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Surface modification of PVDF membranes by sputtered TiO_2: fouling reduction potential in membrane bioreactors

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ABSTRACT

This study investigates activated sludge filterability of a commercial poly(vinylidene fluoride) microfiltration membrane with and without titanium dioxide (TiO_2) coating. Deposition of a TiO_2 thin film on the membrane surface was made by direct current reactive sputtering from a high purity Ti target in Ar/O_2 atmosphere. The modified membrane was characterized by X-ray photoelectron spectroscopy analysis, water contact angle measurement, scanning electron microscopy, and activated sludge filtration measurement. The results showed about 52.5% contact angle reduction of the modified membrane. The modified membrane exhibited less flux decline in activated sludge filtration due to the improvement of surface physical properties of the membrane. A comparison of filtration index (I_{40}) between the modified and the neat membranes showed about twofold increase due to the TiO_2 coating. The loss of nano-TiO_2 particles was revealed by energy dispersion of X-ray analysis after an ultrasonic washing test, and this influenced stability of the modified membrane.

Keywords: PVDF membrane; Surface modification; TiO_2 coating; Sputtering; Fouling

1. Introduction

Polymeric membranes are commonly used in wastewater treatment due to their ease of implementation, flexibility, high quality effluent, and low cost in comparison with ceramic ones [1,2]. These advantages make them very attractive in this filed, considering increasingly stringent environmental regulations. It is possible to use membranes as stand-alone or in conjunction with traditional wastewater treatment units.

As an example, coupling of membranes and common activated sludge wastewater treatment process in membrane bioreactor (MBR) technology, results in treating wastewater at relatively higher concentrations of sludge and rates of loading [3,4] and improvement of the quality of effluent [5]. In MBR systems, pollutants are degraded by activated sludge and clean permeate is obtained by filtering through membranes under pressure gradient [3]. However, membrane fouling during operation has greatly hindered their application. Studies have suggested that a coating of titanium dioxide (TiO_2) nanoparticles on membranes may reduce membrane fouling by enhancing the hydrophilicity of the membrane [6,7].

Among various membrane forming polymeric materials suitable for MBR, polyvinylidene fluoride

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(PVDF) has drawn much attention due to its outstanding mechanical and physicochemical properties besides good thermal and chemical resistance to acid and basis cleaning [8]. However, current applications suffer from low fouling resistance of PVDF membranes due to their intrinsic hydrophobic properties [8]. Fouling in its strict form is coverage of the membrane surface (external and internal) by deposits which adsorb or simply accumulate during operation and subsequently causes the reduction of the membrane flux [9]. This leads to frequent cleaning of membranes causing momentarily stopping filtration. Hence, reduction of fouling to maintain permeability of membranes during filtration process has been subjects of many literatures and research efforts [9–13]. Surface modification of membranes by incorporation of inorganic nanoparticles has been proposed as an effective method to improve membranes hydrophilicity and antifouling properties [14–17]. Among different nanoparticles, TiO_2 has received most attention because of its stability, availability, and stronger chemical resistance to acids and bases compared to other metal oxides [14,18–20]. Some different techniques could be applied to entrap TiO_2 in polymeric membrane matrix or to deposit it on membrane surface [15,21]. Knowledge of contribution of each resistance in the membrane resistance model which is described in the following paragraphs is the key parameter to select the most effective way to immobilize TiO_2 into the membrane matrix.

Formation of a cake layer on the membrane surface increases filtration resistance. Filtration resistance can be expressed according to Darcy's law [22]. For filtration of activated sludge as in the case of MBRs, total permeation resistance, R_t, may be expressed as sum of three components of R_m (intrinsic membrane resistance), R_p (pore fouling resistance), and R_c (cake layer resistance) [23]. Fang and Shi [22] showed that contribution of each resistance is different depending on membrane material. They presented the corresponding resistance values for various polymeric membranes including PVDF. Based on their findings, PVDF membrane fouling resistance is about 2% of total resistance for filtration of activated sludge which is low in comparison with its cake layer resistance. In other words, fouling resistance of PVDF membrane is R_C-dominant.

From this point of view, it seems that deposition of TiO_2 on the PVDF membrane surface to reduce fouling resistance would be more effective in comparison with TiO_2 entrapment into the membrane matrix, since large amount of nanoparticles can be located on the membrane surface in the former method. This conclusion has been confirmed in the literature [17,24]. However, common deposition techniques such as dip coating have some drawbacks such as short lifetime, instability of deposited nanoparticles, and hydrophobicity recovery within hours [25]. Direct current (DC) reactive sputtering is recognized as an enabling technology, particularly for deposition of dielectric materials. Marques et al. applied the unbalanced DC pulsed reactive magnetron sputtering method to produce titania films on glass substrate [26] and also on PVDF polymers for self-cleaning applications [27]. Niu et al. [28] reported the preparation of TiO_2 films on poly(dimethylsiloxane) (PDMS) substrate by DC reactive sputtering to change its surface physical properties. They claimed that the modifications were stable and permanent after three months of applications. N-doped titanium dioxide (titania) photocatalytic thin films were deposited by unbalanced reactive magnetron sputtering on PVDF substrates by Tavares et al. [29]. They illustrated that the polymer substrates reveal a synergistic effect with the top titania coating with respect to the self-cleaning property. To our knowledge, there are many publications about the utilization of DC reactive sputtering method to prepare titania thin films on glass or dense polymeric substrate, but so far few researches have applied DC reactive sputtering for TiO_2 nanoparticles coating on porous polymeric substrates such as membranes. Bergamasco et al. [30] presented filtration results for drinking water treatment obtained with a commercial cellulose acetate membrane deposited with TiO_2 by pulsed-frequency DC reactive magnetron sputtering. They concluded that the applied method for TiO_2 coating is suitable for membrane morphology modification, mitigating the fouling effects, even without using TiO_2 photocatalytic properties. To our best knowledge, there is a lack of information regarding effect of this kind of surface modification on filterability of activated sludge and its potential for being used in MBRs to mitigate fouling. One of the most important factors for economical operation of a MBR is filterability of activated sludge [31,32] which is strongly dependent on the membrane properties.

In this study, surface of a commercial PVDF membrane was modified by deposition of TiO_2 via DC reactive sputtering from a high purity Ti target in Ar/O_2 atmosphere. The modified membrane was characterized by scanning electron microscopy (SEM), energy dispersion of X-ray (XPS), and contact angle measurement. Stability of the titania thin film on the membrane surface was also investigated. The main objective of this study was to investigate potential of the TiO_2 coated PVDF membrane to reduce fouling in activated sludge filtration.

2. Experimental

2.1. Membrane modification

TiO_2 was deposited on the surface of flat PVDF microfiltration (MF) membrane with an average pore size of 0.2 μm provided from Sepro (Oceanside, CA). The deposition was performed by DC reactive magnetron sputtering similar to the method explained in previous research efforts [27–29]. According to this method, an electric field generated by a power supply ionizes a working gas (argon), accelerating Ar^+ ions toward a Ti target and subsequently ejecting neutral Ti atoms that react with oxygen and condense on substrate surface as a thin film of TiO_2. In this study, we used Ti target with purity of 99.97% and the diameter and thickness of 98 and 2 mm, respectively.

Before TiO_2 sputtering, the membrane samples were immersed in ethanol for about 2 h to remove dirt from their surfaces. The samples were then placed in the chamber of DC reactive sputtering system. The films were deposited in mixtures of Ar (99.999%) and O_2 (99.9995%). The target-substrate distance was 65 mm.

Before deposition, the chamber was evacuated to 2×10^{-3} Pa. Ar was then injected to the chamber and it started to discharge at the current of 100 mA and 3 Pa pressure. For oxide layer removal from the surface of titanium target, the pre-sputtering process was first carried out for about 20 min at 60 W which corresponds to 100 mA × 600 V. After that the deposition of a thin film of TiO_2 was performed reactively at a DC input power equals to 22.5 W (450 V × 50 mA) and a sputtering pressure of 1.8 Pa in constant oxygen flow rate of 0.8 sccm. The deposition rate was 0.1 nm/min. A piezoelectric thickness measurement software (model SQM-242, Sigma Instrument) was used to measure the thickness of TiO_2 layer which was equal to 23.6 nm. During the deposition process, the temperature of substrate was set to 50˚C.

The sputtering process parameters were chosen as starting values based on the previous work performed for the deposition of photocatalytic TiO_2 thin films on glass [29], PVDF [27], and PTFE [33] surfaces, using the same sputtering source.

2.2. Membrane characterization

2.2.1. SEM and energy dispersion of X-ray

Surfaces of the modified and the neat membranes were analyzed using scanning electron microscopy technique (SEM, TESCAN, Czech Republic) at magnification of 2 Kx. Membrane samples were sputtered with a thin layer of Au to render them conductive. The existence and content of TiO_2 on the surface of membranes were determined using EDX (energy dispersion of X-ray, VEGA3, TESCAN, Czech Republic).

2.2.2. XPS analysis

Surface analysis of the membranes by X-ray photoelectron spectroscopy (XPS) was performed using 8025-BesTec twin anode XR3E2 X-ray system. The X-ray radiation source was Al Kalpha, 1486.6 eV and Mg, 1253.6 eV. Binding energies were calibrated using containment carbon (C 1s = 285 eV). Survey spectra were run in the binding energy range of 0–1,100 eV. In this method, the samples are irradiated with soft X-rays to eject electrons from the core energy levels of the atoms present. Those generated with characteristic low energies within the top few atomic layers of the surface can escape into the high vacuum spectrometer and be energy analyzed to form a spectrum. The peak energy position provides an elemental analysis, and precise chemical specification can be obtained from the detailed peak shapes using curve resolving procedures. The detection depth of XPS is typically in the range of 5–10 nm.

2.2.3. Contact angle measurement

The contact angles formed by water droplets (4 μl) on the membranes surface were measured using sessile drop technique (OCA15 Plus, Dataphysics, Germany). The average of at least five measurements was reported.

2.2.4. Membrane performance

The modified membranes were evaluated in the filtration system operating with a vacuum pump at the permeate side to promote the driving force. The system had a main feed tank with capacity of 2 L to store water and/or activated sludge to be filtrated. Additionally, there was a recycle to keep the level of water and mixed liquor suspended solids (MLSS) of activated sludge constant. The flat membrane was fixed in a round filtration module as shown in Fig. 1. The effective membrane surface area was 15.89 cm^2. Permeate flux was determined by weighing the permeate mass with an electronic balance. The membrane cell and the filtration setup are illustrated in Fig. 1.

The activated sludge sample was taken from the recycled stream of the wastewater treatment unit of Tehran oil refinery and sedimented with phenol to reach the total suspended solid (TSS) concentration of 3,000 mg/l.

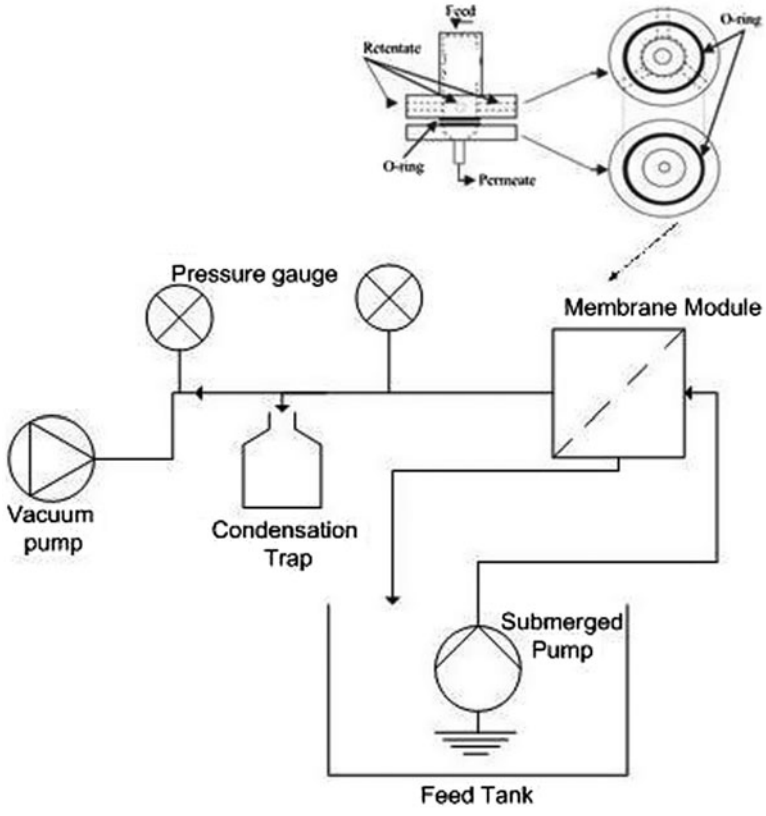

Fig. 1. Membrane cell and filtration setup.

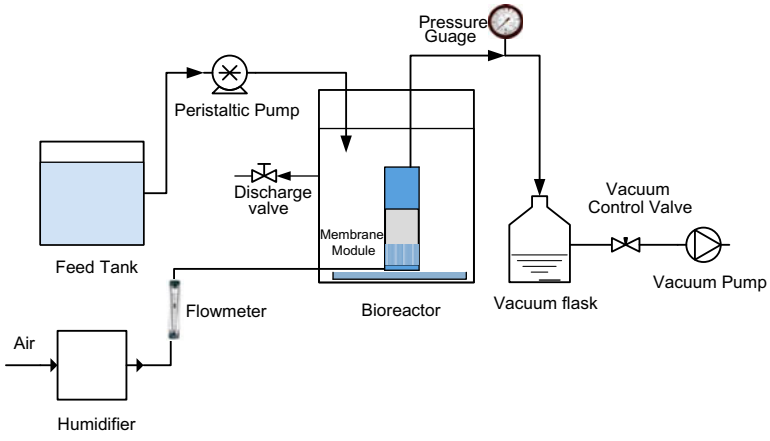

Fig. 2. Submerged MBR schematic diagram: (1) feed tank (10 L), (2) peristaltic pump, (3) discharge valve, (4) membrane module, (5) bioreactor, (6) air pump, (7) humidifier, (8) flow meter, (9) pressure gage, (10) vacuum flask, (11) vacuum control valve, and (12) vacuum pump.

There were two sets of filtration experiments in this study. The first set was conducted to determine the various resistance values for the modified and the neat membranes for which a pattern of 3 steps was applied. The steps comprise filtration of distilled water to determine (R_m), filtration of activated sludge and calculation of the total permeation resistance (R_t) and removing the cake layer by surface cleaning of the membranes to determine the pore fouling resistance (Rp).

Table 1
SMBR feed specification

Component	Purity (%)	Concentration (ppm)
C_6H_5OH	99	1,000
K_2HPO_4	99	360
KH_2PO_4	99	280
NH_4Cl	99.99	200
$CaCl_2{\cdot}6H_2O$	–	67
$MgSO_4{\cdot}7H_2O$	98.5	248
$FeSO_4{\cdot}7H_2O$	99.5	0.5

The values were calculated using Eqs. (1)–(3) [22].

$$R_m = \frac{\Delta P}{\mu J_{pw}} \quad (1)$$

$$R_p = \frac{\Delta P}{\mu J_w} - R_m \quad (2)$$

$$R_t = \frac{\Delta P}{\mu J_{AC}} = R_m + R_p + R_c \quad (3)$$

The second set of experiments was conducted to evaluate the membrane fouling behavior to be used in MBRs by determining the activated sludge filtration index (I_{40}) according to the procedure presented by Rosenberger and Kraume [32]. The filtration index was given as the ratio of permeate flux after 40 min of operation to pure water flux.

The effect of TiO_2 coating on the performance of the PVDF membrane has been studied in a submerged membrane bioreactor (SMBR) as shown in Fig. 2. The SMBR feed specification and operating condition were illustrated in Tables 1 and 2, respectively.

Chemical cleaning of the membrane was performed according to the protocol reported by Nguyen and Roddick using 10 mM SDS solution for 45 min [34]. In this way, the fouled membranes were backwashed by placing them upside down in the filtration cell and applying 0.1 bar vacuum for 5 min. The backwashed membranes were then soaked with gentle shaking in solutions of 10 mM SDS solution at 24°C for 45 min. The pure water flux of the chemically cleaned membranes was determined after rinsing them thoroughly with distilled water.

Table 2
SMBR operating conditions

Parameter	Amount
MLSS	6,000–7,000 mg/l
SRT	70–100 d
HRT	25–28 h
Input phenol concentration	1,000 mg/l
Input COD concentration	2,300–2,500 mg/l

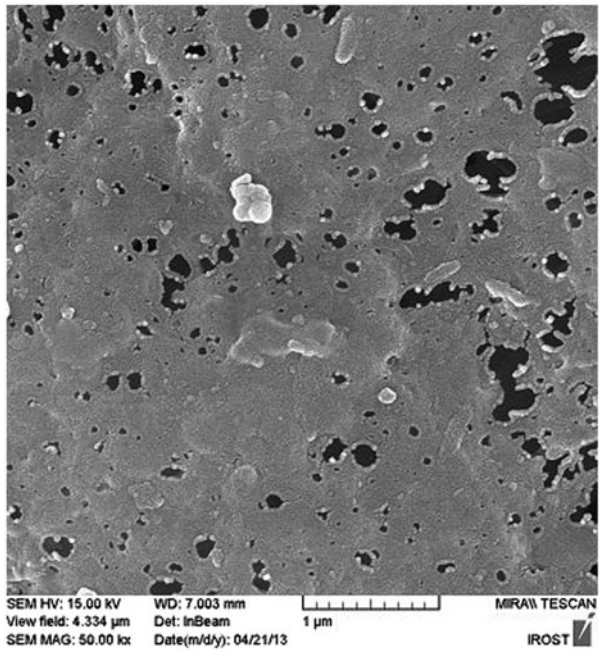

Fig. 3. SEM image, the neat PVDF membranes.

2.2.5. Ultrasonic washing of TiO_2-sputtered membrane

To evaluate stability of the TiO_2 coating on the membrane surface, an ultrasonic washing test was performed. Freshly sputtered and ultrasonic washed modified membranes after 30 and 60 min were analyzed using energy dispersion of XPS analysis (EDS) to determine the Ti content on the membrane surface.

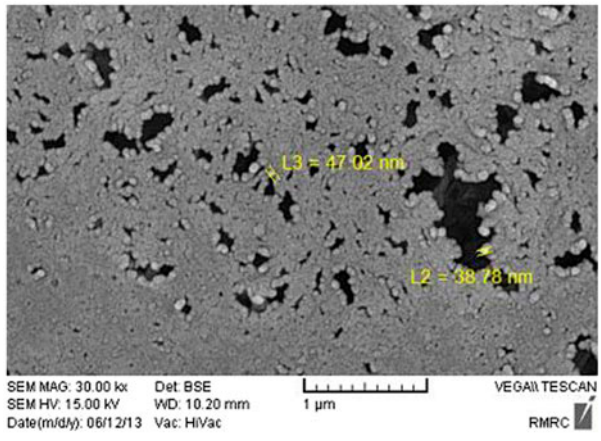

Fig. 4. SEM image, the modified PVDF membranes.

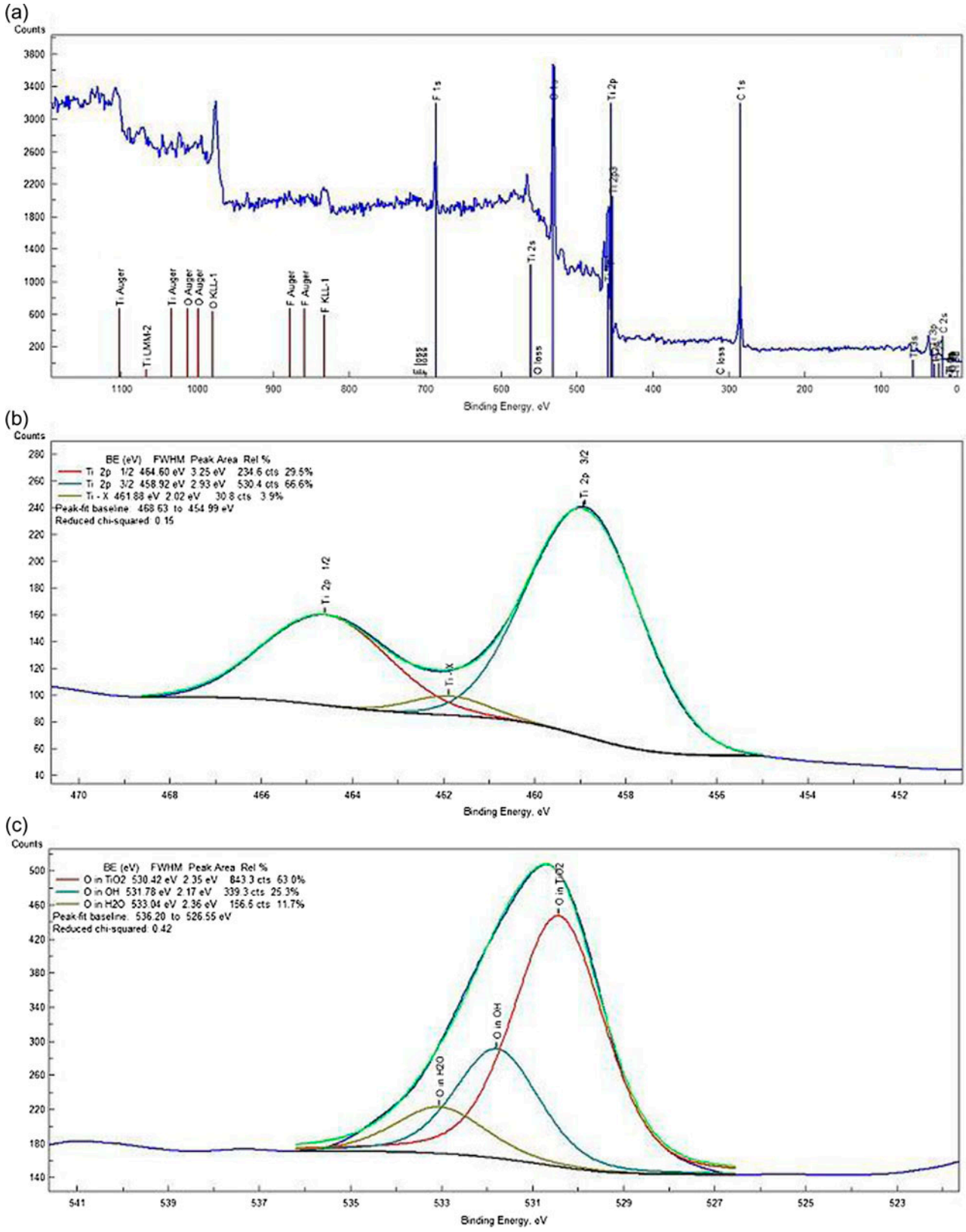

Fig. 5. (a) XPS survey peak of the modified membrane, (b) XPS spectra of Ti (2p region) on the modified membrane, and (c) XPS spectra of oxygen on the modified membrane.

3. Results and discussion

3.1. Characterization of membrane

Surface morphology of the neat and the modified membranes was studied using SEM images as shown in Figs. 3 and 4, respectively. As it is observed, there are deposited materials on the membrane surface probably due to the presence of TiO_2. Similar results were observed by Syafei et al. [35]. Marques et al. [27] also observed that TiO_2 deposition increases the occurrence of isotropic spherulites. In this study, TiO_2 particles with the average size less than 50 nm was deposited on the membrane surface, as illustrated in Fig. 2(b). The size of nanoparticles deposited by this method is small enough not to plug the surface pores of the MF PVDF membrane.

The presence of TiO_2 was investigated by energy dispersion of XPS confirming the existence of TiO_2 on the top surface of the modified membranes. Indeed, surface chemistry of the neat and the modified PVDF membranes and the analysis of possible interactions between nano-TiO_2 were examined by XPS. The results are demonstrated in Fig. 5((a)–(c)). Fig. 5(a) presents XPS survey spectra of modified PVDF membrane, showing the positions of all of the photoelectron peaks, which is in agreement with the values reported by other researchers. The presence of Ti peaks provides evidence that TiO_2 has existed on the modified membrane surface through certain interactions. In addition to the survey spectra, high-resolution XPS studies were also carried out to better understand the possible interactions between polymer and TiO_2.

Considering the peaks of 464.64 and 458.98 eV which correspond to $2p_{1/2}$ and $2p_{3/2}$, respectively, as observed in Fig. 5(b), confirms the presence of Ti^{+4} or TiO_2 on the surface of the modified membrane. Complete fitting can be obtained by adding the third peak called as Ti-x, which shows Ti bond with other elements (about 3.9%) which is negligible in comparison with Ti–O bond, but can be an evidence for unknown bond of TiO_2 with elements of the membrane surface. Such bonds have important roles in durability and stability of TiO_2 on the PVDF membrane surface. However, due to the relatively low contribution of this bond, it may not have an effective role in stability of the TiO_2 sputtered on the PVDF membrane surface. The mechanism of TiO_2 attachment to the membrane surface can be explained as the following. Actually, considering the existence of oxygen element on the neat PVDF membrane before sputtering, it can be concluded that during sputtering, a C=O…Ti complex may develop and its formation can be attributed to the coordinated reaction between partial C=O and nano-TiO_2 particles. However, since no peak was detected corresponding to the chemical bond between Ti and C, it could be said that the TiO_2 nanoparticles are deposited on the PVDF membrane due to physical adsorption.

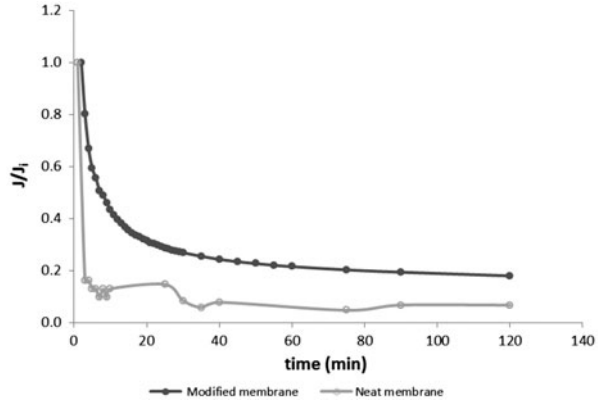

Fig. 6. The dimension-less flux decline behavior of activated sludge filtration.

Fig. 5(c) demonstrates XPS spectra of oxygen which exists in the sample in different types. As can be observed, 63% of oxygen belongs to TiO_2 at 530.42 eV and 11.7% relates to H_2O chemically and physically absorbed on the film and situated at energy bonding of 533.04 eV. Another O 1s peak at 531.78 eV corresponds to the remaining 25.3% which may belong to OH groups [28]. In this way, a Ti–OH complex may develop between (OH) hydroxyl group and nano-TiO_2 particles [28].

One of the most important parameters affecting the antifouling properties of the polymeric membranes is the surface hydrophilicity of membranes which can be evaluated using water contact angle measurements. The hydrophilicity of the modified membrane improves due to the TiO_2 deposition on the membrane

Table 3
Pure water flux, different resistance values, and filtration index of activated sludge filtration

Membrane	J_{PW} (LMH/bar)	R_m ($\times 10^{11}$ m^{-1})	R_c ($\times 10^{11}$ m^{-1})	R_p ($\times 10^{11}$ m^{-1})	R_t ($\times 10^{11}$ m^{-1})	I_{40}
Neat	889.06	2.43	89.45	9.72	101.60	0.0239
Modified	1,244.69	1.74	28.83	5.21	35.77	0.0485

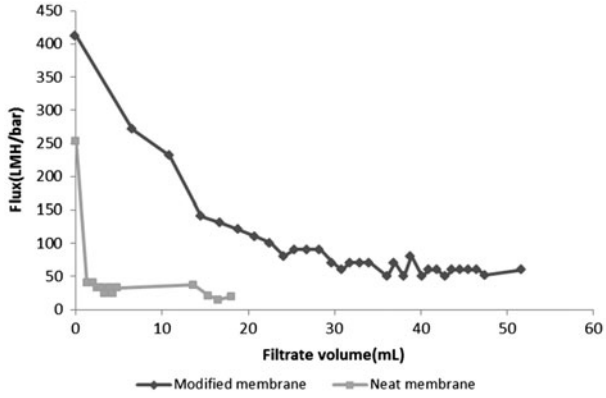

Fig. 7. The permeation flux behavior of activated sludge filtration.

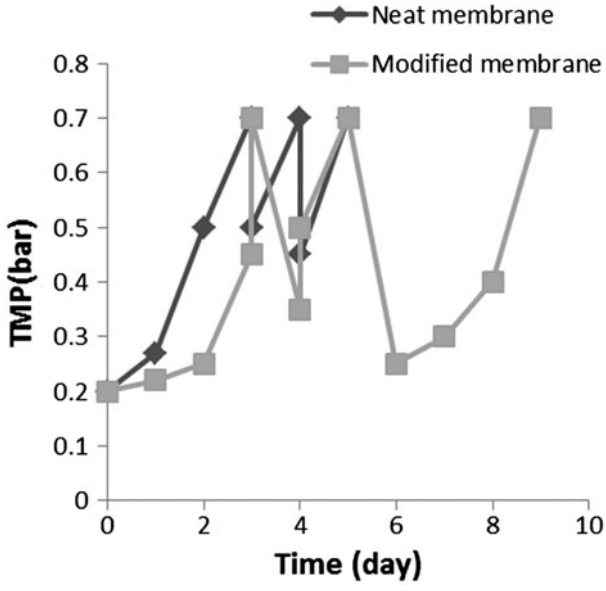

Fig. 8. TMP increase for the neat and modified membrane.

surface. It must be mentioned that the angle was reduced from about 92.5 to 43.9 after the modification and this improvement was stable during several measurements in weeks after the deposition. This extent of reduction was reported in the literature [28]. This good hydrophilicity of the modified membrane can be attributed to the effect of OH groups as detected by the XPS analysis. Coating the surface of PVDF membrane with TiO_2 nanoparticles results in formation of a layer of chemisorbed H_2O on the surface. Such H_2O layer can absorb more water layer through van der Waals forces and hydrogen bonds. The formation of these layers of water prevents direct contact of the foulants and the surface of the membrane and consequently improves the antifouling ability. The water layer on the surface prevents attachment of the foulant on the surface of the membrane and, on the other hand, facilitates removing the cake layer on the surface of the membrane. This phenomenon induces a self-cleaning ability to PVDF membrane coated with TiO_2 nanoparticles [19]. Hence, it can be concluded that low membrane fouling rate in more hydrophilic surface is attributed to a lower rate of adsorption of dissolved organics on the PVDF/TiO_2 membrane surface.

3.2. Membrane filtration

The filtration performance of the modified and the neat membranes was also explored. Table 3 summarizes the respective pure water flux and resistance values. Relative to the neat membrane, the modified PVDF membrane showed improved pure water flux following the surface modification. Such an improvement in the flux should be attributed to the uniform deposition of the hydrophilic TiO_2 nanoparticles on the membrane surface. Although, after deposition of TiO_2, it is expected to observe a flux decline due to reducing pore size of the membrane as it is reported in similar surface modifications [30,35], the hydrophilicity enhancement during the deposition especially at moderate deposition rate and thicknesses can be a reason for pure water flux improvement as observed in this study. The results clearly showed the resistance reduction of the modified membrane after the TiO_2 coating which is more significant for the cake layer resistance (from 89.45 to 28.83 ($\times 10^{11}$ m^{-1})) as previously discussed is the dominant resistance of the PVDF membranes.

The results of flux decline behavior of activated sludge filtration are presented in Fig. 6. As observed, dimension-less flux (J/J_i) reduces significantly for both the membranes; however, its final value is significantly higher for the modified membrane. It must be mentioned that J_i is the initial permeation flux. The results clearly showed that the extent of fouling for the modified membrane is significantly less than that for the neat membrane. This fouling reduction can be interpreted by the fact that surface of the TiO_2 coated membrane is more hydrophilic than that of the neat polymeric membrane due to the higher affinity of metal oxides to water. Therefore, the extent of adsorption between the sludge particles and the TiO_2 coated membrane is less, and the deposited particles can be removed easier by physical cleaning. Sputtering in the way used in this study is a surface modification method which is more effective for the cake layer resistance dominant polymeric membranes, since it deals with surface of the membranes and reduces their hydrophobic adsorption tendency.

Table 4
Relative weight percent of elements remaining on the membrane surface after various ultrasonic washings

Sample	Weight percent of elements			
	C	O	F	Ti
Neat PVDF membrane	31.53	5.58	62.89	0.00
Freshly sputtered membrane	27.25	9.54	60.45	2.76
After ultrasonic washing for 30 min	27.01	6.03	65.45	1.51
After ultrasonic washing for 60 min	27.31	5.81	65.31	1.57

Flux decline behaviors of the modified and the neat membranes vs. filtrate volume are shown in Fig. 7. The difference between the both membranes is much clearer.

Filtration index (I_{40}) was also determined for the both modified and neat membranes as presented in Table 3. A comparison of filtration index (I_{40}) values for the modified and the neat membranes shows about twofold increase due to the TiO_2 coating, and this significantly improves results in activated sludge filtration.

The result of TMP increase due to membrane fouling in a submerged membrane reactor was illustrated in Fig. 8. As shown in the figure, the surface modification of the PVDF could reduce the fouling potential of the membrane and improve the performance of PVDF membrane in SMBR system.

3.3. Stability of sputtered TiO_2 on modified membrane

Table 4 summarizes the relative weight percent of elements remaining on the membrane surface after pure water flux measurement. After ultrasonic washing for 30 min, the weight percent of titanium element decreases from 2.7 to 1.5%. No significant further reduction of Ti is observed with longer washing. Therefore, it seems that the loosely attached TiO_2 particles are lost in the first couple of minutes of the ultrasonic washing. This amount of TiO_2 loss may be due to the lack of such a tight bond between the TiO_2 nanoparticles and the polymer as discussed in previous sections. It should be noted that the PVDF membrane which has been used in this study was a commercial membrane and as it is known various additives containing oxygen element for example pore forming agents such as polyethylene glycols or some other ones such as esters and ethers may be used during membrane preparation and may be remained in the membrane matrix and be the source of this observed oxygen peak in the XPS and EDS analysis. It should be noted that such oxygen element may also be removed during ultrasonic washing similar to the ones belong to sputtered TiO_2 as can be observed in Table 4.

4. Conclusion

TiO_2 was coated on the surface of PVDF MF membrane using DC reactive sputtering. The XPS spectra confirmed that a uniform TiO_2 film is deposited on the membrane surface successfully. TiO_2-sputtered PVDF membrane exhibited improved hydrophilicity of the surface resulting in higher pure water flux. The modified membrane showed lower fouling resistance in activated sludge filtration, and this was mainly due to the reduced cake layer resistance. As a result, it can be recommended that the TiO_2-based surface membrane modification especially for polymeric membranes with higher cake layer resistance offer as a promising method to improve activated sludge filtration. However, since no tight chemical bond can be developed in this method, the sputtered TiO_2 nanoparticles may be removed in vigorous membrane cleaning processes, for example, by ultrasonic washing and this reduces its applicability in long-term filtration processes. It can be concluded that to obtain the benefit of good antifouling ability and improved hydrophilicity of PVDF modified membranes by TiO_2 DC reactive sputtering, some strategies may be needed to tightly bond the TiO_2 nanoparticles to the membranes surface.

Nomenclature

I_{40}	—	sludge filtration index
J	—	permeation flux (LMH)
J_i	—	initial permeate flux (LMH)
J_{pw}	—	pure water flux (LMH)
J_w	—	pure water flux of the membrane after cleaning with water (LMH)
J_{AC}	—	flux of activated sludge at steady state (LMH)
R_c	—	cake layer resistance (m^{-1})
R_m	—	intrinsic membrane resistance (m^{-1})
R_p	—	pore fouling resistance (m^{-1})
R_t	—	total permeation resistance (m^{-1})
ΔP	—	trans membrane pressure (N/m^2)
μ	—	viscosity (Ns/m^2)

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