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Preparation and characterization of PES nanofiltration membrane embedded with modified graphene oxide for dye removal from algal wastewater

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ABSTRACT

The present work was concentrated to study the ability of nanofiltration membrane as a treatment method of algal colored wastewater discharge from Islamabad refinery, Kermanshah, Iran. The polyether sulfone nanofiltration membrane was modified with sodium dodecyl sulfate (SDS) as an anionic surfactant and applied for treatment of colored wastewater. Water contact angle Scanning electron microscopy (SEM) and were applied to characterization of prepared membranes. The pure water flux, relative flux reduction as a parameter that represents antifouling property of membrane and also dye rejection were studied by dead-end and cross-flow filtration system in the present research. The period of the filtration time was extended about 6 hours to evaluate the stability and flux reduction of membrane. The results indicated 23.26% flux reduction was observed for modified membrane that confirms the antifouling property of prepared membrane. The results demonstrated that the permeate was completely transparent (100% dye removal, 98.2% turbidity removal), and the pure water flux was enhanced for modified membrane to 27.21 **(**Kg/m^2.h). In the present research nanocomposite polymeric membrane are introduced as an appropriate option for the treatment of natural colored wastewater.

1. Introduction

There are some reasons that can make the treatment of water as an essential issue. The increasing population of the world and also the increase in water consumption, make a water reuse as a necessity of the today's world (Nawaz et al .2013). Also the industrial wastewater discharge into environment has a negative effect on that (Qadir et al .2008) . It is harmful to discharge in river water and known as a hinder of water treatment for the different application (Azarian et al .2007). So the water shortage and water pollution are become as one of the big challenge in the world and the water reuse defined as a solution to overcome that (Cosgrove et al .2015). There are different ways for water and wastewater treatment such as physical, chemical and biological treatment. Among them, membrane processes have been used extensively as a wastewater treatment method for dye removal from wastewater (Nawaz et al .2014). Despite all the advantages of the membrane, fouling is a severe problem of them, that affects membrane performance (Mosqueda-Jimenez et al .2006). Membrane fouling can be reduced by increasing of hydrophilicity and it can be possible by different way of membrane modification (sun et al .2017).
In the last years, the properties and performance of membranes was improved by the incorporation of carbon nanofillers into the polymer matrix (Bhattacharya et al .2016). The small amount of these kind of nanoparticles can make an improvement in the properties of their composite materials (Bhattacharya et al .2016). Among different methods for membrane fabrication, blending has some benefits such as: Convenient preparation conditions and sufficiency for industrialization (Yang et al .2017). Due to the hydrophilic nature of graphene oxide, it known as a suitable nanoadditive to enhance hydrophilicity of membrane (Chang et al .2014). Zinadini and his coworkers fabricated an antifouling mix matrix PES membrane by embedding graphene oxide nanoplates (Zinadini et al .2014). The prepared membrane shown high pure water flux and hydrophilicity. Yang et al (2017) prepared a graphene oxide modified poly(m-phenylene isophthalamide) nanofiltration membrane with improved water flux, antifouling property and dye rejection. Shukla et al (2017) fabricated polyphenyl sulfone/GO nanocomposite membrane with improved in an antifouling property. Also the prepared membrane demonstrated an improvement in mechanical property. Ganesh et al (2013) prepared Psf/GO composite membrane with significant improvement in pure water flux and salt rejection. Most of these researches reported agglomeration of nanoparticles as a major problem of nanocomposite polymeric membranes (Zinadini et al.2014-Yang et al.2017). The use of surfactant suggested as a solution of these problem (Morsy et al.2014). Therefore, at the present work graphene oxide was incorporated into PES polymeric matrix and sodium dodecyl sulfate (SDS) was selected as an anionic surfactant to play an important role as dispersing agents. This ionic surfactant contains anionic functional groups at their head. It has been able to coating nanoparticles due to the hydrophilic sulfonated group in the molecules and also increase hydrophilicity. The performance of prepared membrane was evaluated by pure water flux measurement, dye rejection and flux reduction as a parameter to indicate antifouling. The algal colored wastewater was applied to examine the performance of prepared membrane in dye removal experiments.

2. Materials and methods
2.1. Materials

Polyethersulfone (ultrason E6020p, Mw=58000 g/mol and glass transition temperature Tg=225˚c) and dimethyleacetamide (DMAC) was used as solvent from BASF co, Germany. Poly vinylpirolidone

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(PVP) with 25000g/mol molecular weight was provided from Merck as pore former agent. The synthetic Graphene oxide was used as a carbon nanofiller. Sodium dodecyl sulfate (SDS) as an anionic surfactatant was used from Merck for dispersion of carbon nanofillers in the casting solution and increase hydrophilicity of polymer. Algal wastewater (total COD=305.7, turbidity=56 NTU, dye concentration= 800-1000 mg/lit) from Islamabad refinery, Kermanshah, Iran was applied as a natural colored wastewater. Distilled water was used throughout the experiments.

2.2. Preparation of the membrane

The composition of casting solution for prepared membranes are listed in Table 1. The phase inversion techniques were used for preparation of membranes. In the first step 0.5 wt.% of GO and certain amount of SDS were dispersed into the DMAC and was sonicated for 30 minutes using DT 102H Bandelin ultrasonic(Germany). Then, PES and PVP were dissolved in the dope solution by continues stirring for 24 h. After that, casting solution was cast by a film applicator on to a smooth glass plate with 150µm thickness. Then the glass plate was submerged into the non-solvent bath (distilled water at a temperature of 15 ˚C). After membrane formation, the prepared membranes were kept in water for 24 h to allow complete phase separation. Then membranes were drying between two sheets of filter paper for 24h at room temperature.

Table1. The compositions of casting solutions.

Membrane type	PES (wt. %)	PVP (wt. %)	G.O (wt. %)	SDS (wt. %)
M1	20	1.0	0.5	-
M2	20	1.0	0.5	0.5

2.3. Characterization of prepared membranes

The hydrophilicity of the membrane surface was examined by contact angle goniometer (G10, KRUSS, Germany) at 25 ˚C and a relative humidity of 50%. All contact angles are measured by 2µL of de-ionized water. To minimize the experimental error value, the contact angle values in five different locations are randomly measured and reported. The morphology of prepared membrane was studied by a Philips scanning electron microscope (Philips X100). The samples of the prepared membrane were cut into small pieces and were submerged in nitrogen liquid for one minute and were frozen. Then the frozen membrane was broken and kept in air for drying. After sputtering with gold, they were viewed in very high vacuum conditions at 25kV.

2.4. Membrane performance measurements

To evaluation of prepared membranes, pure water flux, dye removal and flux reduction were examined. To measurement of the pure water flux, the dead-end stirred cell (200 ml volume) was used with a membrane surface area of 12.56 cm² conjunct to a nitrogen gas line. Pressurized nitrogen was used to force the liquid through the membrane. The operational pressure was 4 bar .The water flux $J_{w,1}$(kg/m².h) was calculated as follow:

$$J_{w,1} = \frac{M}{A \cdot \Delta t} \quad (1)$$

where, M (kg) is the weight of the permeates , A (m²) is the membrane effective area and Δt (h) is the permeation time. The experiments were done at 25 and the average of three times was represented in Tables. Cross-flow filtration cell was applied for measure of relative flux reduction and evaluation of membrane stability at the pressure of 5 bar and flowrate of 130 Kg/h. The fig 1, showed the schematic of cross-flow filtration cell that used for examination of the membrane modified with anionic surfactant.

2.5. Antifouling performance

The flux of the membrane may be reduced during the algal wastewater filtration due to the fouling. To investigate the antifouling property of modified membrane, the relative flux reduction (RFR) parameter was measured. That was calculated by the following equation:

$$\text{RFR}(\%) = \left(\frac{J_f - J_i}{J_i}\right) \times 100 \quad (2)$$

where J_f is the final flux and J_i is the initial flux. The lower relative flux reduction indicates the higher antifouling property.

Also to examination of antifouling performance of prepared membrane, the flux recovery ratio (FRR) of prepared membrane calculated based on water flux before and after the passing milk powder solution with 800 ppm concentration from the membrane. That was measured according following equation:

$$\text{FRR}(\%) = \left(\frac{J_{w,2}}{J_{w,1}}\right) \times 100 \quad (3)$$

Where $J_{w,1}$ is the initial water flux and $J_{w,2}$ is the water flux after milk powder filtration (kg/m².h).

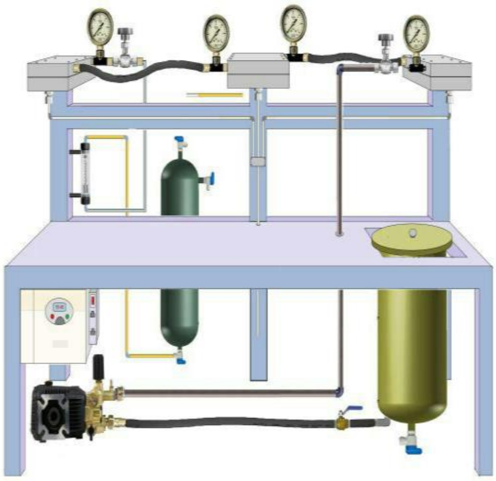

Fig. 1. The schematic of cross-flow filtration system.

3. Results and discussion

3.1. Morphology of the prepared membranes

The SEM technique was used for examine the structure and morphology of the nanocomposite polymeric membranes. The cross-sectional SEM images are shown in Fig 2. Both of the membrane show similar structure with dense top layer and finger-like sub layer. Finger like pores for M_2 is significantly wider than M1. This is due to the hydrophilic nature of GO and SDS that can enhance the mass transfer during the phase inversion and make a wider pore channels (Vatanpour et al.2011).

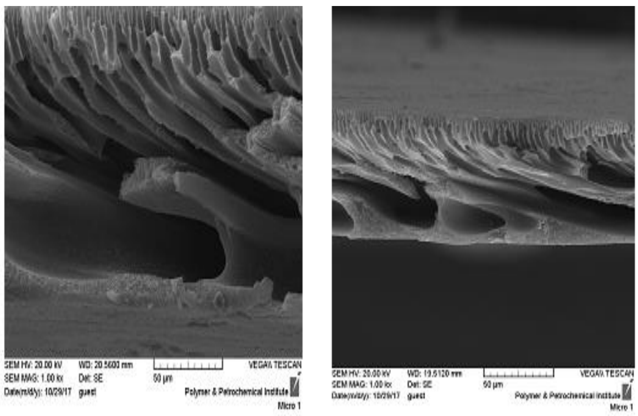

Fig. 2. Cross-section SEM images of the membrane modified with GO-SDS(left) and membrane modified with GO (right).

3.2. Pure water flux and membrane hydrophilicity

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Water contact angle measurement was applied to examine the hydrophilicity of the prepared membrane. More hydrophilic membranes have lower contact angle. As demonstrated in in Fig. 3, the contact angle of membrane modified with GO and SDS was 52.8˚, which is lower than the membrane modified with just graphene oxide (55.3˚). By improving hydrophilicity, water molecules pass more easily through the membrane and the pure water flux will be increase. Fig. 4 showed the pure water flux data of the prepared membrane that indicates higher performance of M_2 membranes.

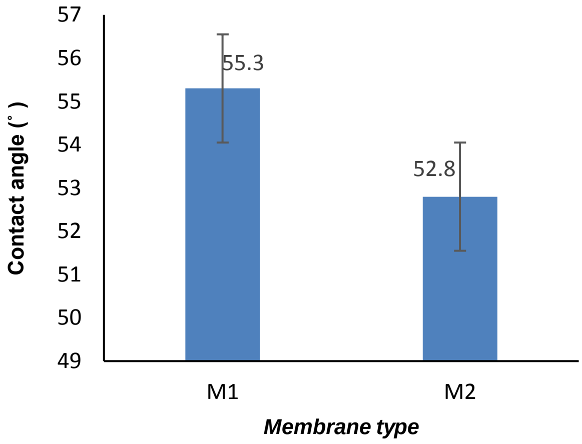

Fig. 3. Static contact angle of the prepared membranes.

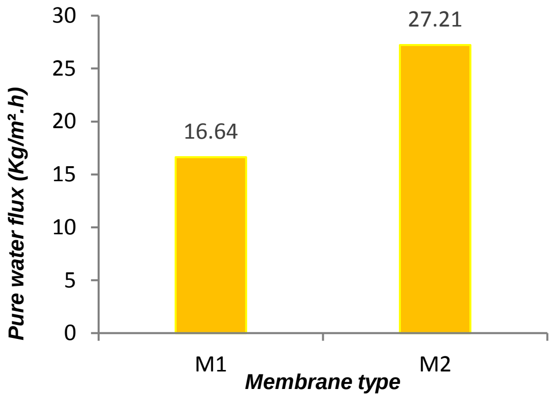

Fig. 4. Pure water flux of the prepared membrane (after 30 min).

3.3. Nanofiltration performance

To investigate the nanofiltration performance of the prepared membrane, the algal wastewater was selected and the removal of algal colored was examined. After filtration, the permeate flow was quite transparent and free of any dyes (100% algal colored removed). Also, the turbidity was measured about 56 and 1 NTU for influent and filtrated respectively that shows 98.2% turbidity removal. It can be attributed to the electrostatic charge of membrane surface and dye. When the pH value is in the range of 2-9, the graphene oxide (Yang et al.2017) and anionic surfactant are negatively charged Which causes repulsion between dye and the negative charge of the membrane surface. The image of influent and permeation solution before and after the filtration was shown in Fig 5.

3.4. Antifouling properties of the membranes

To evaluate the stability and antifouling property of membrane modified with GO and SDS, the cross-flow filtration cell was applied at the flow rate of 130 Kg/h and the pressure of 5 bar. During the long term filtration of the algal wastewater, the pores of the membrane are fouled and the flux decreased. The period of the filtration time was extended about 6 hours and the amount of flux reduction was measured. The relative flux reduction for M2 was calculated about 23.26 %, that shows the antifouling property of the modified membrane. Fig. 6, demonstrated the graph of flux (Kg/m².h) versus time (hour) for M2.

Fig. 5. Comparison of the wastewater appearance before (right) and after membrane treatment (left).

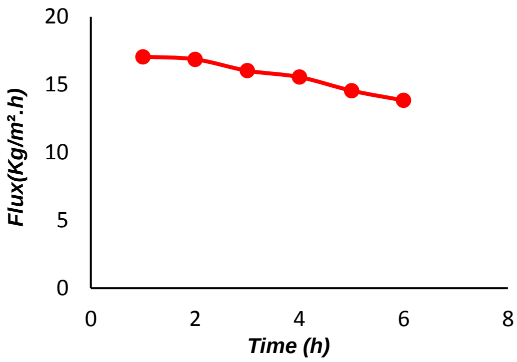

Fig. 6. The flux of algal wastewater during the 6 hours filtration by cross-flow filtration cell.

Also the results of FRR are demonstrated in Fig. 7, and determined as a parameter to indicates the antifouling property of prepared membrane. As shown in Fig 7, the FRR parameter for modified membrane with GO and SDS is 83.79 %, that is higher than bare PES membrane. These results shows that the modified membrane with hydrophilic nanoparticles such as graphene oxide and surfactants such as SDS shows more antifouling properties.

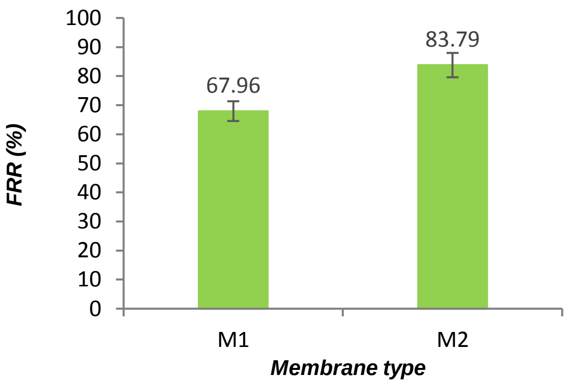

Fig. 7. Flux recovery ratio of the unfilled and modified PES membranes after 90 min milk powder solution filtration at 4 bar by dead-end cell.

4. Conclusions

In this research, polyether sulfone nanofiltration membrane modified with GO and SDS by blending method. The addition of constant concentration (0.5 wt.%) of graphene oxide and anionic surfactant (SDS) into the PES nanofiltration membrane, decrease the contact angle and increase hydrophilicity and pure water flux and improved antifouling property. The morphology of prepared membranes

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studied by SEM images. The modified membrane with GO and SDS showed the wider finger-like structure. Also the modified membrane showed significant nanofiltration performance and eliminate near 100 % algal waste dye. Also after 6 hours the flux reduction of modified membrane was 23.26% that shows the good antifouling property of that. All the results demonstrated that, PES membrane modified with GO and SDS considered as a suitable option for dye removal from algal wastewater.

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