Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1057528

57 (2016) 12941–12955
June

Manufacturing of antibiofouling polymeric membranes with bismuth-BAL chelate (BisBAL)

Suleyman Ovez[a,b], Turker Turken[a,b], Borte Kose-Mutlu[a,b], Selin Okatan[a,b], Gamze Durmaz[a,b], Mehmet C. Guclu[a,b], Serkan Guclu[a,b], Shankar Chellam[c], Ismail Koyuncu[a,b,*]

[a]*Civil Engineering Faculty, Environmental Engineering Department, Istanbul Technical University, Istanbul, Turkey, Tel. +90 543 726 98 90; email: ovez@itu.edu.tr (S. Ovez), Tel. +90 505 554 54 52; email: turken@itu.edu.tr (T. Turken), Tel. +90 554 521 36 37; email: kosebo@itu.edu.tr (B. Kose-Mutlu), Tel. +90 506 428 03 46; email: eylulselin09@hotmail.com (S. Okatan), Tel. +90 537 563 90 31; email: gamze989@hotmail.com (G. Durmaz), Tel. +90 534 264 34 32; email: guclu.mehmetcan@gmail.com (M.C. Guclu), Tel. +90 536 977 93 67; email: gucluse@hotmail.com (S. Guclu), Tel. +90 505 933 17 21; email: koyuncu@itu.edu.tr (I. Koyuncu)*
[b]*National Research Center on Membrane Technologies (MEM-TEK), Istanbul, Turkey*
[c]*Civil and Environmental Engineering Department, University of Houston, Houston, Texas, email: schellam@central.UH.EDU*

Received 20 March 2014; Accepted 20 May 2015

ABSTRACT

Recent developments indicate an increase in demand of water supply and protection of natural water source quality with a requirement of advanced wastewater treatment systems. Formation of biofilms on the membrane surfaces and in the pores of membranes which are caused by extracellular polymeric substances and soluble microbial products has been identified as the main source of biofouling in membrane operation. The secretion of total polysaccharides and proteins by micro-organisms can be lowered when they are exposed to the bismuth-BAL chelate (BisBAL) at near minimum inhibition concentration. Our study aimed at controlling the population and co-products of micro-organisms that cause biofouling. After successful studies with the inhibition of *Escherichia coli* and *Streptococcus pyogenes* in activated sludge, BisBAL-containing membranes were fabricated. The effect of BisBAL on membrane performance was also observed. FTIR, SEM, contact angle, and surface roughness analyses were performed for the characterization of the membranes. Originality of this study comes from the usage of BisBAL for the first time for membrane synthesis.

Keywords: Antibiofouling membrane; Membrane manufacturing; PSf membranes; PES membranes; BisBAL; Xanthan gum; Membrane resistances

1. Introduction

In recent years, membrane processes have widely been used for the treatment of drinking waters [1], various industrial [2,3], and municipal wastewaters [4]. They have been accepted as an alternative to conventional treatment processes. Recently, increase in the need of wastewater reusage and stringent discharge regulations make membrane bioreactors (MBRs) attractive for the treatment of wastewaters. MBRs offer many advantages over the conventional

*Corresponding author.

wastewater treatment systems, including high effluent quality, high loading rates, low sludge production, with no need for chemical additions, compactness, and lower energy costs. These aforementioned advantages highlight the application of MBRs in the treatment of wastewater [5].

Although MBRs have been in use commercially for more than two decades, membrane biofouling remains one of the major issues of MBRs [6]. Biofouling is caused by the formation of biocakes on the membrane's surface. Recent studies related to advanced molecular biological techniques have revealed that the characteristics of the biocake formed on the membrane, such as porosity and biovolume, are closely associated with the permeability loss in MBRs [7]. Currently, extracellular polymeric substances (EPS) and soluble microbial products (SMP) in either bound or colloidal forms are considered as the major cause of membrane fouling in MBRs [8].

Biofilms are microbial communities that are adapted to disinfection and conditions of low nutrient content. In general, biofilms consist of rarely colonized surfaces, the nested structure of the extracellular polymers, ion channels formed by the microbial cells, and the complex layers show various structures depending on the depth [9,10]. Antibacterial nanomaterials are effective when applied on the surface; however, they are more effective when used as blends. The reason for choosing this nanomaterial is due to its cost-effective production processes.

Different types of nanomaterials like copper, zinc, titanium [11–13], carbon nanotubes, magnesium, gold [14], alginate [15], and silver have antibacterial properties. So far, silver nanoparticles have proved to be the most effective antimicrobial agent against bacteria, viruses, and other eukaryotic micro-organisms as well as membrane biofouling [16]. Bismuth has also been used for medical treatments throughout history. Bismuth thiols are one of the most important and well-known antibiotics. They have the ability to reduce the production of EPS and biofilm formation. Concentrations of 0.6 to 1 ppm Bisbal capsule are known to inhibit the formation of biofilm around 70–90%. As compared to other nanoparticles, it is safe and less toxic [18,19]. With the onset of the biological treatment processes in wastewaters, EPS and SMP have gradually increased [20,21]. Bismuth-BAL (BisBAL) can inhibit the secretion of EPS substances by bacterial genuses such as *Staphylococcus*, *Klebsiella*, and *Pseudomonas*. This inhibition reduces the formation of biofilms on membranes which in turn increases the life span of MBRs [22].

The scope of this study was to investigate the effect of BisBAL in reducing membrane biofouling. Also, the membranes were characterized and their performances observed. To the best of our knowledge, this has been the first study to use BisBAL for membrane synthesis.

2. Material and method

Within the scope of this study, optimization of BisBAL synthesis, inhibition tests for bacteria with BisBAL, and manufacturing of polyethersulfone (PES) flat sheet membrane having antifouling property have been included.

2.1. BisBAL synthesis

For optimizing the conditions for BisBAL synthesis, three different parameters, such as temperature, pH, and Bis:BAL molar ratio have been used. BisBALs were synthesized both at room temperature (25°C) and high temperature conditions (45°C). pH values were selected as pH 4, pH 7, and pH 10 in order to represent the acidic, neutral, and basic conditions, respectively. In order to optimize the molar ratio of Bis:BAL, 3:1, 2:1, and 1:1 ratios were selected.

BisBAL was synthesized by mixing bismuth nitrate pentahydrate ($Bi(NO_3)\cdot 5H_2O$ acs reagent ≥ 98.0%, Sigma–Aldrich, Germany), propylene glycol ($C_3H_8O_2$ ≥ 99.5%, fcc, Sigma–Aldrich, Germany), and 2,3-dimercapto-1-propanol (Sigma–Aldrich, Germany). The stock solution was prepared and then mixed with BAL at different temperature and pH conditions. pH adjustments were made with 1-N NaOH (extra pure, Sigma–Aldrich, Germany) and temperature values were adjusted using a hot stirrer constantly. Eighteen different BisBAL combinations were used. The combination names and synthesis conditions have been listed in Table 1.

The inhibition effects of BisBAL on Gram-negative bacterium, *Escherichia coli*, and Gram-positive bacterium, *Streptococcus pyogenes*, were investigated. Pure cultures of these bacterial species were provided as lyophilized pellets by "Microorganism Culture Collection Research and Application Center (KÜKENS) of Turkey".

For the inoculation and growth of bacteria for inhibition tests, Lactose broth (LB) agar was prepared (For 1,000 mL LB agar, 10 g Tryptone, 5 g yeast, 5 g NaCl, and 15 g bactoagar were used). For the inhibition tests, 5 ml LB broth was poured into autoclaved falcon tubes. After cooling, the tubes were inoculated using automatic pipettes and sterile pipette tips. Dilutions for bacterial species were prepared using isotonic water to obtain approximately 40 bacterial cells in each falcon tube. After pouring the LB broth, 0.2 mL

Table 1
Combinations used for BisBAL synthesis optimization

Sample name	Synthesis temperature (°C)	pH of the solution	Molar ratio (Bismuth/Thiol)
S1	25	4	3:1
S2	25	4	2:1
S3	25	4	1:1
S4	25	7	3:1
S5	25	7	2:1
S6	25	7	1:1
S7	25	10	3:1
S8	25	10	2:1
S9	25	10	1:1
S10	45	4	3:1
S11	45	4	2:1
S12	45	4	1:1
S13	45	7	3:1
S14	45	7	2:1
S15	45	7	1:1
S16	45	10	3:1
S17	45	10	2:1
S18	45	10	1:1

bacteria solution was added to obtain lower measurable optical density values after 24 h. After inoculation, BisBAL was added at different molar concentrations to analyze its inhibition efficiency. Bacterial cultures were incubated for 24 h.

Inhibition efficiency of BisBAL on *E. coli, S. pyogenes,* and the activated sludge had previously been tried with different molar concentrations (5, 12, 15, 20, 30, and 40 μM).

In this study, we used the same BisBAL molar concentrations. After 24 and 48 h of BisBAL addition, bacteria was incubated in the broth medium using Heraeus incubator and optical densities of the samples were analyzed at 420 and 570 nm wavelengths.

Minimum inhibition concentrations (MIC) were determined for all BisBAL concentrations and for both bacterial species. Optimum synthesis conditions were found according to the results found from the inhibition experiments.

In the literature, it was mentioned that the inhibition effect of BisBAL is not stable. In our study, experiments were conducted for several weeks to observe the stability of BisBAL inhibition.

After the basic inhibition tests, five optimum BisBAL concentrations had been selected. With these selected concentrations, further tests were performed which include the measurements of EPS and SMP for both control and BisBAL added samples after 24 h incubation. Optimized BisBAL concentrations were S1, S3, S6, S11, and S14, as they were found to be the most inhibitive combinations for *E. coli and S. pyogenes* species. Twelve and thirty μM BisBAL concentration were found as MIC values, and these concentration were used for further experiments. EPS and SMP extraction analysis for proteins and polysaccharides was performed using Lowry and phenol sulfuric acid methods [23], respectively.

2.2. Membrane manufacturing

The optimized BisBAL concentrations (S1, S3, and S14) were selected to be used in the membrane dope solution. Fourteen different types of membranes were casted to the polymer structure of the membranes. Both PES and PSf were selected as polymers. Fifteen and thirty μM BisBAL were the selected concentrations. Polyvinylprolidone was selected as the pore-forming agent [24]. Two different polymer ratios, 16 and 9%, were selected. PVP ratio was selected as 8%. The information related to the fabricated membranes can be found in Table 2. As a control sample, the membranes without BisBAL were fabricated.

To prepare the membrane dope solution, in 100 ml DMAc solvent, appropriate amount (15 or 30 μM) BisBAL was added. Then, PVP (8%) and polymer (PES or PSF, 16 or 20%) were added to the solution, respectively. To obtain a homogeneous solution, all the constituents were mixed at 200 rpm for 1 d at 60–70°C. The homogenized solution was ultrasonicated in order to remove bubbles.

Table 2
Produced membrane combinations

PES 16%	PES 20%	PSf 16%	PSf 20%
Without BisBAL (μM)	Without BisBAL (μM)	Without BisBAL (μM)	Without BisBAL (μM)
S1, 15	S1, 15	S1, 15	S1, 15
S1, 30	S1, 30	S1, 30	S1, 30
S3, 15	S3, 15	S3, 15	S3, 15
S3, 30	S3, 30	S3, 30	S3, 30
S14, 15	S14, 15	S14, 15	S14, 15
S14, 30	S14, 30	S14, 30	S14, 30

Water-induced phase inversion method combined with dipping method has been preferred for flat sheet membrane production. Ninety-micromolar thick textile was used as the support layer. The polymer solution was poured into a rectangular glass plate and membranes were casted. These glass plates were placed on the film applicator. Vacuum of the applicator was opened in order to fix the plate. The casting knife speed was adjusted as 50 mm/s. The casting knife was put on the plate in the beginning and the polymer solution was poured in front of the casting knife, then the applicator was started. Membranes were put in the water coagulation bath for 10 s to obtain a solid form. With the support layer, the total membrane thickness obtained was around 180–220 μm. Glass plates were put in a water coagulation bath for 10 s. All casted membranes were stored in distilled water at 4˚C temperature.

2.3. Filtration studies

After membrane manufacturing, permeabilities were measured for all membranes in order to compare filtration capacities of the membranes. To understand fouling resistances of the membranes, model xanthan gum solution and real activated sludge were filtered/used.

2.3.1. Permeability experiments

Pressure-driven, cross-flow filtration cell was used for permeability experiments (Sterlitech). The membrane diameter used in the filtration cell was 49 mm. The active/total membrane area used was 14.6 cm^2. Three different pressure values had been applied. Prior to the permeability test, membranes were compacted for 1 h in order to remove residual polymer, solvent, or PVP using distilled water. The feed volume was taken as 250 mL out of the total volume of the cell, i.e. 300 mL. The maximum pressure was 69 bar, but the applied pressure was changed according to the experiment. The maximum temperature that can be applied to the filtration cell is 121˚C, but during our permeability and fouling tests, room temperature was preferred. At each pressure, the permeate was weighted and flux values were determined (Eq. (1)). A software was used to convert these weight data to computer files. Using the flux values and the pressure data, a graph was drawn and the slope of this graph (as $y = mx$) was found. The slope represents permeability. The water permeabilities of membranes were measured thrice at different locations of the membranes.

$$J_w = \frac{V}{AT} \qquad (1)$$

where J_w: Water flux ($L/m^2/h$), A: Effective membrane area (m^2), T: Time (h), and V: Permeate volume (L).

2.3.2. Fouling experiments

After the BisBAL inhibition effect was determined, antibiofouling properties of BisBAL added membranes were investigated with xanthan gum solution and activated sludge filtration fluxes. These flux values were compared with distilled water flux values.

2.3.2.1. Xanthan Gum Filtration. Xanthan gum, which is widely used in the food industry, is a heteropolysaccharide which has high molecular chains produced by aerobic fermentation by *Xanthomonas campestris*. Xanthan gum can be used to understand the fouling mechanisms on membrane surfaces. Xanthan gum consists of homogeneous fouling substances. Model xanthan gum solution can be used to understand the fouling mechanism easily for each sample, in place of a complex and heterogeneous activated sludge.

Prior to the xanthan gum filtration studies, membranes were compacted for 1 h. Compaction of the membranes was also done to get rid of the residuals within the membranes. Twenty-five-milligram per liter xanthan gum solution was prepared. Xanthan gum solution was mixed for 1 h and prepared prior to the experiments.

Xxanthan gum filtration studies were performed with the selected membranes (16% PES + 8% PVP, 20% PES + 8% PVP, 16% PSf + 8% PVP, and 20% PSf + 8% PVP) using three different types of BisBAL (S1, S3, or S14 with 15 or 30 μM) concentrations. For fouling experiments, 28 different membranes were used. In each experiment, the membranes manufactured without BisBAL were used as the control. Experiments were conducted in duplicates.

For the fouling experiments, firstly, distilled water was filtered through the membrane for 30 min. During this 30 min period, the pressure increased from 1 to 2 bar, with 0.5 bar increase after every 10 min. After this step, xanthan gum solution was filtered for 1 h at 0.6 bar pressure to see the flux profile changing with time. Flux values were recorded during this step. Finally, distilled water was filtered again for 1 h in order to calculate the relative flux reduction of the membranes.

Furthermore, for the understanding of fouling mechanism, membranes' resistance was also calculated. The resistance values of raw and BisBAL added membranes in xanthan gum filtration were calculated according to the equations given below (Eq. (2)).

$$J_w = \frac{V}{AT} \quad (1)$$

where J_w: Water flux ($L/m^2/h$), A: Effective membrane area (m^2), T: Time (h), and V: Permeate volume (L)

$$R_t = \frac{\Delta P}{\mu J_t} \quad (2)$$

where J: Permeate flux ($m^3/m^2/h$), ΔP: Transmembrane pressure (Pa), μ: Viscosity (Pa s), and R_t: Total filtration resistance (m^{-1})

$$R_t = R_m + R_p + R_c \quad (3)$$

$$R_m = \frac{\Delta P}{\mu J_o} \quad (4)$$

$$R_p = \frac{\Delta P}{\mu J_1} - 1 \quad (5)$$

$$R_c = R_t - R_p + R_m \quad (6)$$

where R_m : Membrane resistance, R_p: Pore resistance, R_c: Cake resistance, J_t: Steady-state flux at xanthan gum filtration ($m^3/m^2/h$), J_o: Initial steady-state flux of water ($m^3/m^2/h$), J_1: Steady-state flux of water after removing the cake layer slowly ($m^3/m^2/h$), and J_2: Initial steady-state flux of water after removing the cake layer slowly ($m^3/m^2/h$).

The relative flux (FR) reduction can be calculated as:

$$FR = \left(1 - \frac{J_2}{J_0}\right) \times 100 \quad (7)$$

2.3.2.2. Activated sludge filtration. After using the model xanthum gum solution, a real activated sludge was filtrated. Activated sludge was taken from a full-scale advanced domestic wastewater treatment plant which is located in Istanbul. The filtration tests with activated sludge were done twice. Mixed liquor suspended solid value was around 4,000 mg/l. The procedure used for the activated sludge experiments was the same as the xanthan gum filtration.

2.4. Membrane characterization

After the membrane fabrication, membranes were characterized. The morphology and performance of membranes without BisBAL have been investigated.

2.4.1. Electron microscope scanning

Morphology of the membranes was observed using FEI Quanta FEG 250 Scanning Electron Microscope (USA). Before scanning, the surface of the membranes was coated with 3–4 nm gold–palladium (Pd–Au) using Quorum SC7620 model sputter coating machine (UK).

2.4.2. Surface roughness

Surface roughness is important to understand the fouling properties of the fabricated membrane. The surface roughness measurements were conducted using Zygo Brand Optical profilometer (USA). The concentration and angle of dense light reflected by the membrane surface were determined by the detector and the roughness of the membrane surface was obtained by the same instrument. Scanning size was 0.187 mm × 0.140 mm. Roughness was determined in μm.

2.4.3. Surface contact angles

Membrane hydrophilicity, which shows wettability of the membranes, was measured by KSV Attension Theta Brand contact angle measure instrument (Sweden). The relationship between the contact angle and hydrophilicity is inversely proportional. Measurements were conducted in triplicates and the average values are presented.

2.4.4. Pore distributions

The pore distributions of membranes were measured by a porometer. Experiments were done by applying pressure to the membranes and passing the chemical (porophyll) from the interface.

2.4.5. Surface charges of membranes

Membrane surface charges were measured by an electrokinetic measurement instrument (Anton Paar Surpass).

2.4.6. Total organic carbon (TOC)

In order to check the organic substances' removal efficiency of the membranes, TOC analysis was done with permeates obtained from membranes w/o BisBAL. TOC instrument from Shimadzu was used and the removal efficiency between the feed and permeate was calculated.

2.4.7. BisBAL release control

It is important to control Bismuth release from membranes during filtration. Deionized (DI) water was filtered at dead-end stirred filtration cell after one hour of operation and the total bismuth concentrations in the permeate were analyzed using the ICP equipment. The total bismuth concentrations were quantified using a Perkin-Elmer (Norwalk, CT) Optima 3,000 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

All the measurements were carried out in the axial mode. A 999 ± 0.2-μg/mL standard solution from Inorganic Ventures including bismuth, water, and 5% HNO_3 (v/v) were used as internal standards for calibration as recommended by the ICP manufacturer and correlation coefficient was 0.9998. All samples and ICP standards were acidified using 0.5% trace metal grade HNO_3.

3. Results and discussion

3.1. BisBAL synthesis optimization

In this study, for the optimization of BisBAL synthesis, three parameters (temperature, pH, and BisBAL molar ratios) were selected. BisBALs were synthesized both at room temperature (25˚C) and high temperature conditions (45˚C). pH 4, 7, and 10 values were selected in order to represent the acidic, neutral, and basic conditions, respectively, for the optimization of pH. Another parameter was the molar ratio of bismuth and BAL. After synthesis, BiBAL S3 combination was determined to be the best for synthesizing membranes.

3.2. Antibiofouling membrane manufacturing

3.2.1. Water permeabilities

Permeability results are given in Fig. 1. Membranes produced with 30 μM BisBAL had generally greater permeabilities than the membranes produced with 15 μM BisBAL. In this study, the membranes were manufactured by phase inversion method. In this method, when the coagulation time is slow due to the extended solvent to non-solvent exchange rates, the created membranes have a thicker and more porous active surface layer. However, when the exchange rate between the solvent and non-solvent is shortened, the membrane morphology changes with a thinner and dense surface.

The conductivity of metallic bismuth (solid form) is lower than its liquid form. Bismuth in polymer solution can affect the heat transfer during phase inversion and favor the exchange rate. The hydrophilicity of the bismuth thiols also decrease the coagulation time. Because of these reasons, BisBAL-added membranes have a denser selective layer than non-BisBAL pristine membranes. Having a dense selective layer can lower permeability results.

Increase in polymer concentration (16 or 20%) caused the permeability to decrease since pore nucleation is limited. Higher polymer concentration resulted in smaller pores and this created resistance. However, this type of membranes can show higher treatment efficiency.

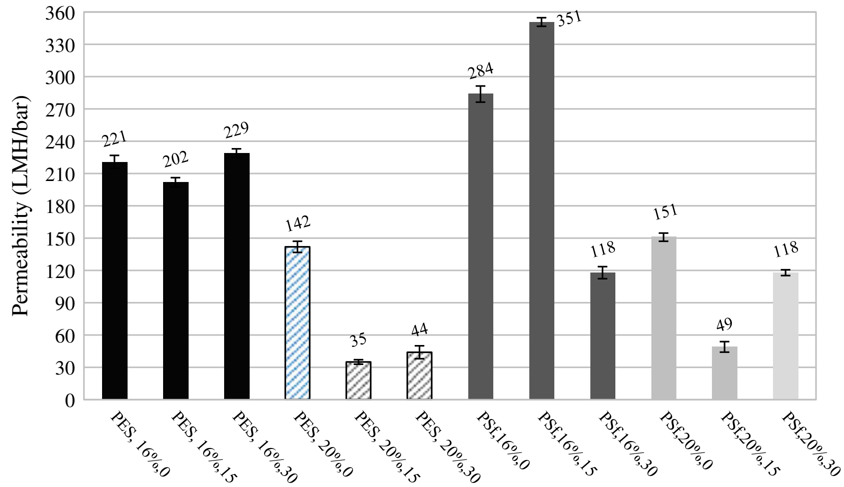

Fig. 1. Pure water permeability values of membranes (Ex.; PES, 16%, 0: nonmodified PES (16%) membrane Ex.; PSF, 20%, 30: modified PSf (20%) membrane with 30 uM BisBAL).

3.2.2. Xanthan gum filtration and membrane resistances

In order to evaluate membrane resistances and BisBAL effects on fouling, xanthan gum filtration studies were conducted. After the distilled water filtration, 25-mg/L xanthan gum solutions were filtered through each membrane. After that, the cake layer on the membranes was rinsed slowly with water. After the hydraulic washing, water filtration was carried out again thrice to calculate membrane resistances. All resistance value results can be seen on the graphs plotted in Fig. 2.

As seen in Fig. 2, the membranes manufactured with PSf polymer have higher membrane resistances. While the total resistance of PES membranes was around $1.4–1.6 \times 10^7\ m^{-1}$, PSf membranes had membrane resistances between 3.0 and $6.0 \times 10^7\ m^{-1}$. PSf membranes were used at two different percentages as 16 and 20% because of resistance properties. Resistances decreased up to 30% with the addition of BisBaL. Additionally, BisBAL had a significant impact on the blocking of the membrane cake layer formation. Up to 65% decrease in pore resistance could be obtained with BisBAL addition. BisBAL also prevented the pore blockage with 50% success. In addition to these, flux reduction values were also calculated and are given in Table 3. According to Table 2, the flux recovery (FR) values decreased from 60 to 2.2%.

3.2.3. Activated sludge filtration

In order to evaluate the antibiofouling effect of the membranes with real activated sludge, filtration test was carried out, results of which are presented in Fig. 3.

According to the data presented in Fig. 3, flux values were higher in BisBAL added membranes. Flux decrease in the pristine membranes was 81%. However, in the 15 μM and 30 μM BisBAL added membranes, flux decreases were 55 and 63%, respectively. In the PSf membrane groups, the percentage decrease in fluxes was higher than the PES membranes.

3.2.4. BisBAL Release Control Results

To control the BisBAL elution from the membranes during filtration, Bi metal analysis was performed with permeates after every 1 h filtration using the ICP Instrument. Also Bi concentration in the raw BisBAL solution was examined and the results are given in Table 4.

As can be seen in Table 4, Bi release was minimum. The membranes fabricated with 20% polymer concentration had lower Bi release than the membranes fabricated with 16% of polymer concentration. The PSf membranes were more impervious than the PES membranes in terms of releasing of Bi. In order to get detailed information about Bi release into the environment, chronic effect analysis would be carried out in future studies.

3.2.5. Characterization of membranes

Before and after the filtration studies, membranes were characterized and their surface morphology was examined by a scanning electron microscope and optic profilometer. In addition to the morphologic structure,

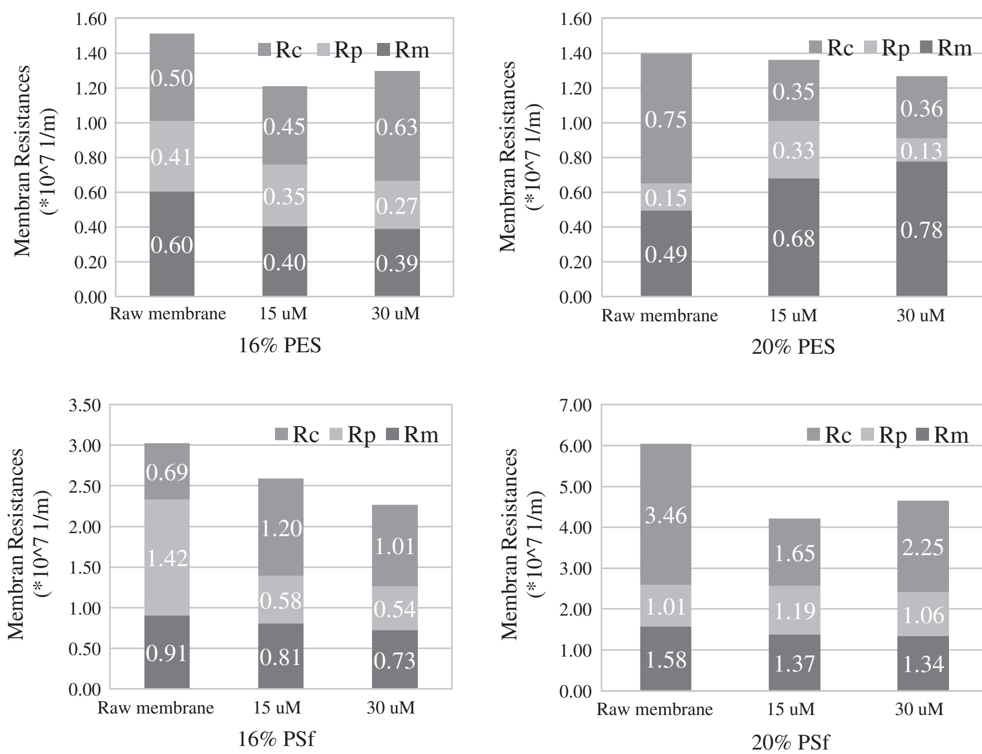

Fig. 2. Membrane resistances.

Table 3
Fouling resistance (FRdw) values after xanthan gum filtrations

	FRdw (%)			
	PES 16%	PES 20%	PSf 16%	PSf 20%
Raw membrane	33.3	57.0	38.5	11.1
15 μM BisBAL	8.3	33.3	5.5	11.1
30 μM BisBAL	2.2	7.1	4.2	1.7

chemical structure and wettability of surfaces are also important. FTIR analysis and contact angle determinations were performed in order to check chemical bond structures on the surface and hydrophilicity, respectively.

3.2.5.1. SEM analysis. SEM analysis of the membranes before filtration was done at two different magnification points which were 8,000× and 120,000×. 8,000× magnification was used to obtain general the morphology of the membranes to detect defects on them. On the other hand, 120,000× magnification was used to see the detailed morphology (pore structure, etc.). After the filtration experiments, membranes were examined under 2,000× magnification to analyze accumulation of organic matter on the membrane surfaces. All SEM results are given in Fig. 4.

Both membranes (PES and PSf) including 16 and 20% polymer concentrations were analyzed and there was no defect on the membranes due to fabrication. Pores on the membranes having both 16 and 20% polymer concentrations at 120,000× magnification can be seen in Fig. 4. Pores do not have round shapes. Their structures can be defined as fissures. The width of these fissures was in the range of 3–10 nm and the length was about 30–40 nm. Although the pore sizes were similar between the surfaces of membranes having both 16 and 20% polymer concentrations, the membranes having 20% polymer concentration had lower flux values than the membranes having 16% polymer concentration. It can be explained by the fact that the membranes having 20% polymer concentration had thicker selective layer which can lead to the decreased flux values.

There were no defects on the membrane surfaces caused by the casting knife. There were some small lines on the surfaces because of the polymer solutions; however, these lines were not important when they were compared to the total membrane area. It can be said that they had no negative effects on the membrane quality.

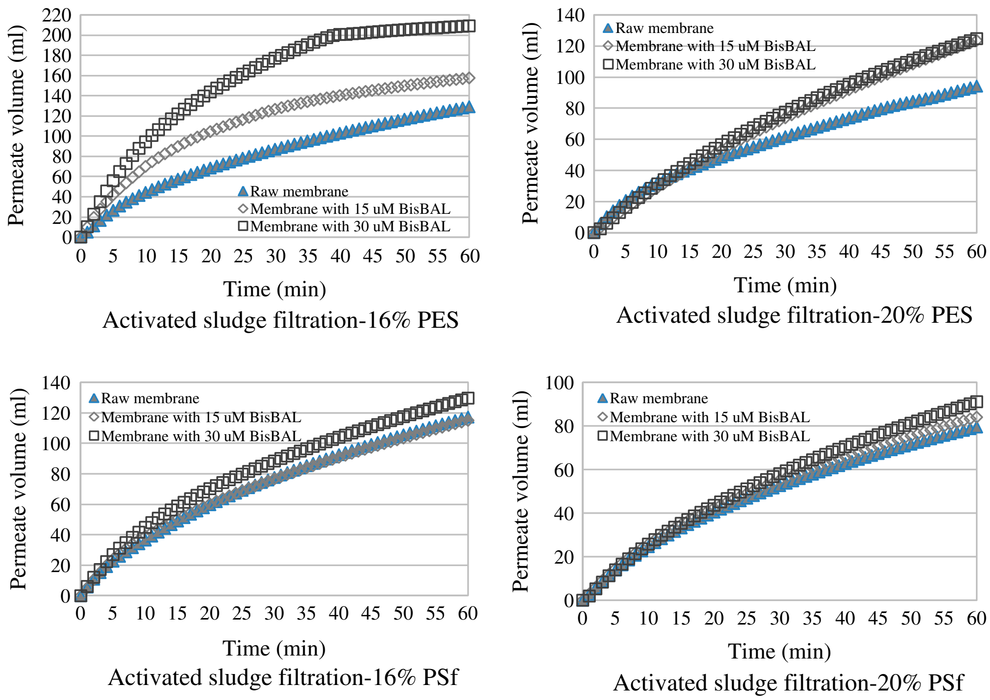

Fig. 3. Activated sludge filtration permeate profiles.

Table 4
Bi concentrations in permeates from related membranes

Sample	Bi concentration (ppm)
Raw 15 μM BisBAL(solution added to the membrane dope solution)	0.9250
Raw 30 μM BisBAL(solution added to the membrane dope solution)	1.2280
PES (16%, 15 μM)	0.0320
PES (16%, 30 μM)	0.0300
PES (20%, 15 μM)	0.0310
PES (20%, 30 μM) membrane	0.0320
PSf (16%, 15 μM) membrane	0.0139
PSf (16%, 30 μM) membrane	0.0131
PSf (20%, 15 μM) membrane	0.0073
PSf (20%, 30 μM) membrane	0.0126

After the activated sludge filtration, a biofilm layer can be seen on the membrane surfaces. The biofilm layer on the membranes having 20% polymer concentration was thicker than the membranes having 16% polymer concentration. The biofilm layer was more thicker on the PSf membranes after the activated sludge filtration. With the increase in the BisBAL concentration within the membrane matrix, the biofilm layer on the surfaces decreased.

BisBAL-added membranes were produced from the organic matters which were built-in flocs. Higher BisBAL concentration caused more compactness and lesser amount of flocs. After hydraulic washing, the biofilms could not be seen anymore. The BisBAL-added membranes were washable after the activated sludge filtration as compared to the non-BisBAL added membranes. It can be said that the adhesion of the organic matter onto the membrane surface was less when it was modified with BisBAL. The PES membranes were better and the flux recovery percentage was more than the PSf membranes regarding biofouling. It can be seen in the SEM figures in detail.

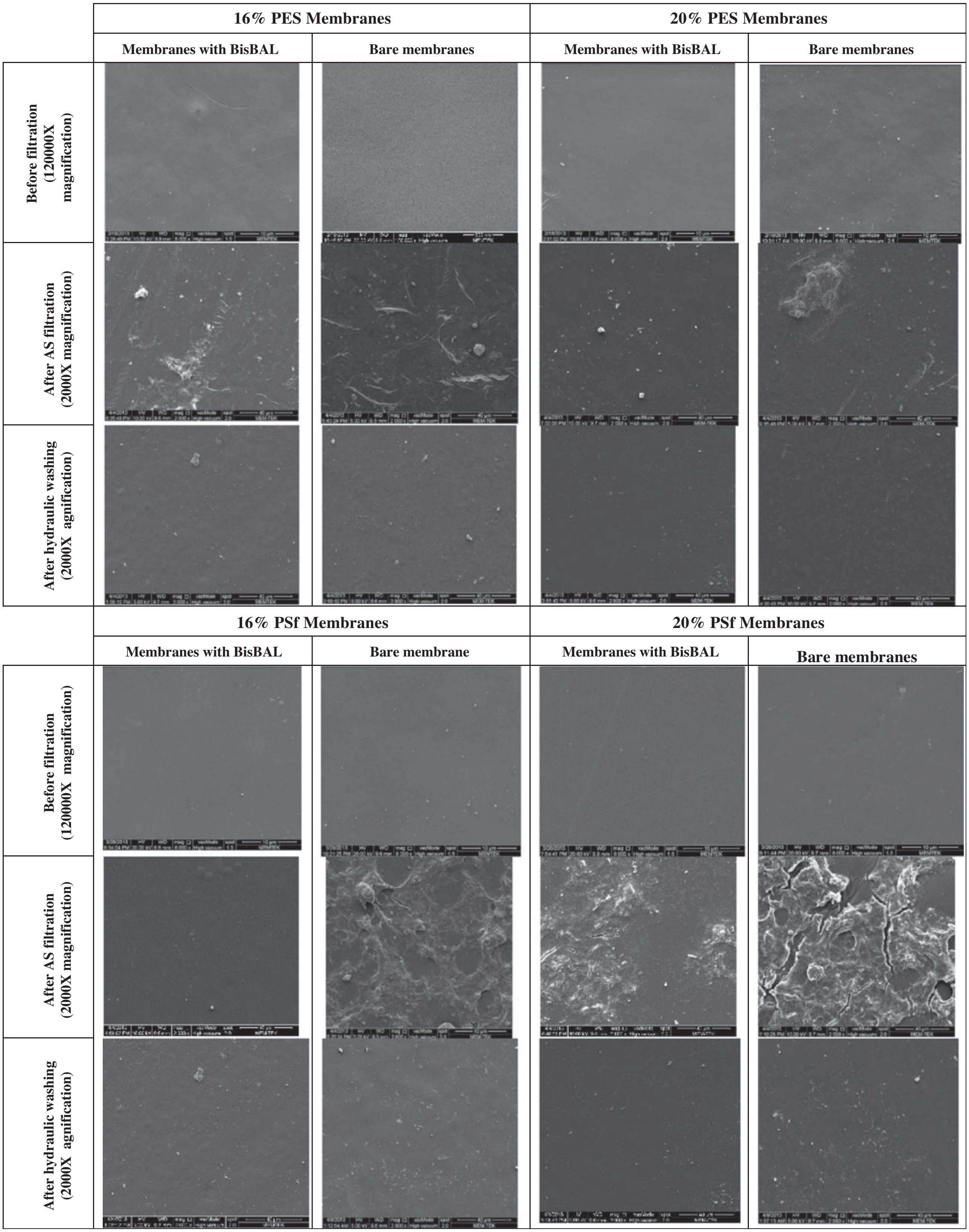

Fig. 4. SEM images of without BisBAL and produced antibiofouling membranes before filtration, after activated sludge filtration, and after hydraulic washing, following activated sludge filtration.

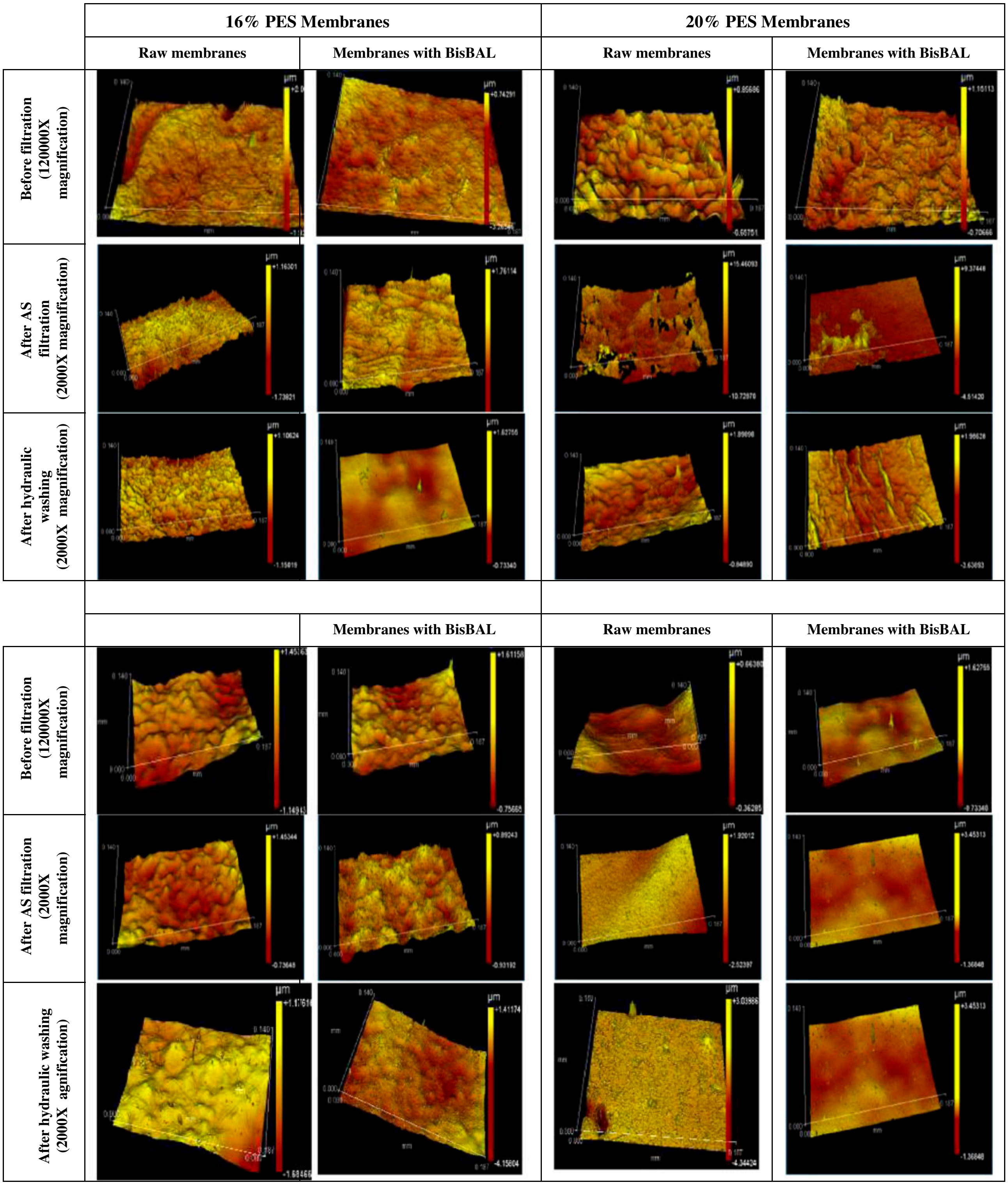

Fig. 5. Optic profilometer result images of without BisBAL and produced antibiofouling membranes before filtration, after activated sludge filtration, and after hydraulic washing, following activated sludge filtration.

Table 5
Ra values of membrane surfaces

Membrane type	BisBAL Additions (μM)	Ra (nm) values		
		Before filtration	After AS filtration	After washing
16% PES	0	275	127	108
	15	122	115	110
	30	177	176	137
20% PES	0	2,270	202	106
	15	429	118	117
	30	599	262	130
16% PSf	0	310	215	165
	15	231	161	143
	30	219	215	133
20% PSf	0	174	139	133
	15	1,464	162	71
	30	812	172	107

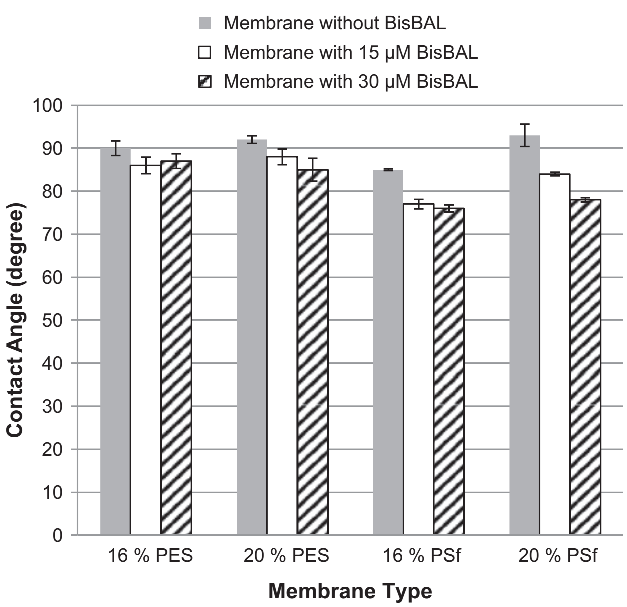

Fig. 6. The contact angle values of membranes.

Table 6
Pore sizes of the membranes

Sample name	The pore sizes of membranes (μm)	
	PES	PSf
Membrane without BisBAL	0.08–0.02	0.15
Membrane with 15 μM BisBAL	0.20	0.03
Membrane with 30 μM BisBAL	0.20	0.03

3.2.5.2. Surface roughness. Surface roughness values of membranes were found to be important to understand the fouling properties of the manufactured membranes before filtration, after the activated sludge filtration, and hydraulic washing. All the results provided from the optic profilometer are given in Fig. 5 and all roughness values are given in Table 5.

Roughness values of the membranes before the filtrations were in normal ranges. The membranes produced with 20% polymer concentration had smaller roughness values than the membranes produced with 16% polymer concentration.

Looking at the 3D structures of the membrane surfaces, hillocks of the membrane having 16% polymer concentration were closer than that of the 20% polymer concentration membranes. This data supported the fact that membranes having 20% polymer concentration had thicker surface active layers.

After the activated sludge filtration, roughness values of the membranes increased due to organic matter accumulation and fouling. With the increase in the BisBAL concentration, roughness values of the membranes decreased.

Each solid plot was obtained from the same place with the 3D structure. The organic matter accumulation and particles on the surface can be more easily seen on the solid plots.

After the hydraulic washing, roughness values decreased. However, the roughness values were still greater than the first roughness values before the filtration. This could be due to the small irreversible pore blockages. Similar results for sludge aggregation can also be seen from the 3D images on the surfaces

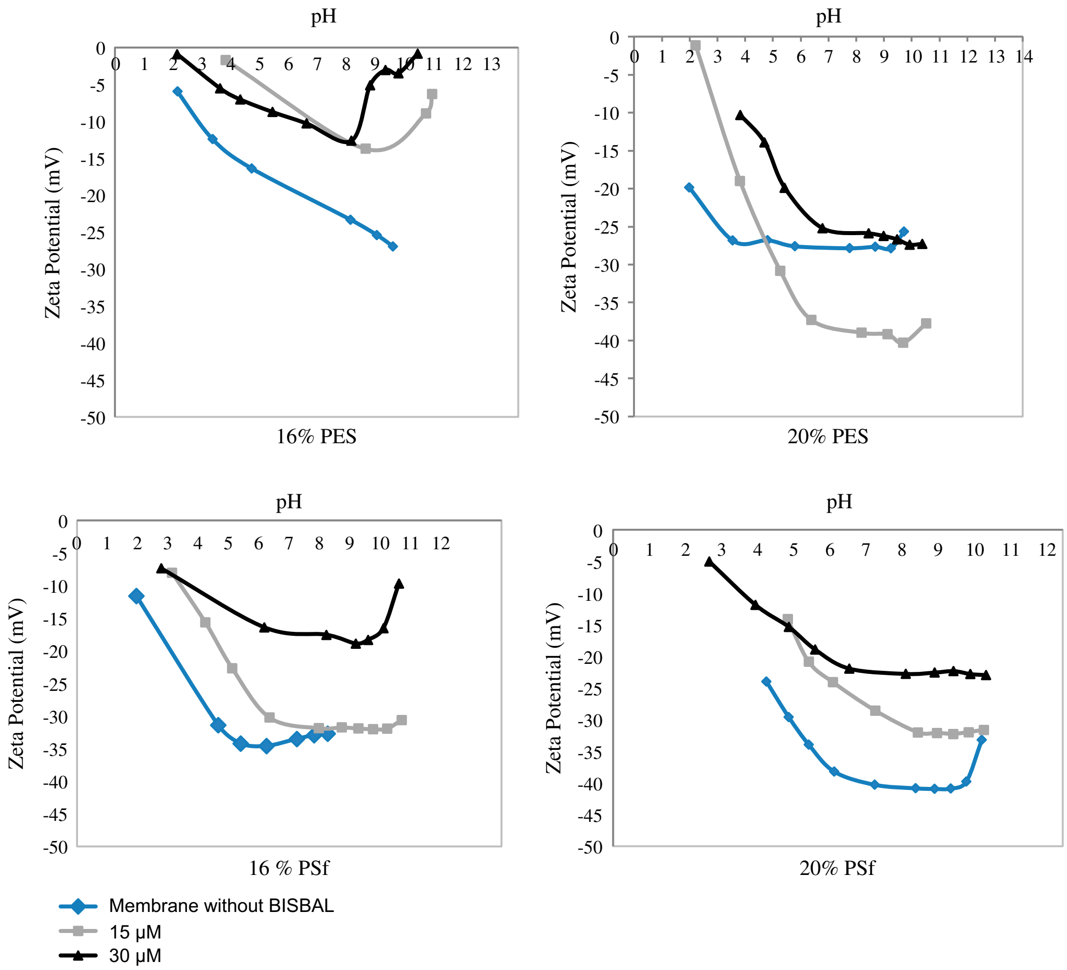

Fig. 7. Zeta potentials of membranes.

of the SEM images. Hydraulic washing showed a more positive effect with the BisBAL-added membranes. The PSf membranes have greater roughness values than the PES membranes.

3.2.5.3. Contact angle measurements. To investigate the hydrophilic properties of the membranes, contact angles of the membranes were measured and the results are presented in Fig. 6. In all cases, contact angle values decreased when the BisBAL concentration in the membrane solution increased. It was related to the hydrophilic Bismuth thiols within BisBAL. However, there was a negligible change in the contact angle values when BISBAL concentration increased. Also, the decrease in contact angle values can result from the functional groups on the membrane surface blended with increased concentrations of BisBAL.

As shown in Fig. 6, contact angle increased due to the nodular structure on the membrane surfaces when the polymer concentration increased in the dope solution.

3.2.5.4. Pore Size Distribution Measurements. The pore size measurements were carried out to evaluate the pore distribution of the membrane samples. However, both PSf and PES membranes having 20% polymer concentration did not give any results because their pore distributions were out of range. Higher polymer concentration made the dope solution more viscous, which led to denser membrane structures and smaller pore sizes. Pore size values of the fabricated membranes are given in Table 6.

Pristine PES membranes without BisBAL had an average 0.02 μm pore size. BisBAL added PES membranes had an average 0.2 μm pore size. However, in the PSf membranes, the pore size decreased with the addition of BisBAL. The reason for this decreased pore size in the PSf membrane is due to the changing speed of precipitation related to the exchange rate between the solvent and non-solvent with differing BisBAL concentrations. The difference between the pore size distributions of the PES and PSf membranes is a result of their different molecular weights. Although differences occurred in pore sizes, there was not much apparent difference between the membranes.

3.2.5.5. Electrokinetic measurements. Changes in membrane zeta potential could be used to investigate the behavior of cake deposition and fouling during the filtration of colloids. The adsorption capacity of a membrane decreases with reduced (more negative) zeta potential. Zeta potential graphs of the membranes are given in Fig. 7.

As can be seen from Fig. 7, the highest zeta potential value belonged to the membranes having no BisBAL. When BisBAL was added to the dope solution, its functional groups made the membrane surface more positively charged. When the BisBAL concentration increased further, this positive charge as well increased on the membrane surface. That is the reason why fouling rates which were caused by colloids increased. However, the membranes having BisBAL were more effective against biofouling due to their greater antibacterial effects.

4. Conclusion

According to our experimental results, BisBAL S3 was found to be the optimum combination for membranes. Minimum inhibition concentration (MIC) value was determined as 15 μM. According to the xanthan gum and activated sludge filtration studies, it was shown that the membranes (both PES and PSf) containing BisBAL had antibiofouling properties when compared to the membranes without BisBAL. Fifteen- and thirty μM BisBAL addition was found to be optimum for the PES and PSf membranes, respectively. The most effective washing was obtained with the PES membrane having 30 μM BisBAL concentration according to the hydraulic washing results.

When SEM images were investigated, the surface morphology showed homogeneous structure. After the activated sludge filtration, the membrane surface was covered with organic matters. Sometimes this accumulation created hillocks on the surface. This resulted in the increase in surface roughness. With the hydraulic washing, these hillocks can be washed off.

Manufactured membranes have different roughness values. The membranes having 20% polymer concentration had lower roughness values than the membranes having 16% polymer concentration. Roughness values after activated sludge filtration may depend on the location and shape of the hillocks on the surface. After the hydraulic washing, the roughness values decreased when compared to after filtration values, but they were even higher than the beginning of the filtration. This meant there was a little irreversible fouling.

According to the FTIR analysis results, there were no important differences between the membranes with and without BisBAL. The secretion of BisBAL within the polymer matrix can be the reason for this. In addition to this, the membranes having BisBAL had lower polysaccharide production when compared to the membranes without BisBAL. In scope of this study, Bismuth release into the environment was also investigated. Each membrane exhibited very low Bi release rates. The PES membranes released more Bi than the PSf membranes.

Pore distribution showed that the fabricated membranes can be classified as tight microfiltration or ultrafiltration membranes. The membranes having 20% polymer concentration were ultrafiltration membranes and the membranes having 16% polymer concentration were tight microfiltration membranes.

Characterization and permeability results are very important for membranes. However, the most important thing about membrane technologies is to create membranes which can treat water or wastewater and at the same time have optimum membrane properties (fouling, cost, etc.). To control the removal efficiencies, TOC analysis was conducted. The BisBAL addition did not show any negative effect on the organic matter removal. The removal efficiencies were between 89 and 90% and 65–75% with the xanthan gum and activated sludge filtration, respectively. BisBAL addition increased the organic matter removal efficiency during the activated sludge filtration.

BisBAL-added membranes had significantly low contact angle values when compared to the pristine membranes without BisBAL. Hydrophilicity of the membranes came from chelate, BAL part of the BisBAL.

According to the surface charge results, our membranes have relatively negative charge and this was an advantage to get rid of organic matters from the surface.

This study aimed transferring the inhibition effect of BisBAL, which is a chelate compound of Bi metal, to membrane technology area and obtaining membranes having antibiofouling capacity to be used in MBRs effectively. BisBAL synthesis and membrane fabrication were optimized by considering respective parameters. Membranes having these types of antibiofouling properties can be considered as innovative and energy friendly technologies for wastewater treatment applications.

Acknowledgment

This study has been supported by TUBITAK (The Scientific and Technological Research Council of Turkey) Project with 111Y273 number.

References

[1] V. Uyak, I. Koyuncu, I. Oktem, M. Cakmakcı, I. Toroz, Removal of trihalomethanes from drinking water by nanofiltration membranes, J. Hazard. Mater. 152 (2008) 789–794.
[2] M. Cakmakci, N. Kayaalp, I. Koyuncu, Desalination of produced water from oil production fields by membrane processes, Desalination 222 (2008) 176–186.
[3] I. Koyuncu, F. Yalcin, I. Ozturk, Color removal of high strength paper and fermentation industry effluents with membrane technology, Water Sci. Technol. 40 (1999) 241–248.
[4] I. Koyuncu, Direct filltration of Procion dye bath wastewaters by nanofiltration membranes: Flux and removal characteristics, J. Chem. Technol. Biotechnol. 78 (2003) 1219–1224.
[5] B. Kose, H. Ozgun, M.E. Şahin, N. Dizge, D.Y. Koseoglu-Imer, B. Atay, R. Kaya, M.Altinbas, S. Sayılı, P. Hoshan, D.Atay, E. Eren, C. Kınacı, I. Koyuncu, "Performance evaluation of a submerged membrane bioreactor for the treatment of brackish oil and natural gas field produced water", Desalination, Vol. 285 (11–12) 01/2012 295–300.
[6] Sang-Ryoung Kim, Oh Hyun-Suk, Sung-Jun Jo, Kyung-Min Yeon, Chung-Hak Lee, Dong-Joon Lim, Chi-Ho Lee, Jung-Kee Lee, Biofouling control with bead-entrapped quorum quenching bacteria in membrane bioreactors: Physical and biological effects, Environ. Sci. Technol. 47 (2013) 836–842.
[7] Yeon Kyung-Min, Cheong Won-Seok, Oh Hyun-suk, LeeWoo Nyoung, HwangByung Kook, Lee Chung -Hak, Beyenal Haluk, Lewandowski Zbigniew, Quorum sensing: A new biofouling control paradigm in a membrane bioreactor for advanced wastewater treatment, Environ. Sci. Technol. 43 (2009) 380–385.
[8] A. Drews, Membrane fouling in membrane bioreactors−Characterisation, contradictions, cause and cures, J. Membr. Sci. 363 (2010) 1–28.
[9] M.W. LeChevallier, T.M. Babcock, R.G. Lee, Examination and characterization of distribution system biofilms, Appl. Environ. Microb. 53 (1987) 2714–2724.
[10] P.S. Stewart, B.M. Peyton, W.J. Drury, R. Murga, Quantitative observations of heterogeneities in *Pseudomonas aeruginosa* biofilms, Appl. Environ. Microb. 59 (1993) 327–329.
[11] G. Canizal, P.S. Schabes-Retchkiman, U. Pal, Hong Bo Liu, J.A. Ascencio, Controlled synthesis of ZnO nanoparticles by bioreduction, Mater. Chem. Phys. 97 (2006) 321–329.
[12] P.S. Schabes-Retchkiman, G. Canizal, R. Herrera-Becerra, C. Zorrilla, H.B. Liu, J.A. Ascenci, Biosynthesis and characterization of Ti/Ni bimetallic nanoparticles, Opt. Mater. 29 (2006) 95–99.
[13] N. Akar, B. Asar, N. Dizge, I. Koyuncu, Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles, J. Membr. Sci. 437 (2013) 216–226.
[14] Z. Gu, K. Wang, J. Wei, C. Li, Y. Jia, Z. Wang, J. Luo, D. Wu, Tensile properties of ultrathin double-walled carbon nanotube membranes, Carbon 44 (2006) 3315–3319.
[15] Z. Ahmad, R. Pandey, S. Sharma, G.K. Khuller, Pharmacokinetic and pharmacodynamic behaviour of antitubercular drugs encapsulated in alginate nanoparticles at two doses, International Journal of Antimicrobial Agents 27 (2006) 409–416.
[16] A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, M. Khavarpour, The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane, Desalination 306 (2012) 41–50.
[17] P. Domenico, L. Baldassarrı, P.E. Schoch, K. Kaehler, M. Sasatsu, B.A. Cunha, Activities of Bismuth Thiols Against Staphylococci and Staphylococcal Biofilms, Japan, (2009).
[18] Bierer, Bismuth Subsalicylate: History, Chemistry, and Safety, Health and Personal Care Division, The Procter & Gamble Company, 11,511 Reed Hartman Highway, Cincinnati Ohio, 45 (1990) 241.
[19] B.J. Marshall, 1991, The use of bismuth in gastroenterology. The ACG Committee on FDA-Related Matters. American College of Gastroenterology, Department of Medicine, University of Virginia Health Sciences Center, The American Journal of Gastroenterology 86(1) (1991) 16–25.
[20] I.S. Chang, P. Clech, B. Jefferson, S. Judd, Membrane fouling in membrane bioreactors forwastewater treatment, J. Environ. Eng. 128 (2002) 1018–1029.
[21] H. Nagaoka, S. Yamanishi, A. Miya, Modeling of biofouling by extracellular polymers in a membrane separation activated sludge system, Water Sci. Technol. 38 (1998) 497–504.
[22] A.R. Badireddy, S. Chellam, S. Yanina, P. Gassman, K.M. Rosso, 2008. BisBAL inhibits the expression of extracellular polysaccharides and proteins by *Brevundimonas diminuta* Implications for membrane microfiltration, Biotechnol. and Bioeng., Vol. 99(3), February 15.
[23] M. DuBois, K.A. Gilles, J.K. Hamilton, A. Rebers, Colorimetric method for determination of sugars and related substances, Anal. Chem. 28(3) (1956) 350–356.
[24] D.Y. Koseoglu-Imer, B. Kose, M. Altınbas, I. Koyuncu, The production of polysulphone (PS) membrane with silver nanoparticles (AgNP): Physical-chemical properties, filtration performances, and biofouling resistances of membranes, J. Membr. Sci. 428 (2013) 620–628.