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Effects of the post-modification using bismuth chelate (BisBAL) on the anti-biofouling and performance properties of flat-sheet microfiltration membranes

Borte Kose-Mutlu[a,b], Turker Turken[a,b], Mehmet C. Guclu[b], Serkan Guclu[a,b], Suleyman Ovez[b], Ismail Koyuncu[a,b,*]

[a] National Research Center on Membrane Technologies, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey
[b] Department of Environmental Engineering, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey

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ABSTRACT

Membrane biofouling defined as the attachment and growth of microorganisms on a membrane surface has been a major problem of membrane bioreactor (MBR) technology. The anti-biofouling properties like the inhibition of bacterial adhesion of a membrane are quite significant for a long-term MBR operation. Surface modification is thought to be one of the most common approaches to improve this property. In this study, polymeric microfiltration membranes were modified by adsorption BisBAL, which is a synthesized chelate using bismuth and have a high anti-bacterial effect on various microorganisms, on the membrane surface using dip coating (DC), spin coating (SC), and low pressure-treated coating (LPtC). The purpose was to increase the surface hydrophilicity, change the surface charge, and gain the surface an anti-bacterial characteristic. It was found that the higher adsorption time, lower feed flow rate and higher spinning velocity, and pressure application increased the efficiency of the process during DC, SC, and LPtC, respectively. Furthermore, improved strategies allow the adsorption of BisBAL on the membrane surface and modified membranes has strong resistance to biofouling. Since modification resulted in a decrease in pore fouling and irreversible fouling for all type of membranes, these membranes can be novel alternatives for energy-saving MBR operation.

1. Introduction

Membrane technology has been one of the proper treatment alternatives used for advanced water and wastewater treatment. The number of these alternatives are limited because of strict standards for the drinking water supply and treated wastewater discharge to a receiving environment [1,2]. Membranes are semipermeable barriers and a technology that has a wide-range of the products with different properties, and a broad usage area. Membranes are separated into four groups according to their molecular weight cut-off's as follows: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis [3]. One of the most common advanced wastewater treatment technology based on the membrane technology has been the membrane bioreactor (MBR) systems, which combines activated sludge process and membrane filtration using microfiltration or ultrafiltration membranes [4]. Researchers had mentioned that MBR has an important commercial importance with its widespread application in municipal and industrial wastewater treatment (Judd, 2008). It was also indicated that the market value of this technology was around US$217 million in 2005 and has an annual growth rate of 11.6–12.7% [5,6]. MBRs have important advantages with its high mixed liquor suspended solids (MLSS) values and fewer area needs [7–9]; however, this highly concentrated microorganism community caused a biofilm formation on the filtration membrane via their tendencies on the adsorption of a surface and vacuum pressure through the membrane resulted from the suction of the permeate flow [10]. The covering of a membrane with biofilm layers in this way is called as biofouling and it can be said that biofouling is the Achilles heel of the MBR technology [11–13].

There have been various commercial membranes that were put on the market by the manufacturers to meet the demand of the users.

Abbreviations: AS, activated sludge; COD, chemical oxygen demand; DI, deionized; DMAc, dimethylacetamide; DC, dip coating; EPS, extracellular polymeric substances; FTIR-ATR, Fourier transform infrared spectroscopy- attenuated total reflectance; ICP-OES, inductively coupled plasma-optical emission spectrometry; LPtC, low pressure-treated coating; -L, manufactured in the laboratory; M, microfiltration membrane; MLSS, mixed liquor suspended solids; P, PES polymer; PES, polyethersulphone; PVDF, polyvinylidene fluoride; PVP, polyvinylpyrrolidone; V, PVDF polymer; SEM, scanning electron microscopy; SMP, soluble microbial product; SC, spin coating; TOC, total organic carbon

* Corresponding author at: National Research Center on Membrane Technologies, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey.
E-mail address: koyuncu@itu.edu.tr (I. Koyuncu).

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Researchers have carried out studies on the treatability of different wastewaters using the commercial membranes purchased from the manufacturers [14–17]. Besides, a prominent research topic in recent years has been the manufacturing of novel membranes in the laboratory and researchers have tried to manufacture membranes with some additions for the creation of special properties to solve present problems in the market. The most important property that is tried to be gained to a membrane is the resistance against the biofouling for a long and economic lifetime. Within this aim, some metal ions and their compounds, of which anti-bio adhesive property are known and used in other industries, like silver, iron, titanium, aluminum, bismuth etc. [18–21] are also preferred for the membrane manufacturing. While Silver ions and silver nanoparticles (nAg) have been used for various water filtration membranes made from cellulose acetate [22], polyimide [23,24], polyamide [25], one of the polymeric membranes manufactured with iron metal is Nafion [26,27]. Besides, titanium and aluminum addition had been mostly studied using polyvinylidene fluoride (PVDF) membranes [28–32]. The anti-biofouling agents can be used while the membranes are manufactured or for the modification of the already manufactured membranes to change the surface characteristics in accordance with a purpose [33] by coating using inorganic additives [28,34–40]. Since membrane fouling is the accumulation of substances on the membrane surface and/or within the membrane pores and adhesive interactions between the bacteria and the membrane surface structure are the main cause of early biofilm development [41–43], surface modification to change the properties of the membranes like roughness, porosity etc. can be a more effective way to prevent the biofouling when compared to changing the polymer blend solution, which can be described as pre-modification [44,45]. Various post-modification methods have been investigated by the researchers for this aim including grafting [42–50], and coating techniques. In the coating method, the membrane surface is generally contacted with a modification solution or dispersion including anti-biofouling agent as an additive and a layer of coating on the membrane surface is formed after evaporation following the contact [2]. In addition, it can be said that the coating method is usually easy to apply compared to the grafting method.

In this study, researchers, who had previously worked on the anti-biofouling properties of a microfiltration membrane prepared with BisBAL-chelate added blend solution [51], had studied the modification of microfiltration membranes using a modification solution including BisBAL. Three flat-sheet microfiltration membranes, which include a PES membrane manufactured in the laboratory and two commercial PES and PVDF membranes, were modified with three coating methods, which are common membrane surface modification method [2], for the physical sorption with dip coating, spin coating, and low pressure treated coating. The anti-biofouling properties of the modified membranes were determined with surface characterizations and activated sludge filtration performances. In the light of the results, it can be said that the novelty of this research that originated from being the first study on the surface modification using BisBAL can make an important contribution to the literature and may result in an inspiration for the researchers who aim to modify their commercial membranes.

2. Materials and methods

2.1. Reagents and materials

Polyethersulphone (PES), Dimethylacetamide (DMAc) and Polyvinylpyrrolidone (PVP) used for membrane manufacturing were supplied from Sigma-Aldrich (Germany). BisBAL, a bismuth chelate, was synthesized by mixing bismuth nitrate pentahydrate ($Bi(NO_3)\cdot 5H_2O$) (Sigma-Aldrich, Germany), propylene glycol ($C_3H_8O_2$) (Sigma-Aldrich, Germany, and 2,3-dimercapto-1-propanol (Sigma-Aldrich, Germany) as described in Ovez et al. [51]. All chemicals in this study were used without any further purification. Reactive Orange 16 (Dye content ≥70%) was also supplied from Sigma-Aldrich (Germany) with its powder form.

Table 1
Properties of the membranes.

	Commercial membranes		Manufactured membrane
	PES membrane (MP005)	PVDF membrane (MV020)	PES membrane (MP-L005)
Pore size (μm)	0.05	0.20	0.05
Flux (LMH)	328.92 ± 37.65	1439.83 ± 176.54	279.83 ± 2.4

*M: Microfiltration, P: PES polymer, V: PVDF polymer, L: Manufactured in the laboratory.
**Pure water flux were determined at 0.6 bar pressure.

2.2. Fabrication of polymeric membranes

Three different polymeric membranes were used for further modification. While two of them were commercial polymeric (PES and PVDF) microfiltration membranes purchased from Microdyn-Nadir (USA), one is PES microfiltration membrane manufacturing in the laboratory using the phase inversion method. The flux and pore size information is given in Table 1. MP-L005 membrane was manufactured using a dope solution including 100 mL DMAc, PVP (8%) and PES polymer beads (16%). This mixture was mixed at 200 rpm for 24 h-duration at a 65 °C temperature to obtain a homogeneous solution. At the end of the 24th hour, the solution was ultrasonicated to remove possible bubbles. The polymer solution prepared for MP-L005 membrane was poured on the surface of a lab-scale membrane casting machine and membranes were cast on the support layers, which have 200 μm thickness, fixated glass plates by means of a casting knife (the speed of the casting knife: 50 mm/s). After the casting, flat sheet polymer films were dipped in the water coagulation bath for 10 s with the glass plates to carry the phase inversion and obtain a solid film structure. All manufactured membranes were stored in distilled water at 4 °C temperature. Commercial membranes were stored according to the manufacturer's suggestions. The pore size distribution graph was given in Figure A1 in the Appendix.

2.3. Modification of polymeric membranes

Membranes were modified using three different modification methods based on the physical adsorption of BisBAL on the membrane surface, and these methods are dip coating (DC), spin coating (SC) and low pressure-treated coating (LPtC). The schematic diagram of the modification methods and the illustration of the physisorption of BisBAL on the membrane surface are given in Figs. 1 and 2, respectively. As seen in Fig. 2, the sorption types of the BisBAL molecules were tried to be described based on the application methods. It is expected that BisBAL molecules can be randomly adsorbed on the membrane surface layer by layer. Since there is not any control on the process in this method, the relationship between the BisBAL molecules and membrane substrata, and between a BisBAL molecule and another BisBAL molecule. An access of the BisBAL molecule is not assumed into the membrane pores. Besides, spin coating results in a single-layer adsorption of BisBAL molecules with a centrifugal force. A certain amount of the BisBAL molecules can be adsorbed on the membrane surface as required by the surface chemistry of the different polymeric substrata. Finally, it may be said that the application of pressure in a filtration cell results in a vertical, multi-layer BisBAL sorption and lets the BisBAL molecules to reach into the pores.

The modification solution was prepared using synthesized BisBAL chelate [51]. For DC modification, the membrane was immersed in the