Self-cleaning properties of RO membrane coated with TiO_2 particles
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Abstract

Fouling is one of the most important problems in membrane processes. The deposition of particles and their sticking on the surface, results in the formation of layers on the surface of membrane. These layers, together with particles left inside the membrane lead to a fluid-passing resistance and as a result the output flux in the lapse of time is reduced. In this research, TiO_2 particles on the surface of composite RO membrane were self-assembled and radiated by UV light. The coating of membrane surface with TiO_2 particles and radiation with UV light, results in a creation of photocatalytic property with an increased hydrophilicity on the surface of membrane. The flux, through a coated and UV light irradiated membrane, has increased to a large extent in comparison with a neat membrane. In this research, the performance of photocatalytic decomposition and ultrahydrophilicity under UV irradiation, which create the self-cleaning specialty in a TiO_2 coated membrane and an increase in the flux, have been studied.

Keywords: self-cleaning membrane, photocatalysis, ultrahydrophilicity, TiO_2.

1) Introduction

Nowadays membrane processes are of great importance in food, chemical, medicine, pharmacy, biotechnology, water, wastewater treatment and many other fields of industries. This is due to the technology's high removal capacity and ability to meet multiple treatment objectives. However, one of the main barriers to greater use of membrane technology is membrane fouling [1]. Fouling is defined as irreversible deposition of materials on the membrane surface which results in flux decline [2]. Membrane fouling affects both the quality and the quantity of products and ultimately shortens membrane life [1]. Hence, the consequence of fouling is always a reduction in separation performance.

Various approaches have been performed to reduce fouling. This generally involves pretreatment of feed solution, adjustment membrane properties, improvement of operating conditions and optimization of module arrangement [3]. Although all the above methods reduce fouling to some extent, cleaning methods is always employed in practice. Among cleaning methods, chemical cleaning is the most important for reducing fouling with a number of chemicals being used separately or in combination [4]. For effective operation of a membrane treatment plant, the filtration process must be shutdown regularly for membrane cleaning to regain membrane permeability. Frequent cleaning means increasing the labour cost and complexity of the membrane filtration process. Furthermore, chemical cleaning of membranes results in increased cost and disposal of waste chemicals and ultimately affects membrane life [1].

In order to solve this kind of problems, many alternative ways have been tried so far with some success. A recently established approach is use UV-catalysts such as TiO_2 for this purpose. The TiO_2 photocatalyst can effectively degrade the pollutants, especially organic materials effectively with UV light. The photo-catalytic, related to the properties of oxidative decomposition and the photo-induced ultrahydrophilicity of titanium dioxide, has attracted much interest from the view points of basic and applied sciences [5]. Among different applications of photoactive TiO_2 thin films, one concerns self-cleaning surfaces, which rely both on photocatalysis and photo-hydrophilicity mechanisms [6].

Some papers have published the good antifouling properties of the membranes with TiO_2. In this field, Kim and coworkers [3] prepared a hybrid thin-film-composite (TFC) membrane by self-assembly of the TiO_2 particles with the COOH functional group of aromatic polyamide thin-film layer. This hybrid membrane was shown to posses the dramatic photobactericidal effect on E-coli under UV light illumination. By means of an ion assisted deposition method, a TiO_2 photocatalyst was prepared on porous teflon sheet (PTS) by Yamashita and coworkers [7]. UV light irradiation of TiO_2 photocatalyst on PTS led to the photocatalytic degradation of organic pollutants. Other works [8, 9] have been carried out in the field of coating nanofiltration composite membrane with titanium dioxide particles and photodegradation under UV irradiation. Kawaguchi and coworkers [10] prepared a polysulfone hollow fiber membrane with TiO_2 particles by the immersion precipitation method. It was shown that the incorporation of TiO_2 is one of the useful ways to prevent the membrane fouling. Other researchers [11] prepared two types of TiO_2 immobilized ultrafiltration membranes, TiO_2 entrapped and deposited membranes. TiO_2 entrapped membrane showed lower flux decline compared to neat polymeric membrane and TiO_2 deposited membrane showed greater fouling mitigation effect compared to TiO_2 entrapped membrane.

In this research, reverse osmosis membrane was coated with TiO_2 particles and the self-cleaning property of the membrane was studied after UV radiation. In order to characterize the coated membrane with TiO_2 particles, FT-IR (Fourier Transform Infrared Spectroscopy) and SEM (Scanning Electron Microscope) were employed.

2) Materials and methods

2-1) Apparatus

All experiments were carried out in a reverse osmosis rig at 23 ± 1 °C. The rig (Fig. 1) consisted of a feed tank, a high-pressure pump, valves, pressure gages and a stainless steel cross flow cell with a membrane area of 0.0023 m^2. The operational mode was cross flow batch concentration, i.e., the concentrate was recycled to the feed tank. The feed was pumped into the cell and the volumetric flux of liquid was measured every 10 minutes. The transmembrane pressure for all experiments was fixed at 20 bars. For radiation of membranes with ultra-violet (UV) light, a 400W, UV lamp (Osram, Germany) was used.

2-2) Membranes

TFC-SR composite membranes with a smooth surface were used for all experiments. This is a hydrophilic reverse osmosis membrane manufactured by the Fluid Systems Company. This composite membrane consists of three layers. The top layer of the membrane is made of poly vinyl alcohol and the support materials are poly aryl sulfone ether and poly ester.

2-3) Materials

Titanium dioxide (TiO_2) was obtained from Degussa. Double distilled water was used for all experiments.

2-4) Feed

Whey from feta cheese manufacturing process was used as feed during all experiments. Whey consists of various proteins.

2-5) Characterizations

The composition of the surface was determined using a fourier transform infrared spectroscopy (FT-IR, IFS48, Bruker, Germany) equipped with a ATR attachment. The surface morphology measurements were carried out with a scanning electron microscope (SEM, XL30, Phillips).

3) Results and discussions

3-1) Photocatalytic and hydrophilicity mechanisms

When a semi-conductor is radiated by a ray equal or greater than the band gap energy in ordinary conditions, an electron is transferred from capacity band to conduction band of the semi-conductor; and therefore a pairs of holes and electrons are created on the surface of the semi-conductor. Since TiO_2 is a semiconductor, the UV ray leads to the appearance of the electrons and holes. The photogenerated electrons react with the oxygen molecules in the environment and produce superoxide radical anions. The photogenerated holes react with the water in the environment and OH radicals is produced. These two types of created groups are among strong oxidant reagents that lead to the decomposition and removal of the dirt especially organic compounds [12-14].

The second phenomenon is the ultrahydrophilicty. In this case, holes and electrons are also created but they react through a different mechanism. The photogenerated electrons tend to reduce Ti (IV) cations to the Ti (III) state and the holes oxidize O_2^- anions. In this process, the oxygen atoms are thrown out and a group of oxygen vacancies are produced on the surface. The water molecules in the environment can occupy the empty sites and adsorbed OH groups are created on the surface which increases the hydrophilicity of the surface [12-14]. On the film composed of TiO_2 particles, there is a layer of chemisorbed H_2O because of hydrophilicity. This layer of H_2O can adsorb more water layers by Van der Waals forces and hydrogen bonds [15]. These layers of water prevent the direct contact between the contaminants and surface and therefore the dirt substances on the surface detach from the surface using the water on the surface; so the surface shows self-cleaning effects.

One of the most interesting aspects of TiO_2 is that the photocatalysis and hydrophilicity can take place simultaneously on the same surface even though the mechanisms are completely different. This is the reason that the film has a self-cleaning effect [16].

3-2) The self-cleaning effect of the membrane surface coated with TiO_2 particles

In order to coat the surface of membrane with TiO_2 particles, the membrane was immersed in a transparent colloidal solution containing 0.003 wt. % of TiO_2 particles for 1 hour. After that, the membrane was washed with an excess amount of distilled water and then illuminated by UV lamp for 10 minutes. The treated membrane was kept in distilled water for 15 minutes before being tested in the experiment rig. The SEM micrographs of TiO_2 coated membrane and neat membrane are shown in Fig.2. TiO_2 particles were uniformly distributed on the membrane surface. However some particles form larger clusters. The modified membrane is covered by the self-assembly of TiO_2 particles and the polymer (poly vinyl alcohol) on the surface of membrane which carries OH functional groups. This self-assembly is made by a coordinance bonding between Ti^{4+} and oxygen. The ATR-IR spectras which were obtained from neat and coated membranes with TiO_2 particles are shown in Fig. 3. The ATR-IR spectrum of the neat membrane indicates a broad peak at 3000-3700 cm^{-1} that is assigned to the stretching vibration of O-H bands in the polymer of membrane surface. The peak at approximately 2935 cm^{-1} is attributed to the stretching vibration of C-H bands. The spectrum of coated membrane with TiO_2 particles, exhibits two peaks at 561 cm^{-1} and 690 cm^{-1} that are attributed to the stretching vibration of Ti-O-Ti and Ti-O bands, respectively. The peak at 2500-3000 cm^{-1} in the spectrum of the coated membrane is completely disappeared. This indicates the complete coating of the membrane surface with TiO_2 particles.

In Fig. 4, the results of the flux of whey through the coated and neat membranes are presented. The feed employed in this test was whey which contains proteins such as alpha-lactalbumin, beta-lactogolubolin, immunoglobulin, fat and lactose. The proteins are more important factors in creating fouling and cake formation in the membrane. Protein molecules do not pass through the membrane and deposit on the surface of the membrane and gradually create a layer on the membrane [17]. The thickness of this layer increases with time and acts as a secondary membrane and hindering the fluid passage. The flux of whey using TiO_2 coated membrane is much higher compared to flux of the neat membrane. This is due to the hydrophilicity and photocatalytic properties of TiO_2 particles radiated on the membrane surface by UV irradiation. The photocatalysis produces oxidant reagents such as: hydroxyl radicals and superoxide radical anions which are among strong oxidant reagents. These groups decompose the contaminations, especially organic compounds. On the other hand, the ultrahydrophilicty created by the TiO_2 particles on the membrane results in increases the membrane flux and spread of water layer all over the surface and the movements of these layers, decontaminate the deposited specimen on the surface.

In summary, TiO_2 particles, by their photocatalytic and ultrahydrophilicity ability in the decomposition and removal of decontaminations, prevent the deposition of proteins and organic compounds, which are the main causes of membrane fouling. When membrane fouling is reduced, the membrane flux increases.

4) Conclusion

In this research, TiO_2 particles were coated on the surface of reverse osmosis membrane and radiated by UV light. The flux of whey of the membrane coated with TiO_2 particles is considerably more than the flux of whey of the neat membrane. This increase in flux is due to creating photocatalytic property and increasing of hydrophilicity in the membrane resulting from TiO_2 particles on the membrane surface radiated by UV light. Pohotocatalytic property of TiO_2 particles results in producing a group of active surface oxidant reagents that decompose and destroy the contaminations, impurities especially organic compounds. The hydrophilicity not only creates self-cleaning through dirt removal, but also increases the membrane flux as well. The photocatalytic and ultrahydrophilicity induced by radiating of TiO_2 particles with UV light avoid deposition and aggregation of organic compounds and proteins on the surface of membrane. So the membrane will clean its surface and in this way it can be said that the membrane has the self-cleaning property.

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Figure 3. ATR-IR spectra of (a) neat membrane and (b) coated membrane with TiO_2 particles.
Figure 5. Flux of whey versus time for neat and coated membrane with TiO_2 particles.

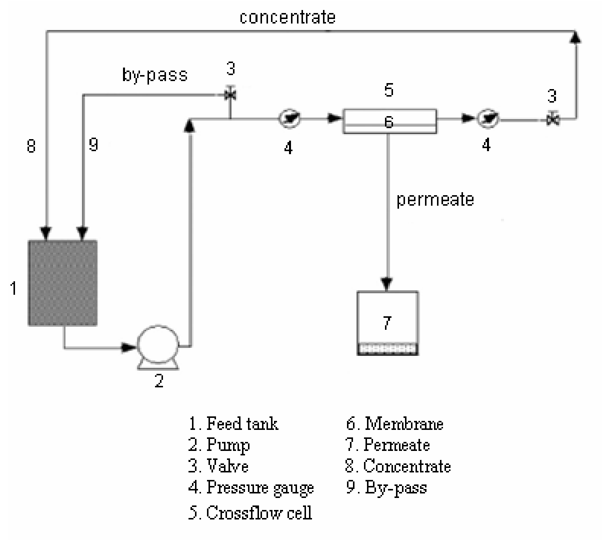
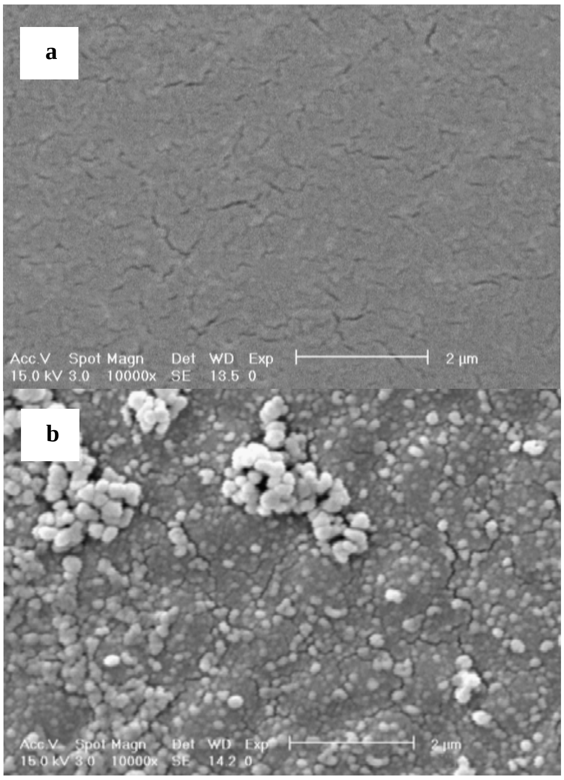

concentrate
by-pass
3
5
6
4
3
4
8
9
permeate
1
7
2
1. Feed tank
2. Pump
3. Valve
4. Pressure gauge
5. Crossflow cell
6. Membrane
7. Permeate
8. Concentrate
9. By-pass

Fig. 1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2 µm
b
Acc.V Spot Magn Det WD Exp
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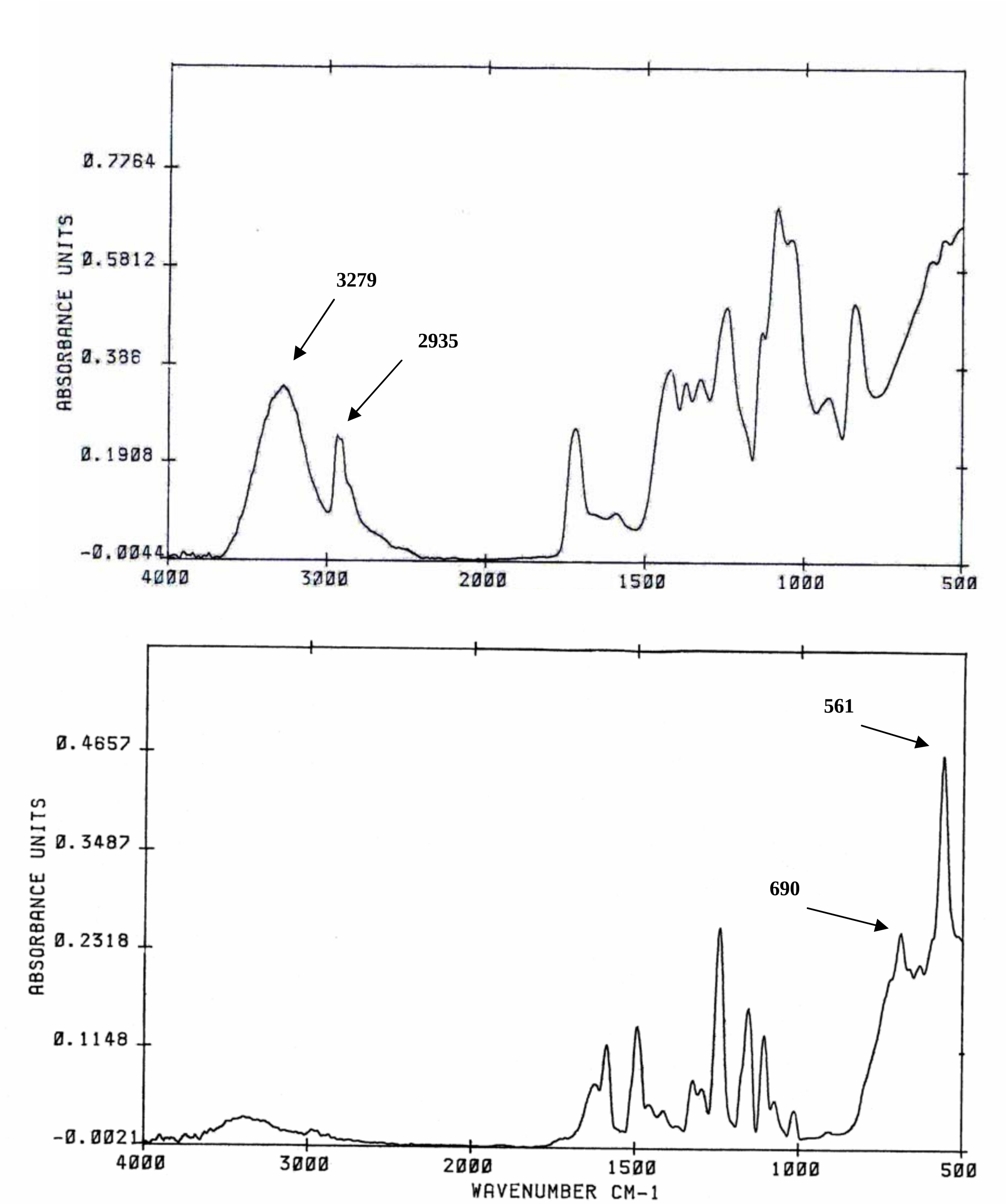
2 µm

Fig. 2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0.5812
0.386
0.1908
-0.0044
ABSORBANCE UNITS
3279
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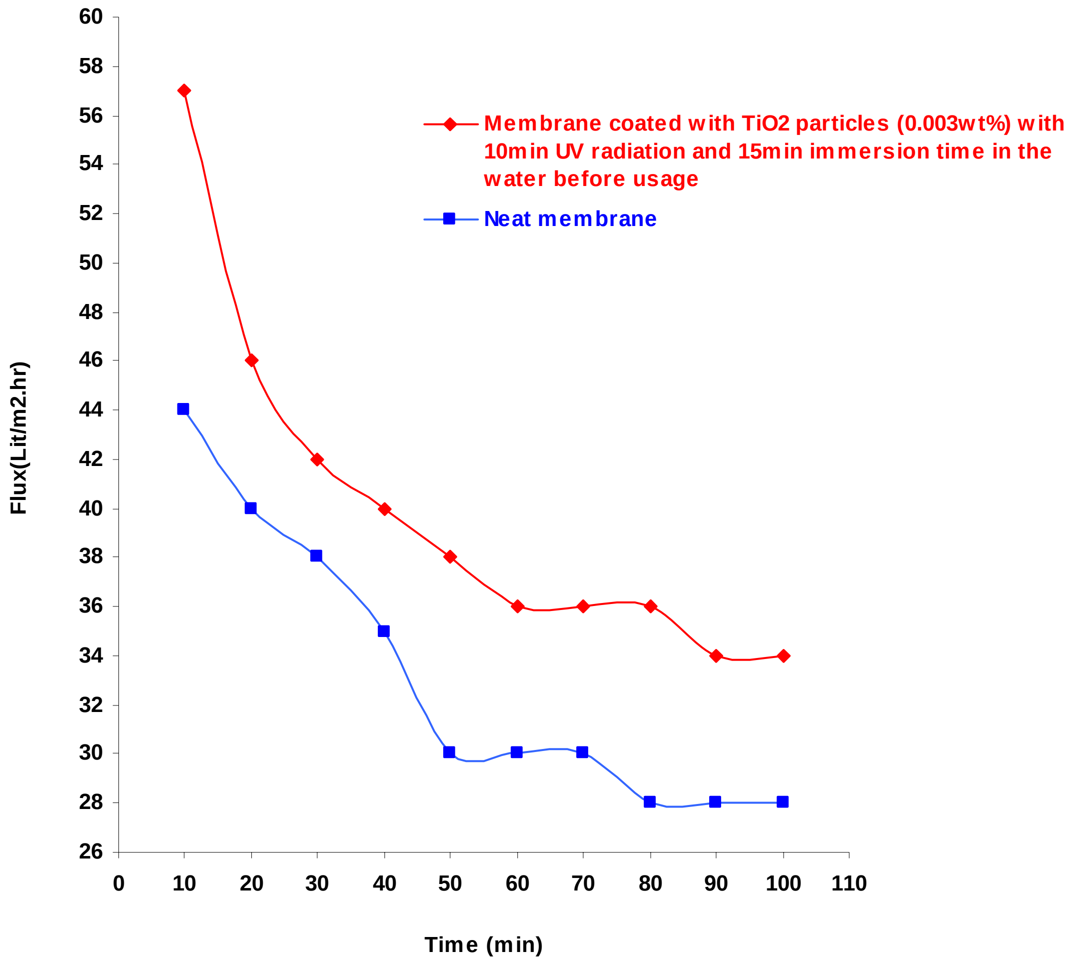
4000
3000
2000
1500
1000
500
0.4657
0.3487
0.2318
0.1148
-0.0021
ABSORBANCE UNITS
561
690
4000
3000
2000
1500
1000
500
WAVENUMBER CM-1

Fig. 3



Membrane coated with TiO2 particles (0.003wt%) with 10min UV radiation and 15min immersion time in the water before usage
Neat membrane
Flux(Lit/m2.hr)
Time (min)
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
0
10
20
30
40
50
60
70
80
90
100
110

Fig. 4