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Research Article

Removal of Dissolved Organic Carbons and some Microorganisms from a Drinking Water Treatment Plant by a Novel Ag Dopped Thin Film Polyamide RO Membrane

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ABSTRACT

Silver nanoparticles can be incorporated into membranes as biocid to remove some microorganisms and dissolved organics from the drinking water. Many conventional water treatments, including filtration, sedimentation and coagulation were not effectively remove the dissolved solids and the microorganisms. In this study, a novel composite membrane namely Thin-Film Composite Reverse Osmosis (TFC-RO)/nano Ag Nanoparticules (NP) membrane was generated to remove some bacteria (*Shigella, Escherichia coli, Vibrio, and Salmonella*), viruses (*Enterovirus and Rotaviruses*), protozoans (*Entamoeba, Giardia, and Cryptosporidium*) and some toxic cyanobacteria (*Microcystis, Gloeotrichia spp., Anabaena Synechocystis spp.*) from the influent of the drinking water treatment plant. The effects of 3 percentage of Ag NP concentration on the removals of Soluble Chemical Oxygen Demand (sCOD), soluble dissolved suspanded solid matter and some organisms (bacteria, viruses, protozoan and toxic cyanobacteria) removals were investigated using RO- nano Ag membrane. The membrane surface was investigated in raw and polluted form after used in treatment of drinking water by performing SEM (Scanning Electron Microscope), XPS (X-ray Photoelectron Spectroscopy), TEM (Transmission Electron Microscopy) and FTIR (Fourier Transform Infrared Spectroscopy) analysis. The effects of different $AgNO_3$: $NaHB_4$ ratios on the yields of the the of sCOD, Dissolved Organic Carbon (DOC), Suspanded Solid (SS), Natural Organic Material (NOM) and organism removals at ambient conditions were studied. The effects of these ratios on the permeability of distilled water and drinking water was studied. The analysis results showed that a RO-Ag NP membrane with a AgNO3 to NaHB4 ratio of 1:4 was effectively remove the pollutants and some resistant bacteria, viruses, protozoa and cyanobacteria. RO membrane without Ag exhibited low removals compared to Ag doped one.

Keywords: RO nano Ag membrane; Thin film polyamide; sCOD; NOM; Drinking water Treatment; Bacteria;Protozoans; Cyanobacteria

INTRODUCTION

Some studies demonstrated the potential to use silver nanoparticles (Ag-NPs) as biocides in membrane separation processes [1]. Silver at optimum concentrations exhibits strong antibacterial activity against numerous types of bacteria [2,3]. Addition of Ag-nanoparticles directly into the influent consume large amounts of silver and therefore will not be economical. Localized loading of small amount of silver in the RO membrane surface is more viable for protecting the membrane from biofouling [3].

Ag-NPs in RO membrane decrease the biofouling. An optimum percentage of Ag nanoparticles overcome the fouling problem [4]. When considering Ag-NP loading procedure on the membrane, the aqueous dissolution of Ag-NPs over time can be exacerbated by the routine chemical cleaning [5].Therefore, the doped of Ag-NPs on the RO membrane should be provide the recharge the Ag-NPs on the TFC-RO membrane. The method must be economical in terms of chemical usage and time [6]. Embedding of Ag-NPs or silver salts in the RO polyamide layer during membrane fabrication resulting in low pollutant removal with RO [7]. The synthesis of Ag-NP and the use of a capping chemical agent increases the cost [8,9]. However, the use of several chemicals such as ammonium-hydroxide, formaldehyde, ethanol at high concentrations necessitates long reaction time Ag-NPs on the TFC-RO membrane by chemical reduction of Ag was found to be more pysible for loading of Ag-NP on the surface of TFC-RO membrane [10].

The conventional drinking water treatment processes were not remove effectively the DOC, sCOD and NOM. The yields for

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these pollutatand are low (68%-73%) [11]. On the other hand some resistant organisms such as viruses, protozoan ana cyanobacteria also were removed with low yields in the conventional drinking water treatment processes (56%-68%) [12]. Therefore, in this study it was aimed to remove the aforementioned pollutants and organisms with high yields in a Thin-Film Composite Reverse Osmosis (TFC-RO)/nano Ag Nanoparticules (NP) membrane system.

MATERIAL AND METHODS

Preparation of RO-Ag nanoparticle membrane

SW-30 RO membrane was purchased and dried. The dried membranes pieces were wetted in immersion oil containing 20% isopropanol and 80% distilled water by mixing the liquids during 30 min. Then, the membrane pieces were rinsed and soaked with distilled water during 37 hours. For doping of 1.0 mm × 10^{-5} mm, 2.0 mm × 10^{-5} mm and 3.0 mm × 10^{-5} mm. Ag-NPs on the RO membrane, the membrane pieces were put in an glass flux. Then 10 mL of diluted $AgNO_3$ solution (1 mm × 10^{-5} mm) was mixed with the isolated RO membrane pieces.

Doping of Ag-NP on the RO membrane surface

$AgNO_3$ was used as reductive matter while deionised water as solvent. Sodium Borohydride ($NaHB_4$) also was used as reducing agent. The ratios of $AgNO_3$:$NaBH_4$ (in mm). The produced excess $AgNO_3$ solution was reused for utilisation in other samples. The thin layer of $AgNO_3$ solution on the RO membrane surface was obtained. Then, this side of the RO membrane was reacted with diluted $NaBH_4$ (1 mm × 10^{-5} mm) solution for 15 min. During this reaction the Ag-NPs were generated on the surface of the RO membrane. Then, $NaBH_4$ solution was removed from the membrane. The produced RO-Ag NPs membrane was rinsed with dissolved water.

RO-Ag NP membrane reactor configuration

The membrane reactor volume was 1.5 liter with a heigth and a diameter of 12 cm and 6 cm respectively. The permeate and the retentate of the reactor were distinguished. The membrane area was 8.87 cm^2.

Operational conditions in the RO-Ag NP membrane reactor

The effects of doping percentages of different concentrations of Ag NPs (1.0 mm × 10^{-5} mm, 2.0 mm× 10^{-5} mm and 3.0 mm × 10^{-5} mm Ag-NPs) on the RO-Ag NP membrane performance was researched. The reactor was operated at 12 bar and at a permeate flux of 8 L/m^2 h to determine the rejections of sCOD, DOC, SS, DOC and organism removals at ambient conditions. The effects of 3 different $AgNO_3$:$NaHB_4$ ratios (1:2, 1:4; 1:6) on the removals of sCOD, DOC, SS, NOM and organisms present in drinking water was investigated at ambient conditions. Furthermore, the effects of these ratios on the permeability of distilled water and drinking water was studied. These ratios were choseen based on the recent studies performed by Yin, et al. [13] and Ben Sasson, et al. [14].

Analytical procedures

sCOD, SS, NOM and DOC measurements were performed according to Standard Methods (2017). Bacteria (*Shigella, Escherichia coli, Vibrio*, and *Salmonella*), viruses (*Enterovirus and Rotaviruses*), protozoans (*Entamoeba, Giardia*, and *Cryptosporidium*) and some toxic cyanobacteria (*Microcystis, Gloeotrichia spp, Anabaena, Synechocystis spp*) measurements were also performed according to Standard Methods (2017).

sCOD permeability coefficient B was calculated from the water fluxes and sCOD rejections according to the method described by Surface contact angle was measured in a contact angle measuremet apparatus [15].

Measurement of the antimicrobial properties of the produced RO-Ag NPs membrane

The raw drinking water was passed from the RO-Ag NP membrane at different operational conditions. The isolation of four organism groups (bacteria, viruses, protozoan and algae) indicating 4 different trophic level were performed in raw and in treated drinking water. Bacteria (*Shigella, Escherichia coli, Vibrio*, and *Salmonella*), viruses (*Enterovirus* and *Rotaviruses*), protozoans (*Entamoeba, Giardia, and Cryptosporidium*) and some algae-toxic cyanobacteria (*Microcystis, Gloeotrichia spp, Anabaena, Synechocystis spp.).* Isolation and enumeration were performed in raw and treated (passed from the RO-Ag NP membrane reactor) drinking water samples.

Calculation of removal percentages

The pollutant and bacteria concentration were measured in raw drinking water before passed from the RO membrane reactor doped with increasing $AgNO_3$:$NaBH_4$ ratios

The removal percenttage was calcuated as follows:

$$R = \frac{C_{\text{raw drinking water}} - C_{\text{after passed from the RO-Ag NP Membrane reactor}}}{C_{\text{after passed from the RO-Ag NP Membrane reactor}}} \times 100$$

Where C is the pollutant concentrations (mg/l) or bacteria number (cfu/100 ml)

Permeability measurements

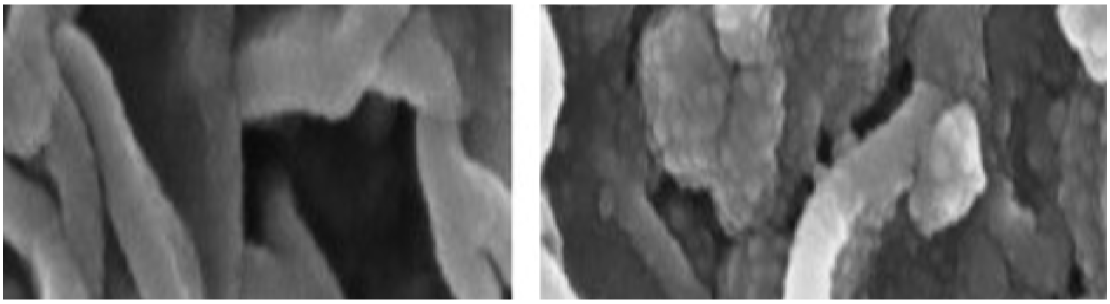
RO membrane permeability measurement: Permeability measurements were performed on a custom made rig consisting of a pressurized liquid reservoir connected to a membrane holder. Pressure transducers were placed at the feed and permeate sides of the membrane to measure the pressure drops.

Distilled water and sCOD permeability measurements: To evaluate the water permeability of distilled water and sCOD; a hydraulic pump (USA) generates a constant volumetric flow, using deionized water ana drinking water, separately, from a temperature controlled fluid reservoir. In addition, two adjustable flow resistances are put in parallel and in series to the sample chamber, respectively while the fluidic pressure on the sample is controlled by adjusting the flow resistances. For a precise measurement of the volumetric flow a doppler sonography flow sensor (Germany) is placed straight in front of the sample chamber. The pressure drops were measured during operation of the chamber with distilled water and drinking water containing sCOD.

RESULTS AND DISCUSSION

SEM analyses results in RO-Ag NP membranes

Figure 1a exhibited the raw RO membrane while Figure 1b indicates the RO membrane modified with Ag-NPs before ued in the



(a) (b)

Figure 1: SEM images of raw RO membrane.; a: RO membrane modified with Ag-NPs before used in the treatment of drinking water; b: Magnification 75.000X.

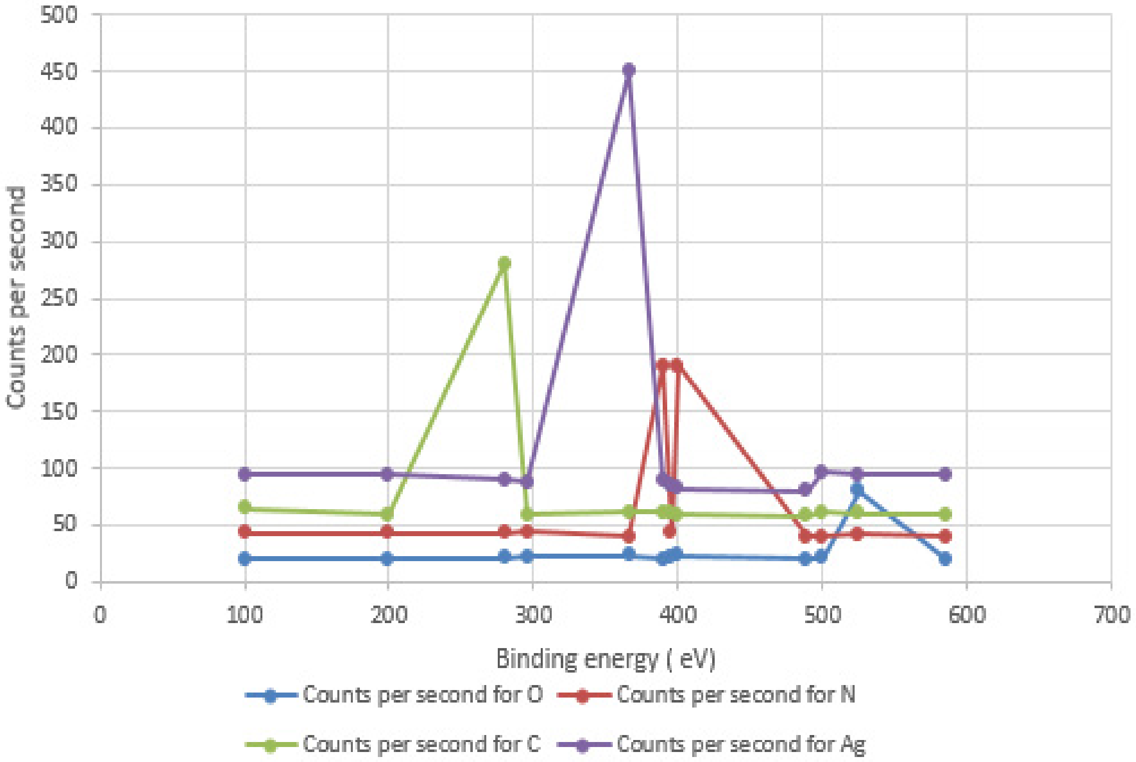


Figure 2: XPS analysis results for raw RO-Ag NP membrane with a AgNO$_3$: NaHB$_4$ ratio of 1:2.

treatment of dringking water in the SEM images (magnification: 75.000X). It was not found significant visual differences in both membranes. In some points the polyamide structures was covered insificantly. In modified membrane, some silver pieces precipitated due to production of small silver precipitate layers on the membrane surface. However, these accumulated small agregates did not cause a significant surface blockage in the membrane permeability.

XPS analysis results in raw RO-Ag NP membrane before used in the drinking water treatment

XPS measurements were performed to detect the elements in the raw RO-Ag NP TFC membrane. Figure 2 showed the XPS spectra of raw RO-Ag NP TFC membrane with a AgNO$_3$ to NaBH$_4$ ratio of 1:2. The presence of a peak at binding energy of 365 eV exhibited the presence of Ag on the membrane. The other XPS peaks at 525 eV and at 280 eV were identified as oxygen and carbon. The nitrogen gives peaks at two points; One of them was at 389 eV while the other one was detected at 401 eV. These results agree with the study performed by Liu, et al., Yin, et al., Ben-Sasson, et al. [3,13,14].

Figures 3-5 exhibit the XPS data of RO-Ag NP membrane samples after used in the drinking water process. No significant differences in the peaks of XPS was detected with AgNO$_3$: NaHB$_4$ ratios of 1:2, 1:4 and 1:6. In the XPS analysis performed with a AgNO$_3$: NaHB$_4$ ratio of 1:6, the maximum peaks values of O, Ag, N and C *versus* binding energies were lowered sligthly. This can be due to high NaHB$_4$ ratio in the RO-Ag NP membrane (Figure 5).

XPS measurements showed that the signal at a binding energy of around 365 eV-366 eV the presence of Ag NPs. Ag NPs signals were detected at all AgNO$_3$: NaHB$_4$ ratios (1:2, 1:4, 1:6) in XPS analysis (Figure 4). These observations clearly showed that Ag NPs embedded to the RO membrane. The XPS analysis indicated that some peaks at binding energies arounds 625 eV, 388 eV, 401 eV and 282 eV were O, N and C spectra, respectively, in the polyamide layer of the RO-Ag NP membrane.No significant difference in the RO membrane with Ag NPs was detected after used in the treatment of drinking water with a AgNO$_3$ to NaHB$_4$ ratio of 1:2.

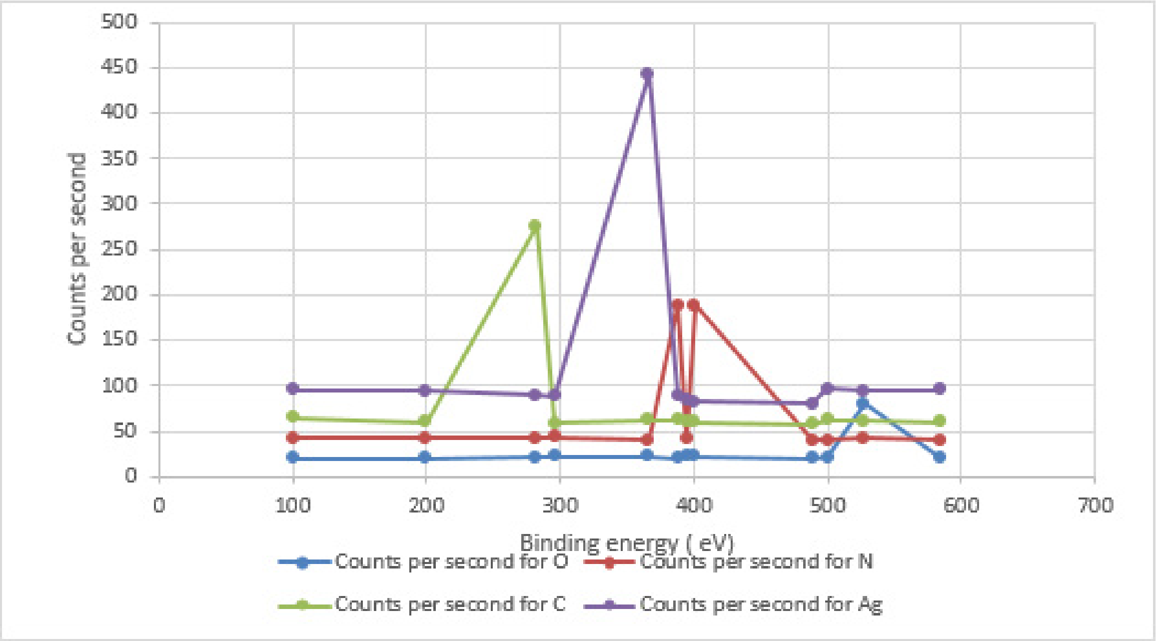


Figure 3: XPS analysis results for treated RO-Ag NP membrane after used in the treatment of drinking water with a $AgNO_3$ to $NaHB_4$ ratio of 1:2.

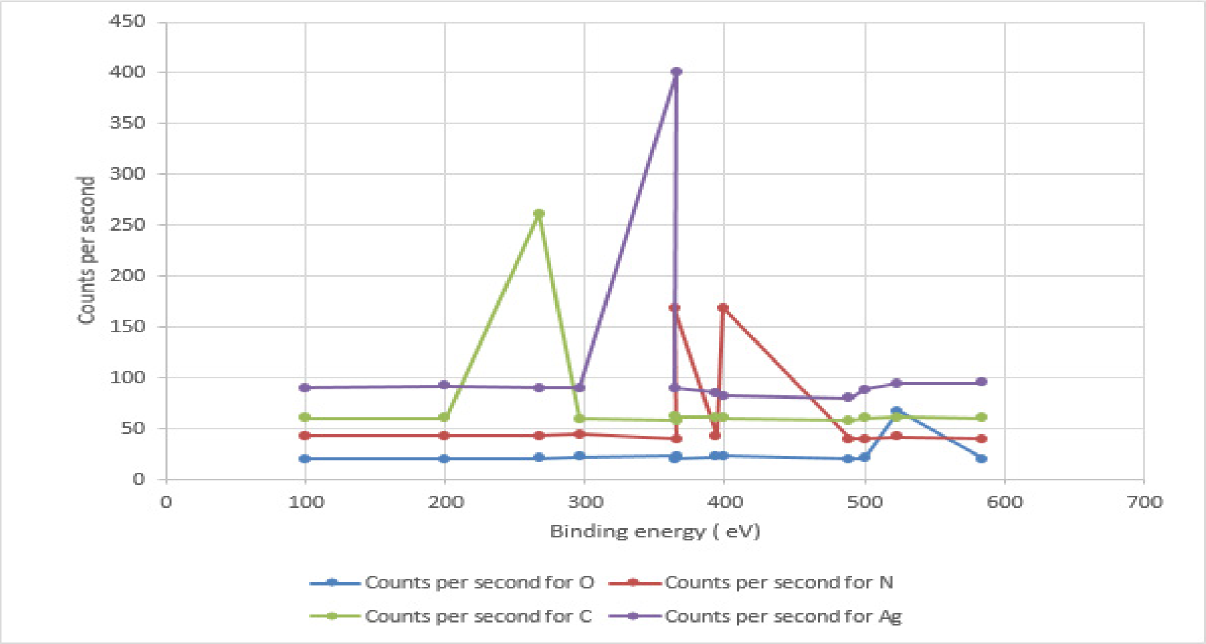


Figure 4: XPS analysis results for treated RO-Ag NP membrane with a $AgNO_3$: $NaHB_4$ ratio of 1:4.

The binding energies lowered sligtly at a $AgNO_3$:$NaHB_4$ ratio of 1:6 (Figure 5). The binding energies were measured as 524 eV, 364 eV, 394 eV, 267 eV for O, N and C while the maximum peak for Ag NP was detected as 364 eV. Although a large amount of $NaBH_4$ was needed to reduce the ionic silver and to stabilize the silver nanoparticles formed at high $NaBH_4$ concentration aggregation began and the colloids broke down and particle settled out $NaBH_4$ as reported by Rashid et al.. As a result, the binding energy of the element lowered sligtly.

The production of the RO-Ag NP membrane included the contact of dilute at a salt solution ($AgNO_3$) with the TFC RO membrane. The hydrolyzed Ag ions diffused toward the membrane surface. Probably, the negatively charged groups were carboxylic and these groups binding with the silver ions electrostatisticaly in RO and contributes to formation of Ag NP [13,15]. It was reported that charged functional groups found in an RO membrane [16,17]. During the contact of dilute silver salt solution ($AgNO_3$) with the RO membrane active layer, the hydrolyzedsilver ions diffused toward the membrane surface. It is likely that the negatively charged carboxylic groups found on the surface of TFC-RO membranes [18-20] form electrostatic pairs with silver ions and contribute to Ag-NP nucleation during the reduction stage [15].

In order to define the carboxylic groups, $pKCOOH_1$, $pKCOOH_2$ should be defined. The equilibrium for the carboxylic groups is given as:

[RCOOH] [H3O$^+$]+[RCOO$^-$] KCOOH [16]

where R represents the polymer backbone in the RO all K and pK-values for chemical equilibria refer to low acidic constants (pH=6.3).

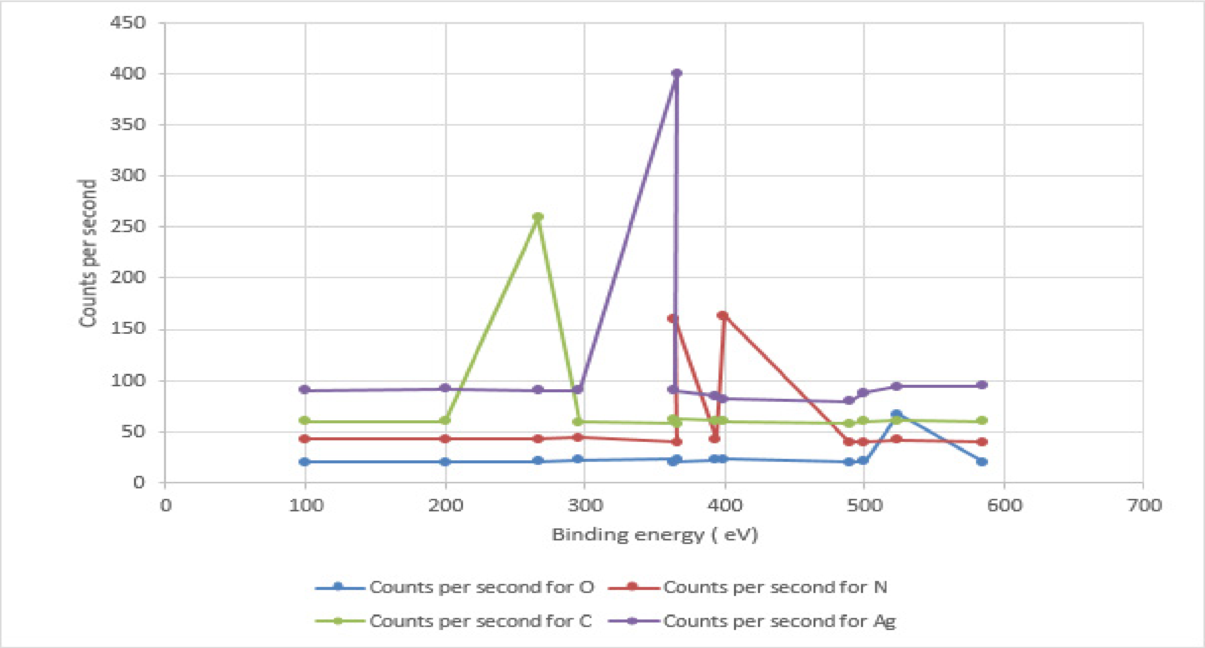


Figure 5: XPS analysis results for RO-Ag NP membrane after used in the treatment of drinking water with a $AgNO_3$:$NaHB_4$ ratio of 1:6.

Table 1: Variation of RO membrane permeability at varying $AgNO_3$ to $NaHB_4$ ratios.

Parameter	**Raw RO-Ag NP membrane with $AgNO_3$:$NaHB_4$ ratio of 1:2**	**RO-Ag NP membrane after used in drinking water treatment $AgNO_3$:$NaHB_4$ ratio of 1:2**	**RO-Ag NP membrane after used in drinking water treatment $AgNO_3$:$NaHB_4$ ratio of 1:4**	**RO-Ag NP membrane after used in drinking water treatment $AgNO_3$:$NaHB_4$ ratio of 1:6**
Membrane permeability ($Lm^{-2}h^{-1}bar^{-1}$)	143.2	143.12	142.6	141.98
	RO without Ag NP (1)	RO without Ag NP (2)	-	-
Membrane permeability ($Lm^{-2}h^{-1}bar^{-1}$)	118.56	116.27	-	

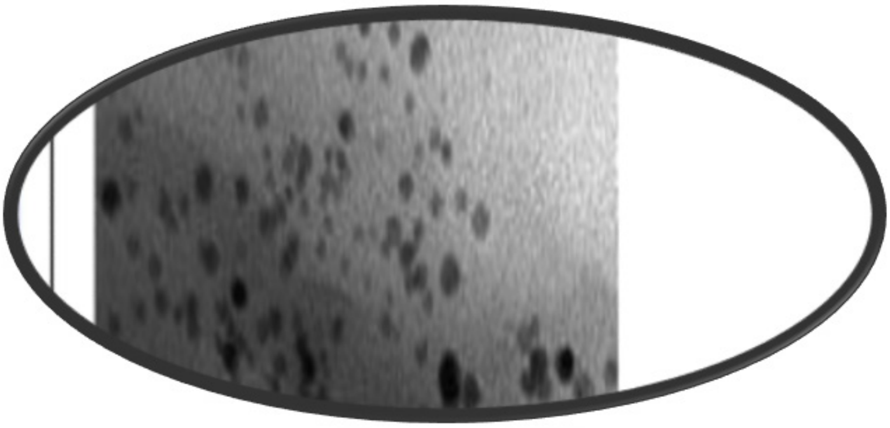


Figure 6: TEM (Magnification 45.000x).

Utilizing the relation betweent concentration and equilibrium constant, KCOOH, we can write

[RCOOH]=[H3O$^+$] [RCOO-] and due to the fixed number of carboxylic groups, at all times [16].

[RCOOH] tot=[RCOO$^-$]+[RCOOH] and with XCOOH=[RCOOH] tot, we can arrived at [RCOO$^-$]=XCOOH/µ 1+ [H3O$^+$] KCOOH [16].

With the addition on of $NaBH_4$ the free silver ions reduced on the RO surface silver can be precipitated on the RO membrane surface [21]. However, in our study, a significant silver precipitation was not detected. A permanent Ag NP precipitation can cause a significant reduction in the produced RO-Ag NP membrane permeability. In this study a significant reduction in the permeability was not detected as shown in Table 1. In the RO membrane reactor without Ag NP exhibited low membrane permeability compared to the Ag doped RO reactor.

TEM analysis results: Figure 6 exhibited the TEM micrographs of the cross section of RO-Ag NP membrane. The Ag NPs remained in the polyamide structure of the RO after formation.

Variation of water permeability of raw distilled water and sCOD after drinking water was passed from the RO-Ag NP membrane

In order to determine the distilled water permeability (B-dis) and sCOD permeability (B-s COD) coefficients in the RO-Ag NP membrane process with $AgNO_3$: $NaHB_4$ ratios of 1:2, 1:4 and 1:6 the RO membrane reactor was operated at a 20 bar pressure at a crossflow velocity of 12 cm/s, and a temperature of 215°C at a pH of 6.7.

The distilled water permeability coefficient (B-dis) firstly increased from 2.00 L/m^2.h.bar to 3.2 L/m^2.h.bar as the $AgNO_3$: $NaHB_4$ ratios was increased from 1:2 to 1:4 (Figure 7) in the RO operated with distilled water. Then the water permeability coefficient (B-dis) in distilled water decreased significantly to 1.4 L/m^2.h.bar at $AgNO_3$ to $NaHB_4$ ratio 1:6. Salt rejection percentages were around 99.4% (Data not shown). When the RO was operated with drinking water, the sCOD permeability (B-s COD) coefficient was recorded as 0.4 L/m^2.bar at a $AgNO_3$:$NaHB_4$ ratio of 1:2 (Figure 8).Then the sCOD permeability increaed to 0.9 L/m^2.bar at a $AgNO_3$:$NaHB_4$ ratio of 1:4. The sCOD permeability coefficient decreased by 58% at a $AgNO_3$: $NaHB_4$ ratio of 1:6 (Figure 9). This shows that some reactions ocurrred in the RO-Ag NP membrane at high $NaHB_4$ ratios [18].

The decrease in membrane water permeability at a $AgNO_3$:$NaHB_4$ ratio of 1:6 can be due to accumulation of Ag-NPs on the RO membrane. At high $NaBH_4$ concentration aggregation began and the colloids broke down and particle settled in the RO membrane durng operation. This decrease the water flux passing from the RO membrane surface. This probably decrease the membrane water permeability at high NaHB4 ratio since the Ag level in the polyamide layers of the RO probably lowered. This decrease the activity of the RO-Ag NP membrane.

Performance of the RO-Ag NP membrane process

Removal of sCOD, DOC, SS and NOM in drinking water in RO without Ag NP and with Ag NP: The removals of pollutant parameters were illustrated in Figure 8. At low $AgNO_3$:$NaHB_4$ ratio (1:2) all the pollutant parameters were remowed with yields as high has 88% and 89%.The maximum yields for all pollutants were around 100% at a $AgNO_3$: $NaHB_4$ ratio of 1:4 However, at high $NaHB_4$ level corresponding to a $AgNO_3$: $NaHB_4$ ratio of 1: 6 the yields reduced to 80%-81%. In the RO without Ag, the yields at all parameters decreased to 80%-81%.

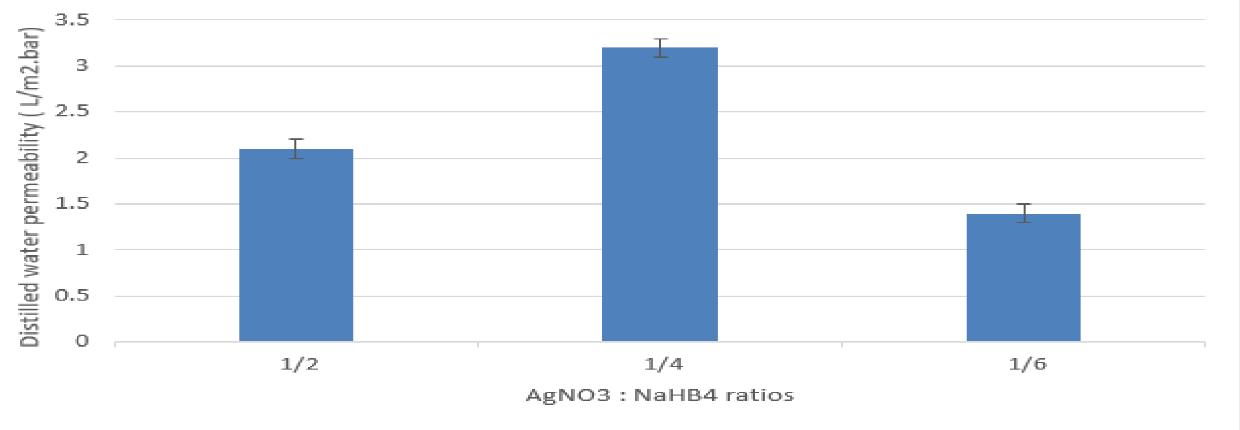


Figure 7: Variation of permeability coefficient (B-dis) in raw s RO-Ag NP membrane process.

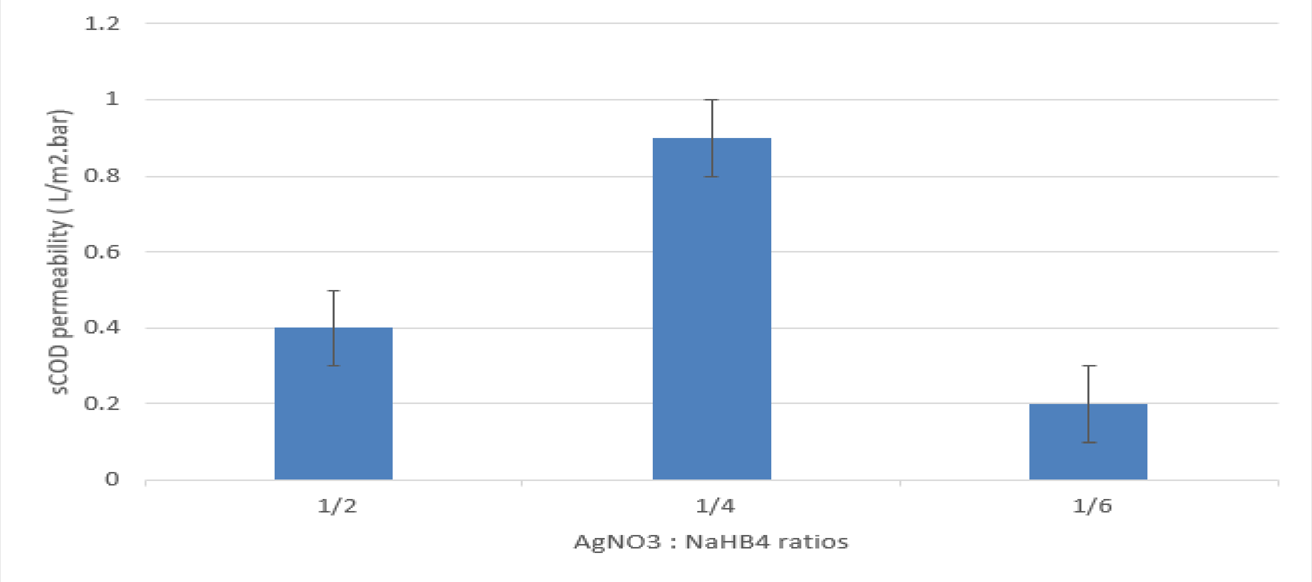


Figure 8: Variation of water permeability coefficient (*B*-sCOD) in treateds RO-Ag NP membrane process.

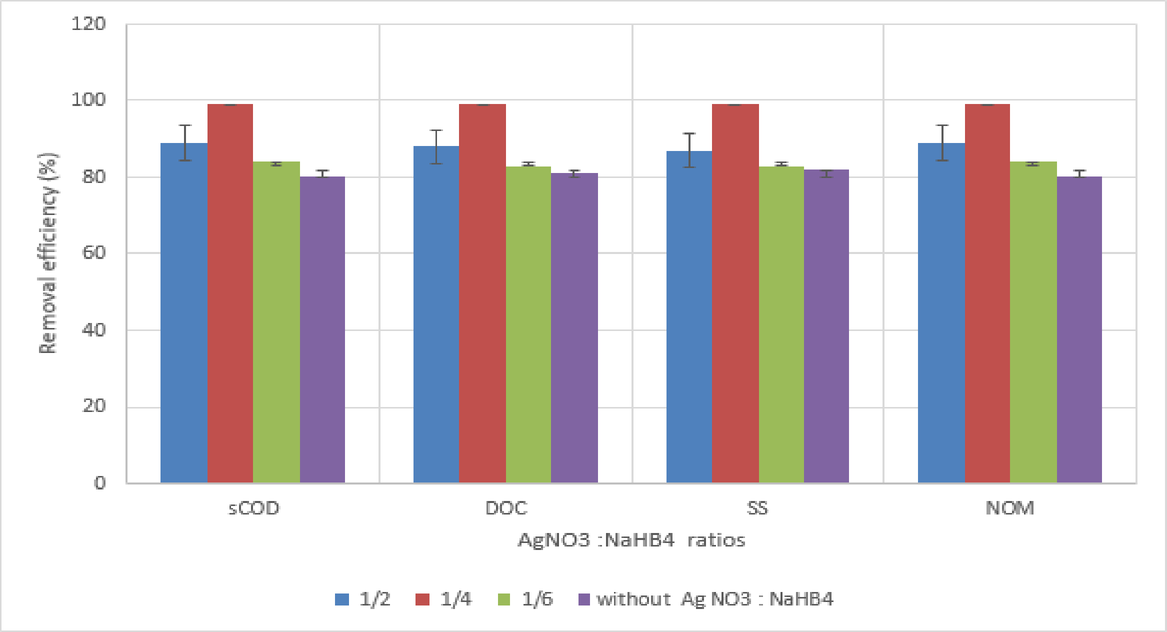


Figure 9: Removal efficiency of pollutants at different $AgNO_3$: $NaHB_4$ ratios in RO.

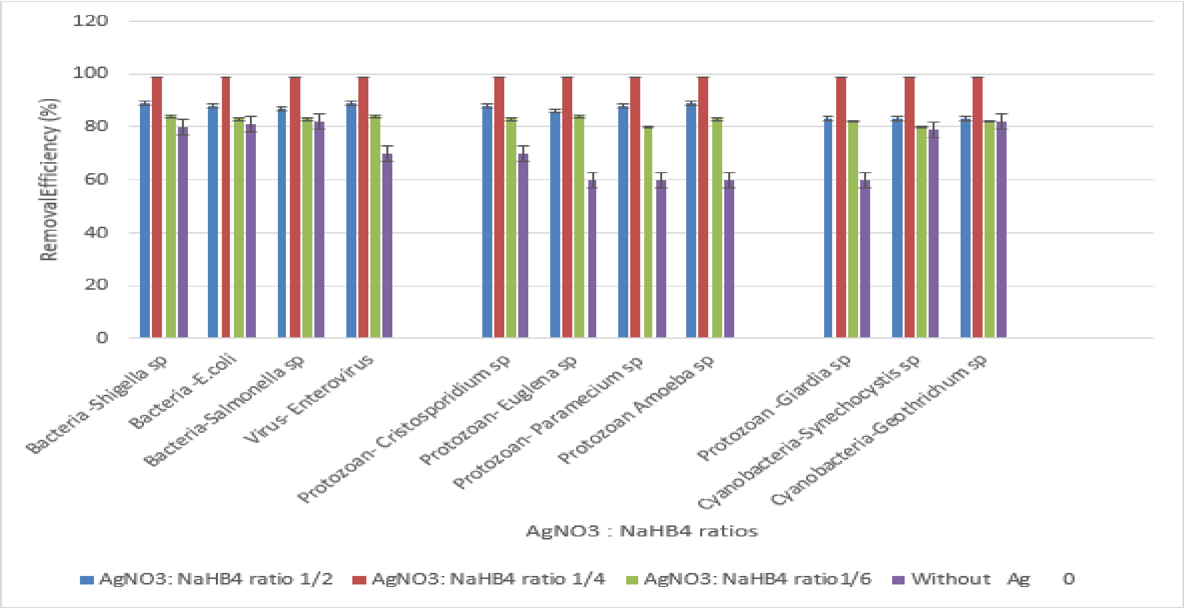


Figure 10: Treatment efficiencies of organisms in RO membrane with and wthout Ag NP.

Removal of organisms present in the drinking water in RO membrane with and without Ag NP : The removals of all organisms present in drinking water in the effluent of the RO were shown in Figure 10. At low $AgNO_3$: $NaHB_4$ ratio (1:2) all the organisms were remowed with yields as high as 82-89% . The maximum organism yields were detected at a $AgNO_3$: $NaHB_4$ ratio of 1:4. However, at high $NaHB_4$ level corresponding to a $AgNO_3$: $NaHB_4$ ratio of 1:6 the organisms yields decreased to 79%-82%.The RO membrane without Ag presented low organism yields (70%-80%). Particularly RO alone without Ag exhibited low removal efficiencies in the removal of some resistant organisms such as protozoan from the grinking water.

CONCLUSION

The results of this study showed that a novel Ag dopped thin film polyamide RO membrane was found to be excellent to remove the sCOD,DOC, SS and NOM from a drinking water. The bacteria, virusus, porotozoan and cyanobacteria also were effectively removed. For maximum pollutant and organism removals the optimum $AgNO_3$ to $NaHB_4$ ratio was found to be 1:4. At this ratio approximately 100% pollutant and organisms yelds were detected. RO membrane without Ag exhibited low removal efficiencies for all pollutants and particularly for resistant protozoan. SEM analysis results showed that in modified RO-Ag NP membrane after drinking water treatment the small Ag agregates did not cause a significant surface blockage in the membrane permeability. XPS analysis showed that Ag NPs embedded to the RO membrane since Ag NPs signals were detected at all $AgNO_3$: $NaHB_4$ ratios. TEM analysis showed that the Ag NPs remained in the polyamide structure of the RO after formation. The maximum distilled water and sCOD permeability constants were detected as 3.2 L/ m^3.bar at a $AgNO_3$: $NaHB_4$ ratio of 1: 4.

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