Influence of nanoparticles on filterability of fruit-juice industry wastewater using submerged membrane bioreactor

Guler Turkoglu Demirkol, Nadir Dizge, Turkan Ormanci Acar, Oyku Mutlu Salmanli and Nese Tufekci

ABSTRACT

In this study, polyethersulfone (PES) ultrafiltration membrane surface was modified with nano-sized zinc oxide (nZnO) and silver (nAg) to improve the membrane filterability of the mixed liquor and used to treat fruit-juice industry wastewater in a submerged membrane bioreactor (MBR). The nAg was synthesized using three different methods. In the first method, named as nAg-M1, PES membrane was placed on the membrane module and nAg solution was passed through the membrane for 24 h at 25 ± 1 °C. In the second method, named as nAg-M2, PES membrane was placed in a glass container and it was shaken for 24 h at 150 rpm at 25 ± 1 °C. In the third method, named as nAg-M3, Ag nanoparticles were loaded onto PES membrane in L-ascorbic acid solution (0.1 mol/L) at pH 2 for 24 h at 150 rpm at 25 ± 1 °C. For the preparation of nZnO coated membrane, nZnO nanoparticles solution was passed through the membrane for 24 h at 25 ± 1 °C. Anti-fouling performance of pristine and coated membranes was examined using the submerged MBR. The results showed that nZnO and nAg-M3 membranes showed lower flux decline compared with pristine membrane. Moreover, pristine and coated PES membranes were characterized using a permeation test, contact angle goniometer, and scanning electron microscopy.

Key words | anti-fouling performance, fruit-juice industry wastewater, membrane coating, nanoparticles, polyethersulfone, submerged membrane bioreactor

INTRODUCTION

Most of the wastewater generated from drink industries contains biodegradable organic compounds including fructose, glucose, sucrose, lactose, artificial sweetener, fruit-juice concentrates, flavoring agents, coloring agents, and mineral salts which are used during production (Ait Hsine et al. 2005). The concentrated-fruit-juice industry uses large amounts of water for washing, and fruit processing can produce large amounts of wastewater with high chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS).

Fruit-juice industry wastewater (FJWW) must be treated properly prior to discharge to a receiving water. Biological treatment methods have been used to treat FJWW because of its high organic content (Pavón-Silva et al. 2009; Braz et al. 2010; Ioannou et al. 2015; Sheldon & Erdogan 2016). In a previous study, the membrane bioreactor (MBR) process was used to monitor and identify the microorganisms that can be indicators to the MBR system treating fruit-juice wastewater and it was reported that fruit-juice wastewaters support almost all kinds of microorganisms, including prokaryotes and eukaryotes (Demirkol et al. 2014). Thus, it can be said that biological treatment of FJWW is feasible due to its composition. However, the presence of bio-resistant compounds in this kind of wastewater prevents efficient treatment. Different process combinations such as physical, chemical, and biological treatment can be used as a possible solution to overcome this problem (Ioannou & Fatta-Kassinos 2013; Ioannou et al. 2013, 2014).

Over the past decades, the use of MBRs for treatment of domestic and industrial wastewater has been increasing. An MBR is a biological process that combines simultaneously secondary and tertiary treatment using a membrane filtration.
process. MBR systems offer many advantages over conventional wastewater treatment plants such as low bacterial counts, low suspended solids and turbidity, compact footprint, and high quality effluent. For these reasons, MBRs are growing in popularity for several wastewater treatment applications (Hoinkis et al. 2012; Coutte et al. 2017).

Membrane fouling, which decreases permeability and increases energy consumption, is still a serious problem in MBRs and the fouling phenomenon limits the widespread application of MBRs (Sabia et al. 2014). The main MBR foulants are colloidal, particulate and dissolved substances secreted by microorganisms present in the biomass, including soluble microbial products and bound extracellular polymeric substances (Meng et al. 2009; Juntawang et al. 2017). Over the last decade, several studies have attempted to prevent membrane fouling. However, recent studies have demonstrated that membrane fouling cannot be prevented in an easy way (Ognier et al. 2004; Brookes et al. 2006; Wang et al. 2013).

Traditional methods to avoid fouling are physical cleanings (relaxation, backwash), chemical cleanings (caustic, acidic, hypochlorite chemicals), low flux operation and cross-flow filtration. An alternative method is the addition of certain materials such as powder activated carbon, FeCl3, chitosan, starch, coagulants and/or flocculants (Huyskens et al. 2012; Mehrnia & Homayoonfal 2016; Aslam et al. 2017). In recent years, coating of the membrane surface with nanoparticles has been applied in the MBR process to reduce membrane fouling or enhance the membrane specialty. One of the most popular nanomaterials is silver (Ag) and zinc oxide (ZnO) nanoparticles. It was reported that flux ratio of the membrane was improved and membrane fouling was decreased when using these nanoparticles (Qiu et al. 2016).

The objective of this study is to treat FJWW using MBR technology and decrease membrane fouling with nano-sized zinc oxide (nZnO) and silver (nAg) coating with different methods. The method providing the lowest flux decline was identified. Moreover, pristine and coated polyethersulfone (PES) membranes were characterized using a permeation test, contact angle goniometer, and scanning electron microscopy (SEM).

MATERIALS AND METHODS

Chemicals and membrane

Silver nitrate (AgNO3), citric acid (C6H8O7), sodium hydroxide (NaOH), ammonium chloride (NH4Cl), di-sodium hydrogen phosphate (Na2HPO4) and COD Cell Test were purchased from Merck. ZnO nanoparticles were purchased from Sigma-Aldrich. D(+-)-Glucose (C6H12O6.H2O) and starch (C6H10O5) were obtained from Lachema. L-Ascorbic acid was provided by Carlo Erba. All chemicals were used without further purification in this study. A flat sheet MP005 PES membrane (with nominal pore sizes of 0.05 μm) was supplied by GE Osmonics.

Procedure of membrane coating

A schematic diagram to illustrate the procedures used to coat nZnO and nAg onto/into the PES membrane is shown in Figure 1. The detailed procedures of membrane coating are given as follows.

nZnO coating of the membrane surface

PES membrane was placed on the flat membrane modules and nano-sized ZnO (5 mg/L) solution was passed through the membrane for 24 h at 25 ± 1 °C (30 mL/min flow rate).

nAg coating of the membrane surface (nAg-M1)

In the first method, 0.1 M silver nitrate (AgNO3), 0.1 M d(+-)-glucose and 0.2% starch solutions were prepared in distilled water. After that, 600 mL of 0.2% starch solution in 3 mL of 0.1 M AgNO3 and 7.5 mL of 0.1 M d(+-)-glucose solution was added. This solution was stirred at room temperature (25 ± 1 °C) for 5 min to form a homogeneous solution and then heated for 210 sec (Raveendran et al. 2006). The PES membrane was placed on the flat membrane module and nAg solution was passed through the membrane for 24 h at 25 ± 1 °C (30 mL/min flow rate).

nAg coating of the membrane surface (nAg-M2)

In the second method, nAg solution was prepared as described for nAg-M1. The PES membrane placed on the flat membrane module was immersed in a glass container and shaken for 24 h at 150 rpm at 25 ± 1 °C.

nAg coating of the membrane surface (nAg-M3)

In the third method, 1.57 g AgNO3 was dissolved in 1 L of distilled water. According to the literature, the optimal L-ascorbic acid solution was determined as 0.1 M and therefore 17.61 mg/L L-ascorbic acid solution was prepared.
The PES membrane was placed in 250 mL of AgNO₃ solution and shaken at pH 2 at 150 rpm for 2 h. Then, the membrane was removed from solution, rinsed with 10 mL of deionized water and shaken with L-ascorbic acid solution at 150 rpm for 24 h. Finally, the membrane was rinsed with 25 mL of deionized water.

Characterization of the coated membranes

The pristine and nZnO/nAg coated membranes were characterized by measuring permeate flux, which is described by Darcy’s law (Lee & Clark 1998).

\[ J = \frac{1}{A} \frac{dV}{dt} \]

where \( J \) is the permeate flux, \( A \) is the membrane filtration area, \( V \) is the total volume of permeate, and \( t \) is the filtration time.

The contact angles of the pristine, nZnO/nAg coated and used membranes were measured on a KSV cam 200 contact angle meter using sessile drop mode on dried membranes. All contact angle measurements were made using 1 μL of deionized water. After the image was captured, the tangential method for low angle was used if necessary. Each contact angle was measured 5–10 times, and average value was calculated.

Surface morphologies of the pristine and nZnO/nAg coated membranes were directly observed by SEM (FEI Quanta 450 FEG-EDS) in high vacuum mode after coating with gold to observe the pore structure.

Characterization of fruit juice processing wastewater

Wastewater samples were provided from a local concentrated-fruit-juice industry, located in Istanbul. The wastewater has a dark color and strong odor. The main physical–chemical characteristics are presented in Table 1. It can be clearly seen from Table 1 that FJWW contains high COD and BOD₃ concentrations as well as high amount of suspend and volatile solids. The BOD₃/COD ratio (0.70) indicates that the wastewater has high biodegradability.

The MBR system

In this study, a laboratory-scale submerged MBR system was used. A schematic representation of the experimental setup is shown in Figure 2. The total volume of the aeration tank was 40 L (effective volume of 35 L) and compressed air was supplied by a diffuser at 6 L/min. The MBR system was cultivated for 30 days before the filtration experiments. Four

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>pH</td>
<td>6 ± 0.3</td>
</tr>
<tr>
<td>COD (mgO₂/L)</td>
<td>1,000 ± 100</td>
</tr>
<tr>
<td>BOD₅ (mgO₂/L)</td>
<td>700 ± 28</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>0.70</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>110 ± 12</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>90 ± 8</td>
</tr>
<tr>
<td>Total N (mg/L)</td>
<td>3.92 ± 0.24</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>0.05 ± 0.01</td>
</tr>
</tbody>
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flat membrane modules made of aluminum material were used; the effective area of each membrane was 49 cm². Pristine membrane and coated membranes (nZnO, nAg-M1, nAg-M2, nAg-M3) were placed on the modules.

A real activated sludge was used and supplied from the aeration tank in Bahçeşehir municipal biological treatment plant located in Istanbul, Turkey, and was cultivated in a laboratory-scale aeration tank treating the FJWW. The mixed liquor suspended solids of the sludge was about 4,250 ± 350 mg/L. The MBR system was operated at sludge retention time of 30 days and 1,600 mg/L organic loading rate. The pH of the bioreactor was adjusted to approximately 7.0 ± 0.5 with NaOH.

Analytical procedure

All analyses were carried out according to Standard Methods (APHA/AWWA/WPCF 1989). The pH of the bioreactor was monitored by a Eutech Instruments-PCD650. Dissolved oxygen was measured by a Hach HQ40d Multi oxygen meter.

COD was analyzed by closed reflux method with a thermoreactor (Eco 16 Velp Scientifica thermoreactor) at 150°C. The COD cell test method was performed with photometric Spectroquant Colorimeter Picco COD/CSB (Merck). BOD₅, total phosphate (TP), and total Kjeldahl nitrogen were analyzed according to Standard Methods 5210, 4500-P, and 4500-Norg C, respectively.

RESULTS AND DISCUSSION

The photographs of the pristine and coated with nZnO and nAg membranes are shown in Figure 3(a)–3(e). Each coating method resulted in different colors on the membrane surfaces. As can be clearly seen in the figure, nZnO appearing white in color was deposited on the membrane surface (Figure 3(b)). The color of the nAg-M1 coated membrane (Figure 3(c)) was similar to the pristine membrane (Figure 3(a)). However, nAg-M2 (Figure 3(d)) and nAg-M3 (Figure 3(e)) coated membrane treated with D-(+)-glucose and L-ascorbic acid solution had a light brown and flavescent color, respectively. It could be observed that nZnO and nAg-M3 were deposited intensively on the membrane surfaces.

The pristine and coated membranes were tested using the submerged MBR. Figure 4 shows the permeate flux decline of the pristine and coated membranes. The results indicated that the nZnO coated membrane showed higher steady-state flux than the pristine and nAg coated membranes. The initial flux for pristine PES membrane was 331 L/m²·h. However, the initial flux for coated membranes was 236, 227, 152, and 52 L/m²·h for nZnO, nAg-M3, nAg-M2, and nAg-M1, respectively. The steady-state flux of pristine membrane was 10 L/m²·h. However, the steady-state flux of coated membranes was 16, 13, 10, and 2 L/m²·h for nZnO, nAg-M3, nAg-M2, and nAg-M1, respectively. The reason why the initial flux of the nAg-M1 and nAg-M2 was lower than the pristine membrane might be that the membrane pores were clogged by the nanoparticles. Vatanpour et al. (2012) coated the surface of MWCNTs (multi-walled carbon nanotubes)/PES membrane with TiO₂ nanoparticles, and they reported that agglomeration of TiO₂ caused the pore clogging (Vatanpour et al. 2012). Moreover, COD concentration was below 25 mg/L for all the membrane permeates.

Table 2 shows the contact angles of the pristine and coated PES membranes before and after filtration. The
surface of the coated membranes had different contact angles. The contact angle of clean pristine membrane was $75 \pm 1.2^\circ$; this indicates a moderate hydrophobic character of the membrane surface. However, coating the membrane surface with nZnO, nAg-M1, nAg-M2 and nAg-M3 decreased the contact angle from $75 \pm 1.2^\circ$ to $51 \pm 1.2^\circ$, $68 \pm 2.2^\circ$, $61 \pm 1.4^\circ$, and $37 \pm 2.6^\circ$, respectively. The lowest contact angle was obtained by nAg-M3. After wastewater filtration, the contact angle of fouled membrane decreased for all membranes except nAg-M3. All membranes coated with nAg had lower contact angle values than pristine membrane. As can be seen from the flux and contact angle results, the nAg-M3 membrane had the highest hydrophilicity and initial flux value. However, nZnO membrane showed higher hydrophilicity and steady-state flux after the filtration. This can be explained by the nanoparticles providing a lower surface tension than that of the pristine membrane (Basri et al. 2011).

The SEM images for clean and fouled membranes are shown in Figure 5. Figure 5(e), 5(g) and 5(i) presents nAg
coated membranes; nAg was deposited and aggregated on the membrane surfaces for all three methods, and the maximum aggregation was observed by nAg-M3 coating method (Figure 5(i)). ZnO particles created thread-like structures on the surface of the membrane (Figure 5(c)). Yan et al. showed that ZnO particles had a tetrapod structure according to transmission electron microscopy (Yan et al. 2003). Moreover, Li et al. (2009) reported that ZnO nanoparticles were irregularly shaped and some were rod-like. Consequently, the thread-like formation on the surface of the membrane could be attributed to the structural properties of ZnO particles. It was also seen that the membrane surface was protected from foulants after the filtration (Figure 5(d), 5(f), 5(h) and 5(j)). However, the surface structure of nZnO coated membrane after the filtration was different than the others (Figure 5(d)). The rougher structure of nZnO coated membrane may cause the higher steady-state flux.

**CONCLUSIONS**

PES membrane characteristics were changed by the coating of ZnO and Ag nanoparticles. The results showed that coated PES membranes with nanoparticles had good anti-fouling properties. nZnO and nAg-M3 coated membranes ensured higher initial and steady-state flux than the pristine and nAg-M1 and nAg-M2 coated membranes. All membranes coated with ZnO and nAg showed lower contact angle values than the pristine membrane before the filtration. The results showed that the coating method is an important factor to create an anti-fouling surface.

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