

# Development of Antifouling Polyamide Thin-Film Composite Membranes Modified with Amino-Cyclodextrins and Diethylamino-Cyclodextrins for Water Treatment

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**ABSTRACT:** The fouling behavior of polyamide thin-film composite (TFC) membranes modified with amino- and diethylamino-cyclodextrins (CDs) through an *in situ* interfacial polymerization process is reported. Modified polyamide TFC membranes exhibited improved hydrophilicity, water permeability, and fouling resistance as compared to the unmodified TFC membranes, while restricting the passage of NaCl salt ( $98.46 \pm 0.5\%$ ). The increase in hydrophilicity was attributed to the secondary and tertiary hydroxyl groups of the CDs, which were not aminated. The membranes modified with amino-CDs had increased surface roughness while the membranes modified with diethylamino-CDs had smoother surfaces. However, despite the surface roughness of the membranes modified with amino-CDs, low fouling was observed due to the highly hydrophilic surfaces, which superseded the roughness. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40109.

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## INTRODUCTION

Thin-film composite (TFC) membranes such as reverse-osmosis (RO) membranes and nanofiltration (NF) membranes are increasingly finding widespread use in water treatment. Among other challenges, membrane fouling is one of the challenges related to using these membranes in water treatment. Membrane fouling decreases the water permeation with time making them expensive to operate.<sup>1,2</sup> Membrane fouling is a process where solutes and particles (foulants) from the feed water physically deposit onto the TFC membrane interfaces resulting in flux decline. In RO and NF membranes, fouling can occur through the formation of a gel layer on top of the membrane as external fouling.<sup>3</sup>

Membrane fouling of TFC membranes is an important problem in water treatment and desalination processes due to high energy consumption and membrane replacement costs required during operation.<sup>4</sup> The typical life expectancy of a TFC membrane is usually 3–5 years. However, fouling drastically reduces the life expectancy of TFC membranes rendering them ineffective within

a short period of time.<sup>5</sup> Hence, much research has been dedicated to finding solutions for reducing membrane fouling, which could ultimately lead to improved performance and extended life expectancy.<sup>4,5</sup>

Researchers seek to reduce the fouling propensity of polyamide TFC membranes by manipulating the surface chemistry of the polyamide thin film. Some of the modification approaches include increasing the hydrophilic properties of the TFC membrane surfaces. Hydrophilic interfaces form a pure water layer, which reduces binding sites for foulants to adsorb and eventually deposit on the membrane surfaces.<sup>6,7</sup> Some studies have focused on the reduction of surface roughness by making smooth membrane surfaces.<sup>8</sup> Smooth surfaces can reduce “valleys” that can act as adsorption sites where foulants can be entrapped and deposited. The disadvantage of smooth membrane surfaces is the reduction of water-adsorption sites, which can ultimately reduce the water permeability of the membranes.<sup>9,10</sup> For example, membranes prepared from 5-isocyanato-isophthaloyl chloride and *m*-phenylenediamine

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**Table I.** Ratios of Amino- $\alpha$ -CDs, Diethylamino- $\alpha$ -CDs, Amino- $\beta$ -CDs and Diethylamino- $\beta$ -CDs Used to Modify Polyamide TFC Membranes

	MPDA (%)	$\alpha$ CDTFC(2A) (%)	$\alpha$ CDTFC(2DA) (%)	$\beta$ CDTFC(2A) (%)	$\beta$ CDTFC(2DA) (%)
Concentration of MPDA	2.00	1.50	1.50	1.50	1.50
Concentration of f-CD	0.00	0.50	0.50	0.50	0.50

Membrane  $\alpha$ CDTFC(2A); membrane modified with 0.5% amino- $\alpha$ -CDs Membrane  $\alpha$ CDTFC(2DA); membrane modified with 0.5% diethylamino- $\alpha$ -CDs Membrane  $\beta$ CDTFC(2A); membrane modified with 0.5% amino- $\beta$ -CDs; Membrane  $\beta$ CDTFC(2DA); membrane modified with 0.5% diethylamino- $\beta$ -CDs.

(MPDA) showed improved hydrophilicity and antifouling properties. It was also shown that the antifouling properties are closely correlated with the hydrophilicity and surface roughness of the membranes.<sup>11–13</sup>

Other studies have also shown that membrane fouling resistance can be improved by incorporating active organic modifiers into the membranes during the interfacial polymerization process. Organic modifiers such as 4,4'-methylene bis(phenyl isocyanates), poly(ethylene glycol) (PEG), and *in situ* hydrophilic surface modifying macromolecules (iLSMM) have been used to improve hydrophilicity and antifouling properties of membranes.<sup>6,14</sup> The downside of using these modifiers is the flux decline that is observed for these modified membranes.<sup>6,14,15</sup> Hydrophilic polymers such as amino PEG monomethylether were also grafted onto membrane surfaces to improve antifouling properties.<sup>16</sup> Relative improved membrane fouling resistance was observed for these membranes because of the enhanced hydrophilicity and steric repulsion effect. However, the drawback was that the reaction between the macromolecules introduced and the membrane surface was sluggish, and these macromolecules failed to cover the entire active membrane surface, which consequently introduced roughness.<sup>16</sup> Therefore, this research study focuses on modifying polyamide TFC membranes with cyclodextrins (CDs) in order to improve their hydrophilicity, water permeability, and fouling resistance.

CDs are cyclic oligosaccharides that consist of 6, 7, and 8 glucose units and are commonly known as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs, respectively. These glucose units are interconnected by  $\alpha$ -1,4-glycosidic bonds and possess exterior hydroxyl groups. CDs have been used in modifying membranes for different applications such as pervaporation and enantioseparation processes.<sup>17</sup> For instance,  $\beta$ -CDs were immobilized onto an ethylene-vinyl alcohol (EVA) copolymer with ethylene using regular extrusion with glycerol as an adjuvant and increased permeability was observed.<sup>17</sup> This was attributed to the internal cavity of the CDs.<sup>17</sup>  $\alpha$ -CDs were cross-linked with hexamethylene diisocyanate to make polymeric membranes, which were used for the separation of *o*-/*p*- and *o*-/*m*-xylene isomer mixtures by pertraction from water.<sup>18</sup>

In our previously reported work, amino functionalized cyclodextrins (CDs) were incorporated into the polyamide active thin-film barrier through *in situ* interfacial polymerization.<sup>19</sup> Mbuli et al. tested these modified TFC membranes for the removal of NaCl and NaSO<sub>4</sub> salts, but the removal of organic molecules and fouling behavior were not reported.<sup>19</sup> Therefore, this article reports on the fouling behavior of the membranes using PEG as model organic foulant.<sup>20</sup> It also focuses on studying the effects of the surface morphology and chemistry of the modified membranes towards the fouling behavior. In this

study, an *in situ* modification of the polyamide TFC membrane was carried out using amino-CDs and diethylamino-CDs for the first time. Fouling studies were carried out using PEG-2000 as a model foulant and the performance of the unmodified and modified membranes was compared.

## EXPERIMENTAL

### Materials

$\alpha$ -Cyclodextrins,  $\beta$ -cyclodextrins, sodium dodecyl sulfate, hexane, trimesoyl chloride, and *m*-phenylenediamine were purchased from Sigma-Aldrich (Germany) and Merck (Germany) as received. PES and ultrafiltration (UF) membranes (Radel 300, 10 kDa) were purchased from Microdyn Nadir (South Africa).

### Preparation of TFC Membranes

The functionalization of the CDs into amino- $\alpha$ -CDs, diethylamino- $\alpha$ -CDs, amino- $\beta$ -CDs, and diethylamino- $\beta$ -CDs was achieved via a process previously reported by Mderawan et al.<sup>21</sup> and Mamba et al.,<sup>22</sup> respectively.

Five PES UF membranes were pretreated in sodium dodecyl sulfate (SDS, 0.5%) solution overnight. The UF membranes were then washed with distilled water for 1 h, after which they were left to air-dry under the fume-hood for 2 h. Samples were immobilized onto different glass plates using double-sided tape together with a paper tape along the edges in order for interfacial polymerization to occur on the surface of the UF membrane. Table I shows the aqueous solutions used for these experiments after pH adjustment (pH 8) using ammonium chloride. Different immobilized PES UF membranes were immersed in different aqueous solutions for 5 min, after which the excess aqueous solution was discarded. A series of aqueous solutions were then prepared using MPDA with either the amino-CDs or diethylamino-CDs as shown in Table I. Trimesoyl chloride (TMC, 1%) organic solution in hexane was reacted with each aqueous solution on the prepared UF membranes to form a series of TFC membranes. These were left to stand for 60 s before being cured in an oven for 15 min at 65°C. They were then washed with deionized water to remove the unreacted monomers.

### Fouling and Rejection Studies

Fouling studies of the membranes were performed using PEG (3.00 g L<sup>-1</sup>) with a molecular weight of 2000 g mol<sup>-1</sup> (PEG-2000). A crossflow system was used for the bench-scale water filtration experiments, where three replicates of each membrane type were tested. The unmodified and modified membranes were compacted with deionized water for 6 h at 15.17 bar pressure before the fouling experiments commenced in the crossflow instrument. Compaction was done until a stable flux was obtained. After compaction, the PEG foulant was filtered through the membrane for 1 h before recording the initial water

flux ( $J_0$ ). In each filtration cycle, the PEG (3.00 g L<sup>-1</sup>) solution was filtered for 36 h at room temperature. The antifouling properties of the membranes were all performed under 13.79 bar pressure and the filtrate flow measurements were taken at intervals ( $J_t$ ). The flux ( $J_w$ ) was calculated using eq. (1)<sup>19</sup>:

$$J_w = \frac{V}{tA} \quad (1)$$

where  $V$  ( $l$ ) is the volume of water collected at a particular time ( $t$ ) (h) and  $A$  is the active surface area (m<sup>2</sup>) of the membrane.

The relative flux recovery ( $J_r$ ) was obtained from the equation:

$$J_r = \frac{J_t}{J_0} \quad (2)$$

The rejection of the PEG-2000 was determined using a refractometer and calculated using eq. (3)<sup>19</sup>:

$$R = 100 \times \left( 1 - \frac{C_p}{C_f} \right) \quad (3)$$

where  $C_p$  is the pollutant concentration of the permeate stream and  $C_f$  is the pollutant concentration of the feed solution.

The rejection of NaCl (1.00 g L<sup>-1</sup>) was measured using a conductivity meter (using the conductivity as a concentration).

#### Zeta-Potential Measurements

Zeta-potential measurements were used to study the electronegativity of the surfaces of the unmodified and modified TFC membranes. The zeta-potential measurements were recorded using an Anton Paar SurPASS Electrokinetic Analyzer. KCl (0.01 M) was used as an electrolyte. The pH of the electrolyte was adjusted using 0.1 M HCl and 0.1 M NaOH.

The zeta-potential measurements were calculated from the measured streaming potentials using the Fairbrother-Mastin equation [eq. (4)]<sup>23</sup>:

$$\frac{\Delta\varphi}{\Delta P} = \xi \frac{\varepsilon_0 \varepsilon_r}{\eta \lambda_0} \left( \frac{\lambda_h R_h}{R} \right) \quad (4)$$

where  $\Delta\varphi_s$  is the measured electrical (streaming) potential in the flow cell,  $\Delta P$  is the applied pressure in the cell used to force the electrolyte to flow over the charged surfaces,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the relative dielectric constant of the electrolyte solvent,  $\xi$  is the zeta-potential and  $\eta$  is the dynamic viscosity of the electrolyte,  $\lambda_0$  is the bulk conductivity of the circulating electrolyte,  $\lambda_h$  is the electrical conductivity of the highly saline reference solution,  $R_h$  is the measured electrical resistance across the flow channel filled with the highly saline reference solution,  $R$  represents the measured electrical resistance across the flow channel filled with the normal experimental electrolyte.<sup>23</sup>

#### Attenuated Total Reflectance Fourier Transform-Infrared (ATR-FTIR) Spectroscopy and Contact Angle Measurements

ATR/FTIR analysis was performed to ascertain the concentration of PEG-2000 on the fouled membrane. The ATR/FTIR spectra were collected using a Perkin Elmer, Spectrum 100, ATR/FTIR spectrometer. The ATR/FTIR studies of the TFC membrane samples were carried out on a germanium crystal. The angle of incidence was fixed at 45° and this gave a probing depth of about 0.4 μm in the IR region. The degree of contact between

all the samples and crystal was the same for all the samples. Dry specimens of the membrane samples were mounted on the crystal with the active layer facing the crystal surface. Therefore, the absorbance peak intensities from the ATR/FTIR spectra of the fouled and unfouled TFC membranes were considered relative to the concentrations of the PEG foulants adsorbed on the membrane surfaces.

Contact-angle (CA) measurements were obtained by using a Dataphysics Contact Angle Instrument (SCA 20, OCA 15EC). Sessile drop water contact-angle measurements were carried out. Sessile drops of deionized water were dislodged onto the dry surfaces of the membranes at room temperature. Five seconds after depositing the water drop onto the sample, images were captured before measuring the contact angles. Five measurements at different locations of the membrane sample were made and averaged to obtain the membrane's contact angle.

#### Morphological Analysis

Scanning electron microscopy (SEM) images of the TFC membranes were viewed by mounting samples on an FEI NovaNano SEM200 SEM and irradiating them with a beam of 20 kV. All SEM samples were carbon coated. The roughness of the TFC membranes was determined using atomic force microscopy (AFM) analysis using Nanoscope 3D Multimode, Veeco. This instrument utilized SNL cantilevers (Veeco Instruments) with spring constant 0.12 N/m through the contact mode in dry air. This was done at proper magnification and accurate focusing for better viewing of the specimens, after drying the samples for 12 h in a vacuum oven.

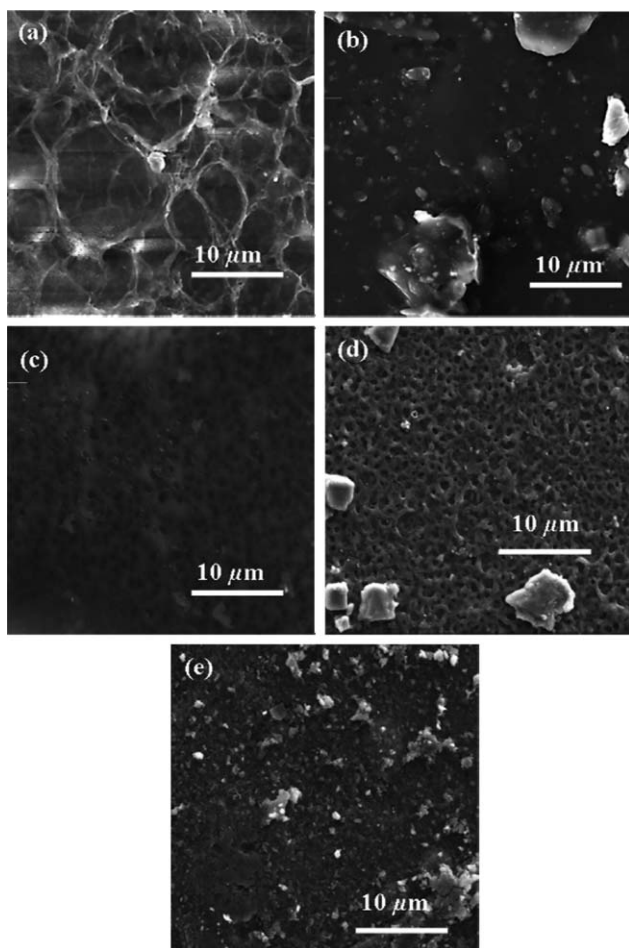
## RESULTS AND DISCUSSION

#### Morphological Analysis of the Polyamide TFC Membranes

SEM and AFM images of the unmodified and modified TFC membranes are shown in, respectively. The SEM images of the top surface of the TFC membranes revealed the nonporous structure of the membranes. The surface of the unmodified membrane was rough with structures that formed a network across the surface of the membranes [Figure 1(a)]. The membranes modified with amino-α-CDs showed structures across the surface of the modified TFC membrane, which potentially increased the roughness of the membranes [Figure 1(b)].

The membrane modified with diethylamino-α-CDs had a rough surface, but not as rough as the surface of the membrane modified with amino-β-CDs [Figure 1(c,d), respectively]. The membrane modified with amino-β-CDs had pore-like structures. These are due to the rearrangement of the polyamide thin film due to β-CDs. The nanosponges interfering with the polyamide thin film matrix caused structural differences as compared to unmodified membranes. Figure 1(A) (Supporting Information) shows SEM images of the modified membranes at a magnification of 20,000×. These highly magnified SEM images clearly show that the pore-like structures are a rearrangement of the polyamide thin film due to the modification.

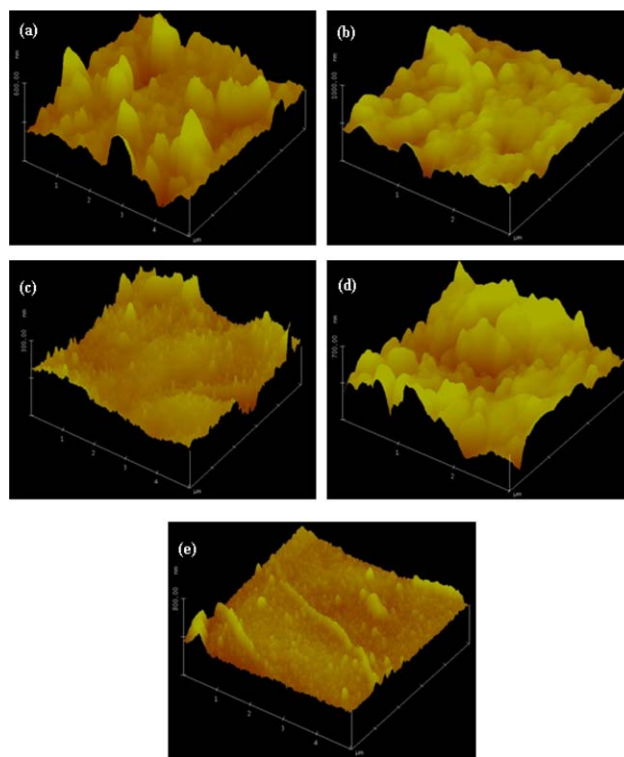
The AFM results confirmed the increase in surface roughness as shown in Figure 2. The AFM surface area projections were 5 × 5 μm<sup>2</sup>. The unmodified membranes showed sharp "peaks" with low "valleys" that could increase fouling propensity due to



**Figure 1.** SEM images of (a) unmodified membrane; (b) membrane  $\alpha$ CDTFC(2A); (c)  $\alpha$ CDTFC(2DA); (d)  $\beta$ CDTFC(2A); and (e)  $\beta$ CDTFC(2DA).

accumulated foulants within the “valleys.” This could lead to entrapment of foulants, which can increase deposition in the “ridges and valleys” of the polyamide thin film. The average roughness of the unmodified membrane was 50.16 nm (Table II). The membranes modified with amino- $\alpha$ -CDs possessed a similar surface roughness of 50.77 nm. This could mean that the membrane modified with amino- $\alpha$ -CDs could be prone to fouling.

It is challenging to avoid membrane fouling as it occurs as a result of the presence of the filtration velocity towards the wall, which becomes a continuous source of foulant particles that keep on increasing in the near-wall region.<sup>24,25</sup> The build-up of the concentration layer is time-dependent because the layer of constant concentration away from the wall resembles a continuous source of particles, which are transported towards the wall by the permeate velocity.<sup>24,25</sup> This results in a progressive build-up of concentration boundary layers. Since this is a mechanical phenomenon that cannot be avoided during filtration, but can be countered by changing the surface chemistry, which prevents foulants from adsorbing onto the interface of the membranes.<sup>24–26</sup> The accumulation of the foulants on the surfaces of the modified TFC membranes was reduced by decreasing proba-



**Figure 2.** AFM images ( $5 \times 5 \mu\text{m}^2$ ) of: (a) unmodified membrane; (b) membrane  $\alpha$ CDTFC(2A); (c) membrane  $\alpha$ CDTFC(2DA); (d) membrane  $\beta$ CDTFC(2A); and (e) membrane  $\beta$ CDTFC(2DA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ble adsorption sites by modifying the membrane with the hydrophilic  $\alpha$ -CDs.

The AFM images reveal that the surfaces of membrane modified with amino- $\alpha$ -CDs were less sharp relative to the unmodified membranes [Figure 2(b)]. The surface “ridges” of the membrane modified with amino- $\alpha$ -CDs had a “hyperbolic” contour whereas those of the unmodified membrane had a “pyramid-like” shape. As a consequence, the “valleys” of the membrane modified with amino- $\alpha$ -CDs were fewer and less deep as compared to those of the unmodified membrane. The same was observed for the membranes modified with amino- $\beta$ -CDs ( $R_a = 66.53$  nm) where the “ridges” were a “hyperbolic” contour. The membrane modified with diethylamino- $\alpha$ -CDs had an average roughness of

**Table II.** Roughness Values of Unmodified and Modified Polyamide TFC Membranes

Membranes	Roughness	
	$R_q$ (nm)	$R_a$ (nm)
Unmodified membrane	70.68	50.16
$\alpha$ CDTFC(2A)	64.75	50.77
$\alpha$ CDTFC(2DA)	17.91	12.70
$\beta$ CDTFC(2A)	87.15	66.53
$\beta$ CDTFC(2DA)	25.93	18.79

12.70 nm (Table II). This was the lowest average roughness observed making this membrane less prone to fouling.

Researchers have reported that preferential locations of resuspension of foulants along the surface exist.<sup>25–27</sup> Under turbulent flow conditions, the local distribution of attached foulant particles may not be uniform because of the presence of near-wall coherent flow structures. These disruptions in the form of membrane roughness could result in spatial fluctuations of the convective flow towards the wall and strong inhomogeneities of wall shear stress leading to foulants detachment.<sup>24</sup> Therefore, having membranes with smooth surfaces is an advantage since this could prevent the adsorption of particles on the surfaces of the membranes. Since, the modified TFC membranes did not have deep “valleys,” there was no deposition of the foulants on the membranes [Figure 2(b)].

The deposition of the foulants on the deep “valleys” of the unmodified membranes could make it difficult to remove the foulants from the membrane surfaces, even with the hydraulic shear force from the water.<sup>25,26</sup> This could result in faster accumulation of the foulants in these “valleys.” Since the unmodified membranes were rougher and hydrophobic, the deposition of the foulants on their surfaces was more favorable as compared to the modified membranes [Figure 2(b,c)]. The explanation was that foulants were readily embedded in the “valleys” of the unmodified membranes and the lifting of deposited material by fluid ejection was not possible [Figure 2(a)]. The foulants were only dispersed by Brownian motion and eventually dragged to the “valleys.”<sup>25</sup>

The membranes modified with amino- $\beta$ -CDs were as rough as the unmodified membrane, whereas the membrane modified with diethylamino- $\beta$ -CDs had smooth surfaces as shown in Figures 1 and 2. These structural differences had an influence on the fouling behavior of the different membranes as well as water permeability and salt rejection properties.<sup>28</sup> Since the surface roughness of the unmodified membranes (50.16 nm) was less than for the membrane modified with amino- $\beta$ -CDs (66.53 nm), their fouling trends were likewise expected to be similar. However, the membrane modified with amino- $\beta$ -CDs [membrane  $\beta$ CDTFC(2A)] was more resistant to fouling than the unmodified membrane. This could be rationalized by considering that the adsorption of foulants onto the membrane surfaces was not only determined by the morphological properties, but also by the hydrophilicity (functional groups) and electronegativity (surface charges) of the polyamide TFC membranes.<sup>29</sup>

As mentioned earlier, the unmodified membrane had a rough surface with sharp and “pyramid-like ridges,” whereas the membrane modified with amino- $\beta$ -CDs [membrane  $\beta$ CDTFC(2A)] had “hyperbolic ridges.” It was noted that the “valleys” of membrane  $\beta$ CDTFC(2A) were shallow in comparison to unmodified membranes. Rough surfaces are more favorable for foulant attachment resulting in more extensive fouling and rapid fouling rates, although in this case, the modified membranes showed resistance to fouling because of their improved hydrophilicity.<sup>30</sup> Here, the hydrophilicity of the modified TFC membranes probably offset its roughness. The membranes modified with diethylamino- $\beta$ -CDs [membrane  $\beta$ CDTFC(2DA)] were

smooth, hence less susceptible to fouling. Since membrane surface roughness has an effect in the flux decline and fouling of TFC membranes, developing membranes with a smooth hydrophilic surface was one of the aims of this study. This was achieved by producing smooth membranes modified with diethylamino- $\beta$ -CDs with relatively high water permeability, selectivity, and fouling resistance.

The average roughness of the membrane modified with amino- $\beta$ -CDs was 66.53 and 18.79 nm for the membrane modified with diethylamino- $\beta$ -CDs (Table II). The membrane modified with amino- $\beta$ -CDs had a higher surface roughness than the unmodified membranes (50.16 nm). This enhanced the water permeability of the membranes because it had a flux of  $22.50 \pm 1.80 \text{ L m}^{-2} \text{ h}^{-1}$ . The unmodified membrane with an average roughness of 50.16 nm had the lowest flux ( $4.55 \pm 1.3 \text{ L m}^{-2} \text{ h}^{-1}$ ), at a pressure of 13.79 bar. The membrane modified with diethylamino- $\beta$ -CDs had a low flux ( $6.70 \pm 1.45 \text{ L m}^{-2} \text{ h}^{-1}$ ), which was comparable to the unmodified membranes. This can be explained by the smoothness of the membrane surface and crystallinity.<sup>31</sup> Smooth surfaces are known to have less projected area than rough surfaces and this means less surface area, which reduces the adsorption sites for water molecules to attach.<sup>28,32</sup> As a result, smooth membranes have reduced water permeabilities as can be observed with the membranes modified with diethylamino- $\beta$ -CDs. Furthermore, from our previous study the membranes modified with diethylamino- $\beta$ -CDs showed higher crystallinity, which can make this membrane impermeable leading to reduced fluxes and higher selectivities (Table II).<sup>31</sup>

The permeability increased with increasing surface roughness because of the unevenness of the membrane skin layer that resulted in the enlargement of the effective membrane surface area.<sup>28,32</sup> This finding was in agreement with the results of Hirose et al.<sup>32</sup> who suggested an approximate linear relationship between membrane roughness, and permeate flux for cross-linked aromatic polyamide RO membranes.

#### Water Permeability and Rejection Properties of the Modified TFC Membranes

The membranes modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs possessed lower contact angles of  $46.78 \pm 0.9^\circ$  and  $51.78 \pm 0.34^\circ$ , respectively (Table III). The modified membranes were more hydrophilic than the unmodified membrane ( $63.35 \pm 0.9^\circ$ ). The improved hydrophilicity of the modified membranes was attributed to the incorporation of the  $\alpha$ -CDs, which contain hydroxyl groups. The unmodified membranes were hydrophobic and this could lead to membrane fouling as it is known that hydrophilic membrane is less prone to fouling.<sup>14</sup>

The unmodified and modified membranes showed high rejection capacities for PEG ( $>99 \pm 0.33\%$ ) throughout the 36 h of the fouling experiment at 13.79 bar pressure. In separate rejection experiments, the membranes modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs rejected NaCl ( $1.00 \text{ g L}^{-1}$ ) salt at  $94.79 \pm 1.4\%$  and  $98.46 \pm 0.5\%$ , respectively, at a pressure of 13.79 bar (Table III). Unmodified membranes rejected  $97.40 \pm 0.12\%$  of NaCl salt at the same pressure. The NaCl salt

**Table III.** Contact Angles, Flux, and Rejection Properties of Modified TFC Membranes

Membranes	Contact angles (°)	Flux (L m <sup>-2</sup> h <sup>-1</sup> )	Rejection (%)	
			PEG-2000	NaCl salt
Unmodified membrane	63.35 ± 0.90	4.55 ± 1.3	>99 ± 0.33	97.40 ± 0.23
αCDTFC(2A)	46.78 ± 0.90	14.37 ± 2.0	>99 ± 0.40	94.79 ± 1.40
αCDTFC(2DA)	51.78 ± 0.34	9.31 ± 1.5	>99 ± 0.50	98.46 ± 0.50
βCDTFC(2A)	40.02 ± 1.10	22.50 ± 1.80	>99 ± 0.31	91.55 ± 1.20
βCDTFC(2DA)	55.10 ± 1.20	6.70 ± 1.45	>99 ± 0.23	97.18 ± 0.78

rejection for all the membranes was comparable. However, the water permeation was improved significantly in the modified membranes relative to unmodified membranes. Membranes modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs were shown to have permeate fluxes of  $14.37 \pm 2.0$  L m<sup>-2</sup> h<sup>-1</sup> and  $9.31 \pm 1.5$  L m<sup>-2</sup> h<sup>-1</sup>, respectively. These values are higher than the permeate flux of  $4.55 \pm 1.3$  L m<sup>-2</sup> h<sup>-1</sup> observed for the unmodified membranes. The advantage of the modification was the improved water flux, fouling resistance, and superior rejection properties in comparison to unmodified membranes.

The contact angle of the membranes modified with diethylamino- $\beta$ -CDs was  $55.10 \pm 1.20^\circ$  with a water flux of  $6.70 \pm 1.45$  L m<sup>-2</sup> h<sup>-1</sup>. The membrane modified with amino- $\beta$ -CDs had a contact angle of  $40.02 \pm 1.10^\circ$  as compared to the  $63.35 \pm 0.9^\circ$  of the unmodified membranes (Table III). The amino functional groups caused the modified membranes to have a more hydrophilic surface than the diethylamino functionality as they had slightly higher contact angles. The improved hydrophilicity of the modified membranes led to increased fouling resistance because hydrophilic surfaces are known to be less susceptible to fouling as a result of fewer hydrophobic interactions between foulants and membrane surfaces.<sup>28,32</sup> The thin water film that is formed on the membrane interface due to the hydrophilicity reduces any hydrogen bonding formation between the foulant and the membrane surfaces.<sup>6,7</sup> The membrane modified with the amino- $\beta$ -CDs was rougher than the unmodified membrane, which could make the membrane prone to fouling. However, the modified membrane was hydrophilic, which resulted in increased fouling resistance. Rough but hydrophilic membranes are prone to fouling than rough membranes that are hydrophobic.<sup>30,33,34</sup> Therefore, the unmodified membranes were more susceptible to fouling due to being rough and hydrophobic.

The membranes modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs also maintained high rejection capacities that were comparable to the unmodified membranes. For example, the membranes modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs rejected NaCl by  $91.55 \pm 1.2\%$  and  $97.18 \pm 0.78\%$ , respectively (Table III). The rejection of the membranes modified with diethylamino- $\beta$ -CDs was comparable to  $97.40 \pm 0.23\%$  NaCl salt rejection of the unmodified membranes at a pressure of 13.79 bar. The membrane modified with amino- $\beta$ -CDs was slightly lower than the unmodified membranes by 5.85%. However, these modified and unmodified membranes rejected  $>99 \pm 0.33\%$  of the PEG-2000. This implies that the modified

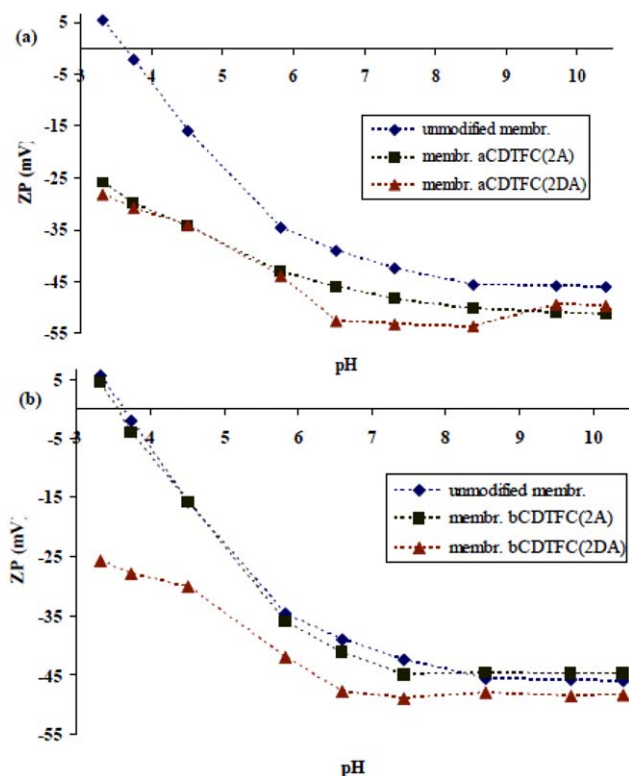
membranes had significantly improved water permeability and fouling resistance, while maintaining high salt-rejection capacities. Furthermore, the electronegativity of the membranes contributed to the high rejection capacities of the membranes. This was unique from these modified membranes because other kinds of modifications have suffered the disadvantage of improving fouling resistance at the expense of water permeability or rejection capacities. For example, membranes that were modified with methacrylic acid showed improved fouling resistance and rejection, but the water permeability declined by 36% when compared to the unmodified membranes.<sup>35,36</sup> Furthermore, membranes that were modified with triglyme with improved fouling resistance had their water permeability decreasing by 18%.<sup>33,35</sup> The incorporation of the CDs onto the membranes proved to maintain high rejection capacities while improving their fouling resistance and water permeability.

#### Zeta-Potential Analysis

The zeta-potentials of the amino-CDs and diethylamino-CDs were determined to ascertain the influence of the CDs on the surface charges and electrokinetic properties of the membranes. The electronegativity, functionality, and hydrophilicity of membranes have an impact on their fouling behavior as it influenced the affinity of fouling materials on the membrane surface.<sup>23</sup> The electrokinetic phenomena relate to the net interaction between a charged surface and a particular electrolyte.

The zeta-potential of the unmodified and modified TFC membranes is shown in Figure 3. The modified membranes are more electronegative than the unmodified membranes. The isoelectric point for the unmodified membranes was at pH 3.6. The modified membranes were entirely electronegative throughout the pH ranges because of the OH groups from the CDs. The zeta-potential was  $-25.88$  mV for membranes modified with the amino- $\alpha$ -CDs at pH 2 and  $-28.19$  mV for the membranes modified with diethylamino- $\alpha$ -CDs [Figure 3(a)].

The membranes modified with diethylamino- $\beta$ -CDs were the most electronegative membranes as they had a zeta-potential of  $-25.66$  mV at pH 3 [Figure 3(b)]. The membrane modified with amino- $\beta$ -CDs had an isoelectric point of 4.34 mV at pH 3.5 [Figure 3(b)]. These zeta-potentials were lower than those of the unmodified membrane of 5.54 mV at pH 3. All the fouling experiments were conducted at pH 6.8. The zeta-potential at that pH was  $-41.24$  and  $-47.83$  mV for the membrane modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs, respectively. These values differed from that of the unmodified



**Figure 3.** Zeta-potential (ZP, mV) as a function of pH for the unmodified membrane, (a) membranes  $\alpha$ CDTFC(2A) and  $\alpha$ CDTFC(2DA); and (b) membranes  $\beta$ CDTFC(2A) and  $\beta$ CDTFC(2DA). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membrane, which had a zeta-potential of  $-39.15$  mV at the same pH.

Other researchers have shown that membranes modified with PEG have an electronegative zeta-potential as a result of the  $-\text{OH}$  groups from the PEG.<sup>10</sup> Moreover, sodium dodecyl sulfate (SDS) was used by some researchers to change the feed-solution chemistry, which consequently altered the polyamide RO membrane surfaces (electronegative zeta-potential).<sup>26</sup> The sulfate was hydrophilic, making the membranes surfaces hydrophilic. The surface of nonsulfated  $\beta$ -CD14C<sub>6</sub> and  $\beta$ -CD21C<sub>6</sub> nanoparticles were negatively charged with zeta-potentials ranging between  $-15$  and  $-20$  mV.<sup>37,38</sup> This was due to  $-\text{OH}$  groups of the  $\beta$ -CDs oriented towards the water and resulting in surface hydrophilicity of the nanoparticles. This clearly demonstrated that the introduction of electronegative compounds and hydrophilic groups such as hydroxyl and sulfate groups on the membrane surfaces resulted in electronegative zeta-potential.

Hydrophilic membrane surfaces with higher electronegative zeta-potentials have previously shown improved membrane organic fouling resistance and this was observed with the modified TFC membranes of this research study.<sup>39–41</sup> The low hydrophobic interactions between the foulant and membrane surfaces increased the fouling resistance of modified TFC membranes.<sup>42</sup> Polyamide thin films possess  $-\text{COOH}$  and  $-\text{NH}_2$  groups that ionize in aqueous solutions resulting in zeta-potentials that vary

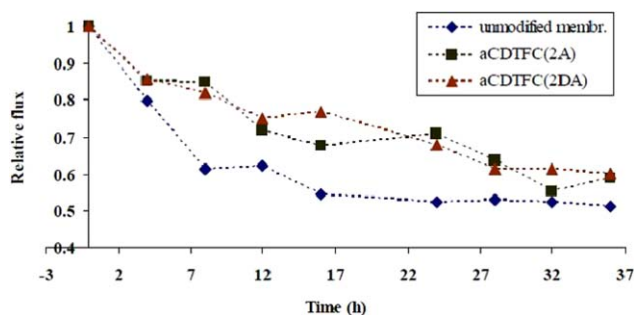
as a function of pH and ionic strength.<sup>42</sup> The introduction of the  $-\text{OH}$  groups into the modified TFC membranes influenced the net zeta-potential towards a more electronegative charge. As a result, the modified TFC membranes were more hydrophilic and electronegative with high rejection capacities of NaCl solute as well as improved water permeabilities (Table III).

### Fouling Studies of the Modified TFC Membranes

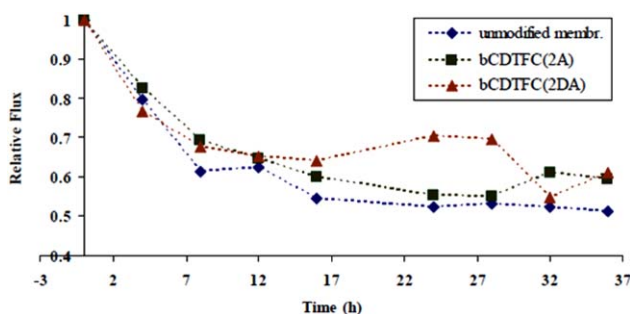
The fouling resistance of the membranes modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs was compared to unmodified membranes by monitoring flux over time. The unmodified and modified TFC membranes were compacted using deionized water for 6 h at 15.17 bar pressure, before the fouling experiments commenced. Compaction was done until a stable flux was obtained and this served as the initial flux for all the membranes. The relative flux for the unmodified membrane and membrane modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs were measured for 36 h as shown in Figure 4. The membranes modified with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs showed higher fouling resistance than unmodified membranes over the period of 36 h. The relative flux of the membranes modified with amino- $\alpha$ -CDs had declined to 59% at the end of the experiment. The membranes modified with diethylamino- $\alpha$ -CDs had a relative flux decline to 60% by the end of 36 h, while unmodified membranes had a relative flux of 51%. Therefore, the unmodified membranes showed a higher relative flux decline than the modified membranes.

Modifying membranes with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs resulted in improved fouling resistance of the membranes as shown by monitoring the relative flux profiles in Figure 4. The membranes modified with amino- $\alpha$ -CDs had relative flux slowly declining from 100% at 0 h to 64% after 28 h. Moreover, the membranes modified with diethylamino- $\alpha$ -CDs had relative flux slowly reaching 61% after 28 h. This differed from the unmodified membrane where a sharp flux decline followed by a steady state of the decline was observed. The sharp flux decline was observed in the first 8 h where the relative flux ratio was reduced from 100% at 0 h to 61% as shown in Figure 4.

To explain these flux declines, we took into account the organic fouling mechanisms of these modified and unmodified membranes. Two types of mechanisms of organic fouling in



**Figure 4.** Relative flux ( $J_r$ ) as a function of time for unmodified membranes and membranes  $\alpha$ CDTFC(2A) and  $\alpha$ CDTFC(2DA). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** Relative flux ( $J_r$ ) as a function of time for unmodified membranes and membranes  $\beta$ CDTFC(2A) and  $\beta$ CDTFC(2DA). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membranes have been identified. The first type involves membrane-foulant interactions that are dependent on the membrane surface chemistry and morphology as well as the chemistry of the foulants.<sup>42</sup> This type is usually demonstrated by membranes that show very sharp flux declines. The second type of fouling mechanism involves foulant-foulant interactions. This type of fouling mechanism is demonstrated by a steady flux decline. In addition, this type of fouling requires that a first layer of foulants is adsorbed on the membrane surface so that a secondary layer can be adsorbed due to interacting with the first layer of foulants. Delaying the adsorption of the first layer of foulants can result in delaying membrane fouling.<sup>32</sup> Thus by making the surface smooth and hydrophilic can reduce adsorption sites for foulants, which could delay fouling. Hence, the membranes were modified with  $\alpha$ -CDs that improved their hydrophilicity. The membranes modified with diethylamino- $\alpha$ -CDs were smooth, which further reduced the adsorption sites for foulants.

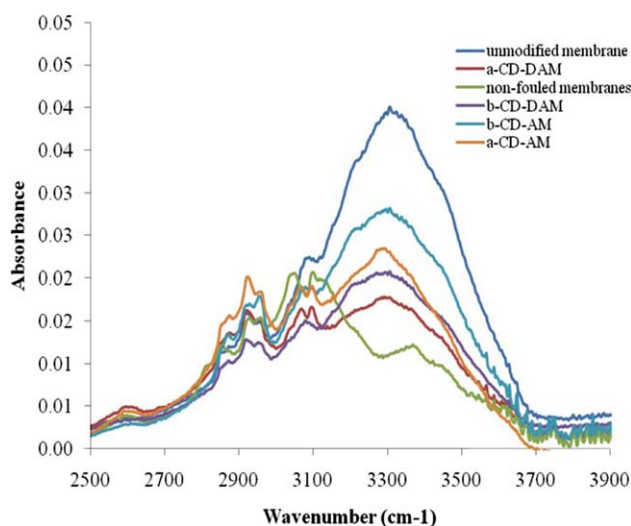
The relative flux profile of the unmodified membrane in Figure 4 shows a rapid and sharp flux decline in the first stages demonstrating membrane-foulant interactions. This type of fouling may result in irreversible foulant films, which can be difficult to remove using backwash methods as the foulants are strongly adsorbed on the membrane surfaces by hydrogen bonding.<sup>39</sup> Membrane-foulant interactions are caused by hydrophobic interactions between the hydrophobic membranes and the foulant, which was observed for the unmodified membranes.<sup>39</sup> The relative flux of the modified membranes exhibited a different fouling behavior because of the slower flux decline than the unmodified membranes (Figure 4). This occurred because the membrane surfaces were hydrophilic, which prevented hydrophobic interactions between the foulants and membrane surfaces, thus preventing hydrophobic membrane-foulant interactions.

It has been reported in the literature that TFC membranes modified with PEG and iLSMM macromolecules have improved hydrophilicity and antifouling performance, but with flux decline.<sup>6,14</sup> In another study, membranes modified with poly(vinyl alcohol) and amino PEG monomethyl ether (MPEG-NH<sub>2</sub>), were grafted onto the membrane surfaces to improve antifouling properties.<sup>15,16</sup> These membranes showed better membrane fouling resistance because of the enhanced hydrophilicity and

steric repulsion effect. However, due to the sluggish reaction between the MPEG-NH<sub>2</sub> macromolecules and the membrane surfaces, these macromolecules failed to cover the entire active membrane surface area causing defects.<sup>16</sup> When compared to what has been reported on other modified membranes in the literature, the modified membranes prepared in this study performed better with respect to reduced roughness, increased water permeability, and fouling resistance.

The membranes modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs were also compared for their fouling behavior with the unmodified membranes over a period of 36 h as shown in Figure 5. As shown, the relative flux of the unmodified membrane as well as that of the modified membranes decreased sharply. The difference between the unmodified membranes and membranes modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs was the reduction of relative flux the unmodified membranes by 38.8% as compared to 30.8% and 32.2% for the modified membranes, respectively. After 8 h of the fouling experiment, the flux decline stabilized for all membranes. The inference is that the fouling occurred at the beginning of the experiment and it involved the membrane surface-foulant interactions.

The modified membranes were hydrophilic; hence the flux decline was reduced contrary to the unmodified membranes that had a further flux decline up to 16 h after the start of the experiment. Thereafter it stabilized until the end of the experiment. Within 36 h, the flux had declined to 51.2% for the unmodified membrane as compared to 59.4% and 61.0% of the membranes modified with amino- $\beta$ -CDs and diethylamino- $\beta$ -CDs, respectively. The decreased flux decline of the modified membranes was due to the electronegativity and hydrophilicity of the membranes that prevented the adsorption of the foulants on the membrane surfaces.



**Figure 6.** ATR-IR spectra of the nonfouled modified membrane, fouled unmodified membrane, modified membranes with amino- $\alpha$ -CDs and diethylamino- $\alpha$ -CDs showing the fouling concentrations. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



### Determination of Foulant Adsorption Using the ATR-IR Spectroscopy

The nonfouled membranes were analyzed and there was a weak peak intensity identified at  $3,275\text{ cm}^{-1}$  characteristic of  $\text{—OH}$  groups from the CDs as shown in Figure 6.<sup>43,44</sup> Since the  $\text{—OH}$  peak intensity showing the presence of the CDs on the nonfouled modified membranes was weak, the  $\text{—OH}$  groups from the PEG could be monitored and estimated using the ATR-IR spectroscopy. One ATR-FTIR spectrum of the nonfouled was chosen as the functional groups were similar for all the nonfouled polyamide TFC membranes. In Figure 6, the nonfouled membrane, which was the control membrane had weak absorbance peak intensity. The absorbance peak intensity of the fouled unmodified membranes was higher than that of the modified membranes. This suggested a higher adsorption of the PEG on the surfaces of the unmodified membranes. This confirmed the fouling degree as elucidated from the fouling trends relative to the flux profiles, which showed more fouling of the unmodified membranes than the modified membranes.

### CONCLUSION

The membranes modified with amino-CDs and diethylamino-CDs were more hydrophilic than the unmodified membranes. They were more hydrophilic because of the presence of the unfunctionalized secondary and tertiary hydroxyl groups from the incorporated  $\alpha$ -CDs and  $\beta$ -CDs. The improved hydrophilicity of the modified membranes translated into improved water permeability and fouling resistance. The amino functionality increased the surface roughness of the membranes for both the  $\alpha$ -CDs and  $\beta$ -CDs when compared to the unmodified membranes. Despite the surface roughness of the membranes modified with amino-CDs, low fouling was observed as compared to the hydrophobic unmodified membranes because of their hydrophilic properties, which off-set the roughness. The rejection of PEG and NaCl salts by all the modified membranes was comparable to the rejection by unmodified membranes. Furthermore, the modified membranes showed significant increase in water permeability coupled with improved fouling resistance.

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