Surface Modification of CTA-FO Membrane by CO₂ Plasma Treatment

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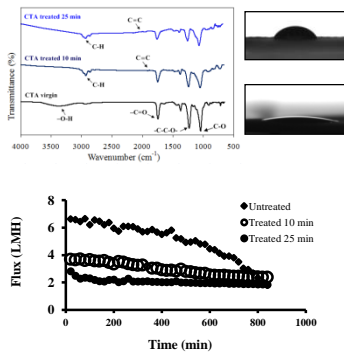
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Abstract

The aim of this research was to examine the influence of CO_2 plasma activation on CTA membrane in order to improve its the hydrophilicity. This research also investigated the enhancement of CTA membrane whether it could increase the anti-fouling in FO process. The plasma power was used varied in the range of 10-50 W and the exposure time was employed at 5-25 min, respectively. The contact angle and hydrophillicity of samples were reduced after CO_2 plasma treatment. The reduction of the contact angle was presented from 64.04° to 9.38°. The optimum condition of plasma power was 20 W with the exposure time at 10 min. The result suggested that the CO_2 plasma etched and changed the functional group of CTA membrane to carboxylic group and their derivative as indicated by FTIR-ATR. The results showed the decreased water flux after the treatment by CO2 plasma and the high salt leakage. Filtration experiments of BSA solution and demonstrated the low water flux fouling due to the surface roughness of modify CTA membrane. The hydrophilic membrane treatment plasma surface could reduce interactions and decreases protein absorption.

Keywords: CTA membrane; plasma treatment; surface modification; hydrophilicity

■1.0 INTRODUCTION

Forward osmosis (FO) is emerging membrane separation process for water reuse and desalination. This process is natural driving force using osmotic pressure difference across a semi-permeable membrane process. However, this process is limited by lower flux, higher fouling and higher salt leakage comparing with reverse osmosis (RO) [1]. The permeate flux decline during the operation due to the concentration polarization and membrane fouling in FO process. As a result, various methods were attempted to reduce fouling and enhance flux such as membrane surface modification, new material synthesis, etc [2, 3]. Hydrophilicity membrane surface tend to foul less than hydrophobicity membrane [4].Therefore, membrane surface modification has been examined in order to increase the surface hydrophilicity. Numerous methods for membrane surface modification including adsorption, coating, blending, surface chemical reaction, plasma treatment, UV irradiation, grafting polymerization were tested [5, 6]. However, one of the most favorable and effective is low temperature plasma treatment. This treatment presents membrane surface properties, which can be tailored to satisfy with a particular request without affecting the bulk of the membrane surface [7, 8]. Additionally, gas plasma treatment can modify cellulose triacetate (CTA) ultrafiltration (UF) and pervaperation (PV) membrane surface to improve hydrophilicity [8-10].

Bhat and Wavhal used ammonia plasma gas treatment to improve pervaperation membrane surface to show high hydrophilicity and it had excellent selectivity for water separation [9]. Riekerink *et al.* modified and investigated CTA and cellulose acetate (CA) membrane treatment by CO_2 and CF_4 plasma etching. The result revealed that the treated UF membrane was more hydrophilic, good flux enhancement and low membrane fouling [11]. Huang *et al.* studied the surface properties of CA membranes using low-pressure plasma. Argon (Ar) and difluoromethane (CH_2F_2) plasma were used to control the surface wettability of CTA UF membranes. It was found that the Ar plasma increased the hydrophilicity. Nevertheless, CH_2F_2 plasma polymerization resulted in membranes more hydrophobic due to the strong of fluorination at the top layer [8]. Wavhal and Fisher. He *et al.* discovered that the CO_2 plasma introduced several oxygen containing moieties, including carboxylic acid, ketone/aldehyde, and ester functional groups [12, 13].

According to the above review, it is clearly seen that the modification of membrane surface by gas plasma treatment could improve the properties of hydrophilic polymer that depended on

the membrane chemical properties, type of plasma gas, hydrophilic monomer, and the condition of testing.

The aim of this research was to examine the influence of CO_2 plasma activation on CTA- FO membrane in order to improve its hydrophilicity. This research also investigated the enhancement of CTA membrane whether it could increase the anti-fouling in FO process.

■2.0 EXPERIMENTAL

2.1 Material

Flat sheet cellulose triacetate (CTA) membrane was supplied from Hydration Technology Inc® (HTI®, Albany, OR, USA). The membrane embedded in polyester mesh to provide mechanical support with 50 µm of thickness was used in this experiment. The CTA membrane samples (7 cm x 14 cm) were prepared for the plasma treatment and were characterized after the plasma treatment.

2.2 Plasma Treatment

The DC glow discharge plasma reactor was generated in the vacuum chamber that consisted of 25.4 cm internal diameter, and 38.1 cm length. The base pressure within the reactor was typically in the range of 5.0×10^{-4} mbar [14]. The CO_2 plasma flow was adjusted to obtain a steady pressure at 0.4 mbar and to create the plasma power by a needle valve. The plasma power used varied in the range of 10-50 Watts and the exposure time was employed at 5, 10, 15, 20 and 25 min, respectively.

2.3 Characterization of Membrane Surface

The hydrophilicity of membrane surface was determined by using water contact angle (Data Physics Instruments OCA15 GmbH, Filderstadt, Germany). The water droplet with volume of 1µL/s was formed on the membrane surface. Each measurement was tested in triplicate and their average value was calculated. The surface chemical structures of untreated and the treatment membranes were analyzed by Attenuated Total Reflectance-Fourier transform Infrared spectroscopy, ATR-FTIR (Tensor 27, Bruker, US).

Statistical analysis was carried out by variance full factorial in random complete block design to identify major factors affecting water contact angle by using the statistics package of social science (SPSS, Version 11.5).

2.4 Permeation Test in RO Experiment System

The performance of CTA membrane was characterization by measuring water permeability coefficients, pure water flux and salt rejection. The water permeability coefficient (A; LMH.bar^{-1}) and salt rejection (R; %) were tested with RO mode. Deionized (DI) water was supplied as feed solution at the applied pressure between 1-5 bars. DI water and 10 mM of NaCl solution were used as feed solution for water permeates flux testing and salt rejection testing, respectively. The water flux (J_w) was calculated as follows:

$$J_w = \frac{\Delta weight}{water\ density \times effective\ membrane\ area \times \Delta time}$$

(1)

The salt rejection was calculated as follows:

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

(2)

where C_p and C_f are the salt concentration of permeate solution and feed solution, respectively.

The salt permeability coefficient (B; LMH) was calculated as follows: [3]

$$\frac{1-R}{R} = \frac{B}{A(\Delta P - \Delta \pi)}$$

(3)

where A is water permeability coefficient (LMH.bar^{-1}), ΔP and $\Delta \pi$ are the difference pressure and osmotic pressure across membrane (bar), and R is salt rejection (%).

2.5 Water Flux in FO Experiment System

The FO experiment was set up as shown in Figure 1. The membrane unit consisted of 20 cm long, 10 cm wide, and 0.3 cm depth on both permeate and feed sides of membrane. The water flux was analyzed with DI water at 0.10 cm/min in the feed side. The draw solution flow was conducted in co-current mode with the velocity at 0.10 cm/min by peristaltic pump (EYELA MP-3N, Japan). The feed solution was BSA 1 g/L. The draw solution (DS) concentration was 2 M NaCl. They were operated for the long run testing (10 h). The water flux and salt reverse flux behavior were observed.
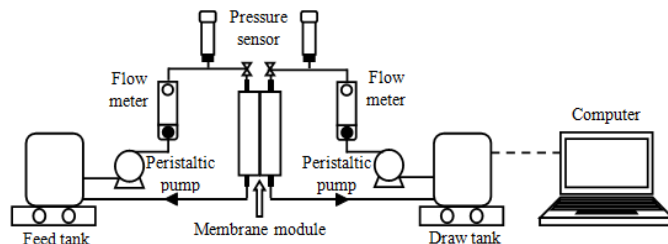

Figure 1 The FO experiment system

Membrane cleaning was done after fouling runs were stopped. The fouled membrane was cleaned using cross flow DI flushing for 10 min, circulate of citric acid (2%wt) for 60 min, circulate of NaOH (1%wt) for 60 min and DI flushing until pH is equal to 7.0 ± 0.1. Each cleaning protocol was done at fixed cross flow velocity 0.1 cm/min for both sides.

■3.0 RESULTS AND DISCUSSION

3.1 Membrane Characteristics

3.1.1 Hydrophilicity-contact Angle Measurement

The hydrophilicity of membrane can be improved by the carbon dioxide (CO_2) plasma gas treated on CTA membrane. In this study, contact angle measurements were used to identify the hydrophilicity of untreated and treated membrane on surface of CTA. Table 1 shows the contact angle results of the untreated membrane and treated membrane for each experiment. The reduction of the contact angle was presented from $64.04 \pm 3.13°$ to 9.38 ± 0.00. The reductions were correlated with high power and long time exposure. The contact angle and hydrophilicity of samples were reduced after CO_2 plasma treatment. It can be concluded from Table 1 that the increase of hydrophilicity

reached almost a constant value after 10 min of plasma exposure. All further experiments were therefore conducted with membranes exposed for 10 min and 25 min of CO_2 plasma irradiation.

Figure 2 shows the comparison of images for contact angles of membranes before and after the treatment. However, the highest power supplies did not obtain the lowest contact angle due to the destroying by the high power or heat. In additional, contact angle data analysis are presented that the contact angle are significant interaction of time and power ($p<0.05$).

The modification of membrane surface by the plasma treatment could improve the properties of hydrophilic polymer that depended on the application of systems. The increasing of the exposure time and power supplies increased membrane hydrophilicity.

Table 1 The contact angle of untreated membrane and treated membrane for each experiment (n=6)

Exposure time	Contact angle (Average±SD) for each plasma power			
	10 W	**20 W**	**30 W**	**50 W**
0	64.04±3.13	64.04±3.13	64.04±3.13	64.04±3.13
5	31.21±1.42	28.98±2.07	27.55±2.07	20.62±1.16
10	20.38±1.91	18.51±1.74	13.89±1.67	31.18±2.82
15	18.77±0.61	19.99±0.76	15.89±1.02	33.74±1.68
20	21.77±2.82	12.54±1.13	14.32±1.41	29.64±0.94
25	23.81±1.80	9.38±0.0	9.01±3.77	30.06±3.92
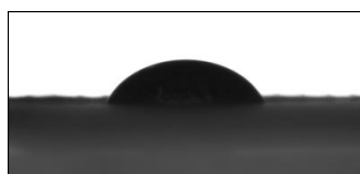
(a) Untreated membrane
Left average   = 64.00 °
Right average = 63.99 °
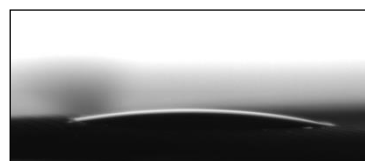
(b) Treated membrane
20 W for 10 min
Left average   = 18.34 °
Right average = 18.34 °
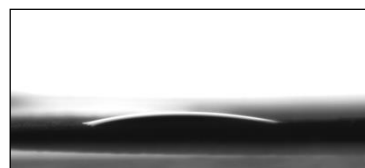
(c) Treated membrane
20 W for 25 min
Left average   = 9.39 °
Right average = 9.39 °

Figure 2 The images of contact angle on CTA membrane (a) untreated membrane; (b) treated membrane with 20 W for 10 min; and (c) treated membrane with 20 W for 25 min

Other studies also observed the water contact angle after treatment by CO_2 gas plasma in the different application as shown in Table 2.

Table 2 The comparison of contact angle with other studies

Membrane	Type of plasma gas	Time (min)	Energy (W)	Application System	CA (°)
CTA untreated[a]	-	-	-	FO	64
CTA[a]	CO_2	25	20	FO	9.39
CTA[a]	CO_2	10	20	FO	18.51
CTA[b]	Ammonia	20	10	PV	35
CTA[c]	CO_2	5	47-49	UF	56
CTA[c]	CO_2	15	47-49	UF	n.a.[d]

[a] This study, [b] Bhat and Wavhal (2000), [c] O. Riekerink *et al.*(2002*),*
[d] n.a. = droplet was absorbed by the membrane

As the results, the contact angle and hydrophilicity of samples were reduced after CO_2 plasma treatment. The gas plasma treatments improve the membrane properties in the different result of hydrophilicity even the same membrane material which depended on the type of plasma gas and the membrane application [9, 11].

3.1.2 FTIR Measured

The FTIR results of CTA membrane are presented in Figure 3. The untreated membrane presented the functional groups of –C-O stretching, Acetate -C-C-O- stretching, –C=O stretching, and –O-H stretching with absorption band wave number detected at 1042.1, 1232.6, 1742.1 and 3371 cm^{-1}, respectively. The CTA membrane treated presented the same band of untreated membrane and appearance of C=C or C≡C stretching,–C-H stretching and the wide peak of O-H stretching on the membrane surface. As the results, the element content of O and N increased with the increasing of plasma treatment time due to the surface oxidation [5].
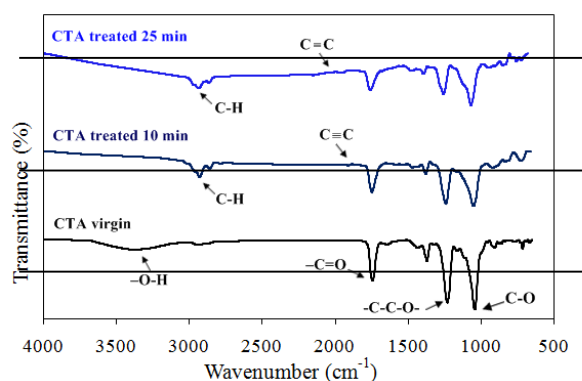

Figure 3 FTIR results after treatment by CO_2 plasma, CTA untreated, CTA treated for 10 min and CTA treated for 25 min

From Figure 3, the possible assignments of the significant FTIR bands (cm^{-1}) appearing after CO_2 plasma modification changed the chemical properties of membrane surface of functional group–COOH and –OH to be their derivative within more hydrogen bonding. it can be concluded that the changing surface structure of CTA and surface oxidation caused the

increasing of polarity. The carbonyl groups were etched in the chain of CTA membrane at the dense top layer and changed to C=C, C=N. This further resulted in more capability of hydrogen bonding [5, 6].

3.1.3 Morphology with SEM

Morphology of CTA membrane at the top layer which was untreated and treated by CO_2 plasma is shown in Figure 4. The untreated CTA membrane at dense top layer was quite rough. After CO_2 plasma treatment, the surface at top layer increased roughness due to the etching membrane on the top layer.
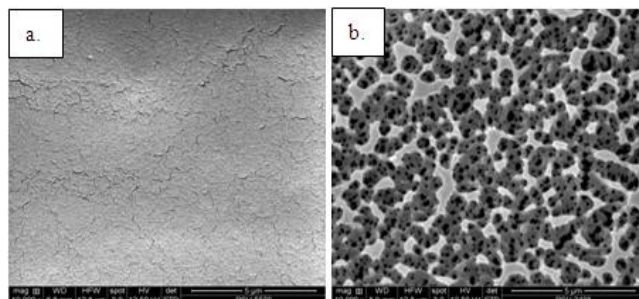

Figure 4 The SEM image of CTA untreated membrane and treated membrane (a) CTA untreated (b) CTA treated for 25 min

3.2 Membrane Performance

3.2.1 Water and Salt Permeability in RO

The water permeability (A) and salt permeability (B) of the treated and untreated membrane are presented in Table 5. The water permeability (A) and salt permeability (B) of the untreated membrane were similar to the results of many previous researches [15, 16, 17]. As the results above, the modification of membrane surface by CO_2 plasma treatment increased water permeability and salt permeability. This phenomenon can be explained that after the CO_2 plasma treatment, the pore size of membrane surface increased, whereas salt rejection was decrease.

Table 5 The different value of A and B for the different treatment

Membrane	Water permeability, A ($Lm^{-1} bar^{-1} hr^{-1}$)	Salt permeability, B ($Lm^{-2} h^{-1}$)
CTA untreated	0.7	0.68
Treated 10 min	1.7	11.50
Treated 25 min	1.8	28.65

3.2.2 Water Flux and Reverse Salt Flux in FO for Long Time Experiment

The effectiveness of plasma treatment for BSA solution filtration for long time experiment are shown in Figure 5.
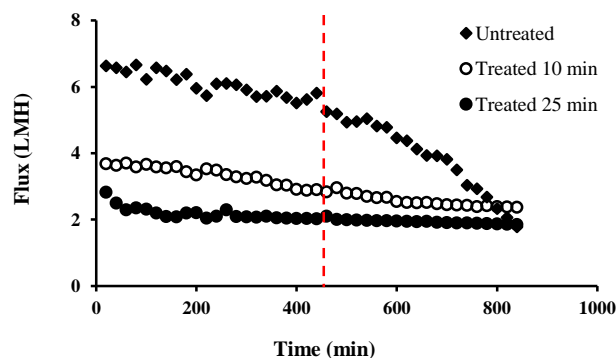

Figure 5 Water fluxes of untreated and treated CTA membrane during the BSA solution filtration

From Figure 5, The results showed the decreased water flux after the treatment by CO_2 plasma and the high salt leakage. BSA solution filtration the treated membrane showed lower water flux for 30% in the beginning and more reverse salt flux than untreated membrane. However, after filtration for 420 min, the water flux of untreated membrane decreased and close to the water flux of treated membrane at 800 min. The modification of CO_2 plasma membrane surface for 10 min and 25 min could improve protein antifouling. The hydrophilic membrane treatment plasma surface could reduce interactions and decreases protein absorption [9]. As the results, the separation performance for BSA solution could also be enhanced by CO_2 plasma treatment. It is, therefore, the treated CTA membrane at 10 min is suitable for protein filtration.

The comparisons of water permeate flux and reverse salt flux of untreated and treated CTA membranes are presented in Table 4.

Table 4 The comparison of water permeability and reverse salt flux for DI filtration and BSA solution filtration with untreated and treated membrane

Type of feed solution	Type of membrane	Water flux (J_w; $L.m^{-2}h^{-1}$)	Reverse salt flux (J_s; $Mol.m^{-2}h^{-1}$)
DI	Untreated	5.85	5.04
	Treated 10 min	3.80	6.12
	Treated 25 min	3.92	8.02
BSA solution	Untreated	5.08	0.03
	Treated 10 min	2.99	2.06
	Treated 25 min	2.30	3.32

From Figure 5 and Table 4, the water flux observed decreased after the CO_2 plasma treatment, reverse salt flux increased. Due to the mass transfer of draw solution at the high molecular density, high osmotic pressure and high water transport resistance retarded the diffusion of water molecule. This made the water molecule unable to diffuse across the membrane.

On the contrary, the greater hydrophilicity may also reduce the water transport resistance, leading to increased water productivity. However, it must be possible that the substrate must make a compromise between high pore size/high flux for avoiding additional resistance to mass transport, and low pore size/ low flux for providing a smooth transition to the top UF membrane which as suggest by Chaharmahali [18]. Hence, the water flux

decreased even though the hydrophilicity increased for FO CTA membrane after treatment by CO_2 gas.

3.2.3 Durability of CTA FO Membrane

In addition, the membrane after chemical cleaning was tested for flux recovery to examine the durability of treated CTA membranes. Their results are presented in Table 3.

Table 3 Permeate flux recovery after chemical cleaning

CTA membrane	Flux recovery (J/J_0) %	
	1st Cleaning	2nd Cleaning
Untreated	96	92
Treated 10 min	98	97
Treated 25 min	98	96

As it is displayed in Table 3, all cleaning conditions are recorded and efficiency of more than 80% after chemical cleaning. The results revealed that the durability of the treated membrane was higher than untreated membrane. The modification of CO_2 treatment could be introduced to the surface which may have better antifouling characteristics of proteins and easily to eliminate.

■4.0 CONCLUSION

CTA membranes treated with CO_2 plasma enhance their hydrophilic nature and their performance. The reduction of the contact angle was presented from $64.04\pm3.13°$ to 9.38 ± 0.00. The optimum condition of plasma power was 20 W with the exposure time at 10 min. The CO_2 plasma etched and changed the functional group of CTA membrane to carboxyl group and its derivative. The results showed the low water permeate flux, high salt leakage flux and high protein antifouling after the treatment by CO_2. The hydrophilic membrane treatment plasma surface could reduce interactions of membrane surface, high roughness and decreases protein absorption.

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