valley layer can be observed in 2D image of the membranes. Similar surface features were observed by SEM-FE image (Fig. 1).
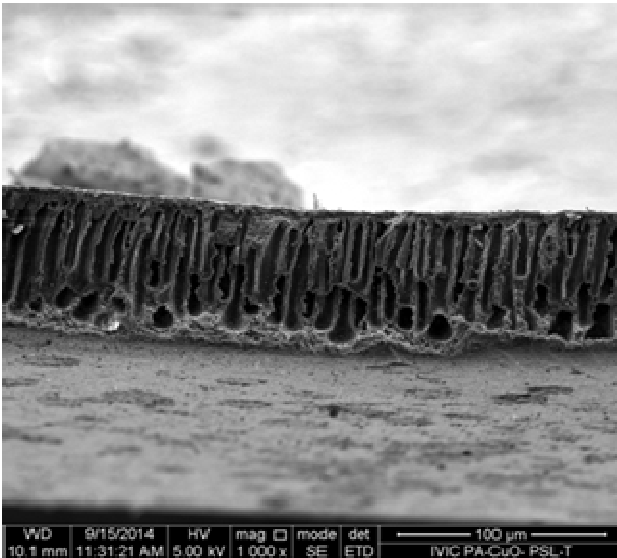

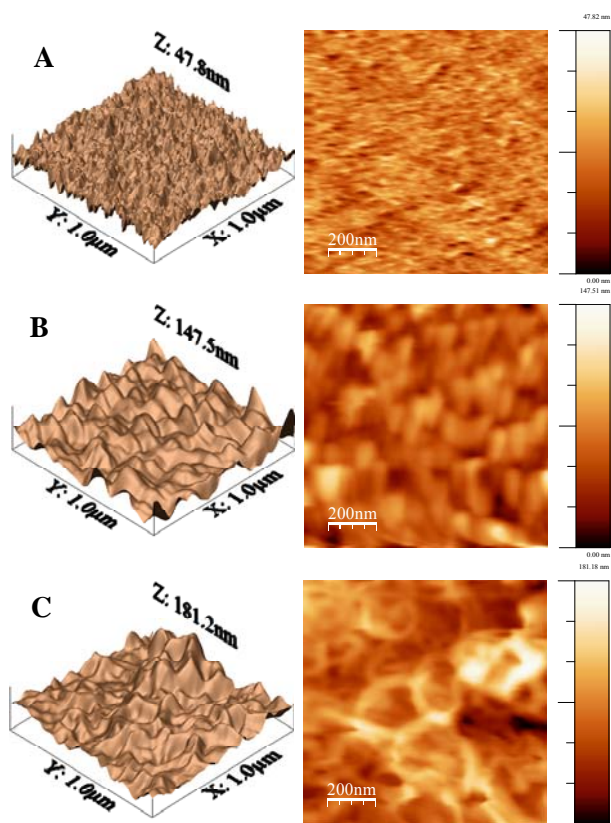**Fig. 3 Cross Sections of (PA-CuO 1%)/PSL membrane.**

Fig. 4 AFM scan of the membranes, A) PA/PSL, B) (PA-CuO 0.25%)/PSL, C) (PA-CuO 1%)/PSL.

Unfavorable changes on surface roughness in modified membranes with respect to unmodified membrane were observed (Fig. 4) exhibiting higher surface roughness with the modification. The root mean square roughness parameter are observed in Table 1.

This detrimental effect on the surface roughness of modified membranes by incorporating CuO nanoparticles (~50 nm) into the membrane during the interfacial polymerization process can be attributed to the agglomeration of nanoparticles in the surface during this polymerization process. The agglomeration could change the height between ridges and valleys

Table 1 Root Mean Square roughness (RMS) of membranes.

Membrane	Root Mean Square roughness (RMS) of the membranes (nm)
PA/PS	18±4
(PA-CuO 0.25%)/PSL	31±3
(PA-CuO 1%)/PSL	103±9

of the polyamide layer increasing its surface roughness. In contrast, authors have modified RO membranes with Cu-Nps (~34 nm)by dipping and no significant changes in the surface roughness were reported [15]. Difference in the nanoparticles size and the type of modification of TFC-RO can be responsible of these behaviours.

3.2 Antibiofouling Effect

The Table 2 shows the anti-biofouling properties of the membranes. Significantdecrease in the number of *E.coli* colonies formed in the medium (CFU) in presence of modified membranes (PA-CuO)/PSL with respect to the pristine membrane were observed evidencingan important bactericidal effect.

Moreover, it can be seen an excellent anti-adhesion capacity of modified membranes (> 80% of bacterial anti-adhesion percentage). A slight increase in these properties was observed when the percentage of incorporated nanoparticles is increased.

The distributions of the bacteria on the modified and unmodified membranes are shown in Fig. 5. It shows that the numbers of cells per mm^2 were significantly lower in presence of the modified membranes confirming their excellent anti-adhesion properties.

These significant bactericidal and anti-adhesion effectcan be mainly attributed to the copper toxicity. CuO is a highly ionic nanoparticulate metal oxide and promote the release of Cu^{2+} ions from the surface of the modified membranes [11-13]. The Cu^{2+} ions released from the CuO nanoparticles have a toxic effect on bacteria, because the ions trigger the production of reactive oxygen species, which damage the DNA of the bacteria [26]. Moreover, the reduction of number of

Table 2 Anti-biofouling properties of the membranes.

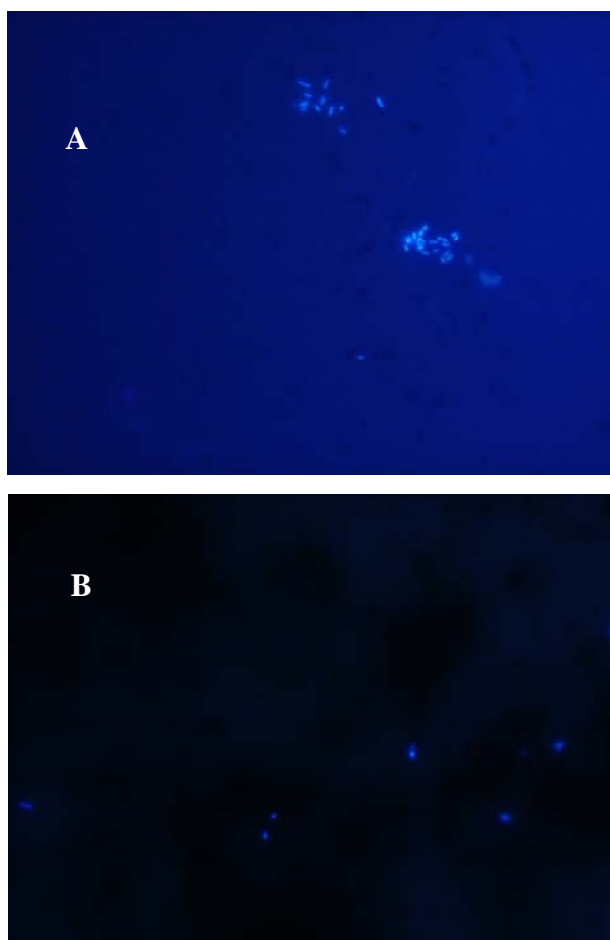| Membrane	Reduction of CFU (%)	Bacterial anti-adhesion percentage (%)
PA/PS	15	0
(PA-CuO 0.25%)/PSL	32	84
(PA-CuO 1%)/PSL	44	88

Fig. 5 Images of distribution of *E. coli* on the membranes by epifluorescence microscopy, A) PA/PSL, B) (PA-CuO 1%)/PSL.

colonies forming units in the aqueous medium decreases the number of bacteria that could potentially attach to the membrane surface [3].

3.3 Desalination Performance

The desalination performance of modified membranes showed an important salt rejection of about 98% with stable water flux during 60min and a recovery of 50%. The presence of CuO nanoparticles into the membranes (0.25 and 1.0 wt%) allowed permeate flux about 11 and 36 $L.m^{-2}.h^{-1}$, respectively. CuO nanoparticles are hydrophilic nanoparticles[20], which favor the water permeability.

3.4 Copper Leaching-Crossflow Study

The results obtained from the cross flow leaching

Table 3 Permeate flux and rejection of salts of the membranes.

Membrane	Permeate Flux $L.m^{-2}.h^{-1}$	Rejection of salts percentage %
PA/PS	12.7±0.2	98±1
(PA-CuO 0.25%)/PSL	11.5±1.2	97±1
(PA-CuO 1%)/PSL	36.4±2.2	98±1

Table 4 Concentration of copper in the permeated flux by using (PA-CuO 1%)/PSL.

Permeate Time (min)	Copper Concentration in permeate water (ppm)
5	0.03
20	0.14
40	0.14
60	0.14

experiments were shown in Table 4. The values represent the percentage of copper in the permeate solution at different intervals of time. Measure copper concentrations in the permeate water shows to be negligible. Copper leaching studies show that very low copper content is leached from the surface of the modified membranes, demonstrating the stability of copper nanoparticles incorporated into the membrane during the polymerization interfacial synthesis. It is important to note that copper ions leachedwould be released by membranes, so would not be in the permeate.

4. Conclusions

It was found that modifying RO membranes by incorporating CuO nanoparticles in the PA layer leading to (PA-CuO)/PSL, resulted in the membranes exhibiting antibiofouling properties. Significant bactericidal and anti-adhesion effect resulting from copper toxicity mainly the release of Cu^{+2} ions from the CuO nanoparticles incorporated in the membranes. The desalination performance of modified membranes showed an important salt rejection of about 98% with stable maximum water flux about 36 $L.m^{-2}.h^{-1}$ and a recovery of 50%. The incorporation of CuO nanoparticles into RO membranes improves the

antibiofouling capacities without impairing the performance of the membrane.

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