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Flux and Rejection of Methyldiethanolamine from Wastewater by Composite Reverse Osmosis Membrane

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Abstract: Amine based sweetening process has been widely used for the removal of carbon dioxide and hydrogen sulfide from sour natural gas. However, during the process of absorption-desorption, a small amount of amine get carries over and discharged into the effluent wastewater stream. Treatment of amine wastewater using existing wastewater treatment plant (WWTP) without any dilution is very challenging due to its high Chemical Oxygen Demand (COD). However, dilution increases the volume of the wastewater and requires extension of the existing WWTP. Therefore, treatment of amine contaminated wastewater is a major concern for amine sweetening plants. Limited work has been done for treatment of amine contaminated wastewater, especially using membrane separation processes. The present study investigated the flux and rejection characteristics of methyldiethanolamine solution across composite polyamide reverse osmosis membrane (AFC99). The experimental work was carried out to investigate the effect of pressure, cross flow velocity and pH. The findings showed that AFC99 membrane was able to reject up to 99% of MDEA depending on the operating conditions.

Key words: Methyldiethanolamine, wastewater, reverse osmosis, Spiegler Kedem model

INTRODUCTION

Sour natural gas must be purified by removing various impurities, particularly carbon dioxide and hydrogen sulfide before it can be utilized as a source of energy for domestic and industrial purpose. Various amine solutions such as monoethanolamine (MEA), methyldiethanolamine (MDEA) and diethanolamine (DEA) are used for the absorption of these gases (Jou *et al.*, 1997; Sohbi *et al.*, 2007). However, during the process of absorption-desorption and maintenance activities, a small amount of amines get carry over and discharged into the effluent stream due to entrainment, foaming, excessive gas velocities, leakage etc. (DuPart *et al.*, 1993; Abry and DuPart, 1995). Amine wastewater is generally characterized by high Chemical Oxygen Demand (COD) typically about 50,000 mg L^{-1} (Isa *et al.*, 2005). Treatment of amine wastewater using existing wastewater treatment plant (WWTP) without any dilution is very challenging and endangers the process performance of the activated sludge. However, dilution increases the volume of the wastewater and requires extension of the existing WWTP. In addition, the slow degradation rate, requirement of large surface area and disposal requirement of excess sludge are the other drawbacks of existing WWTP (Hospido *et al.*, 2004; Hawthorne *et al.*, 2005). Therefore, the development of a technology which is suitable for effective removal of amines in the high COD amine wastewater is required. Thus, it is the main objective of this study to investigate the removal of methyldiethanolamine (MDEA) from artificial wastewater using reverse osmosis (RO) membrane separation process and predictions of the membrane performance using combined film theory- Spiegler kedem model (CFSK).

Under present study, RO membrane is used due to its high rejection efficiency and ability to meet discharge standards. Modeling of the separation process is essential in the design of membrane separation processes in order to estimate the performance of the process and the corresponding size of the treatment plant required to meet the discharge limit

MATERIALS AND METHODS

Spiegler Kedem model: The working equations of the Spiegler-Kedem model is expressed as (Murthy and Gupta, 1997; Murthy and Chaudhari, 2009):

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad (1)$$

$$R = \frac{\sigma\left[1-\exp\left(-J_v\frac{(1-\sigma)}{P_m}\right)\right]}{1-\sigma\exp\left(-J_v\frac{(1-\sigma)}{P_m}\right)} \quad (2)$$

Corresponding Author: H. Mukhtar, Department of Chemical Engineering, Universiti Teknologi PETRONAS, 31750, Tronoh, Malaysia where, J_v (l/m^2.h) is the permeate flux, L_p (l/m^2.h.bar) is the hydraulic permeability coefficient, ΔP (bar) is the pressure gradient across the membrane; $\Delta\pi$ (bar) is the osmotic pressure gradient across the membrane, σ is reflection coefficient, P_m (m sec^{-1}) is solute transport parameter and R is the true rejection.

The true rejection is the relative change in concentration from the membrane interface to the permeate stream and can be expressed as:

$$R = 1 - \frac{C_p}{C_m} \tag{3}$$

where, C_p (mg L^{-1}) is the permeate concentration and C_m (mg L^{-1}) is the concentration at the membrane interface. The observed rejection, R_o is obtained by replacing the concentration at the membrane interface, C_m in to bulk concentration, C_b (mg L^{-1}) It is expressed as:

$$R_o = 1 - \frac{C_p}{C_b} \tag{4}$$

Film theory model: As membranes are permselective, they allow solvent (water) to pass through while rejecting the solutes and subsequently develops a concentration gradient at the membrane-solution interface due to the accumulation of rejected solutes. Thus, in order to model the transport mechanism of solvent and solute across the membrane, the intersection between the bulk solution and the membrane interface is crucial to be studied. This relation is described using film theory as (Murthy and Gupta, 1997),

$$\ln\frac{1-R_o}{R_o} = \ln\frac{1-R}{R} + \left(\frac{J_v}{k}\right) \tag{5}$$

where, k (m sec^{-1}) is the boundary layer mass transfer coefficient.

Combined film theory-Spiegler Kedem model: In order to model the separation mechanism of the membrane, the Spiegler Kedem membrane transport model is combined with film theory model in order to incorporate the effect of concentration polarization during the separation process. Thus, (Eq. 2) is inserted into (Eq. 5) and rearranged to give,

$$\frac{1-R_o}{R_o} = \frac{1-\sigma}{\sigma}\left[1-\exp\left(-J_v\frac{1-\sigma}{P_m}\right)\right]^{-1}\left[\exp\left(\frac{J_v}{k}\right)\right] \tag{6}$$

Equation 6 is the combined film theory-Spiegler Kedem model (CFSK). The dependent variables ((1-R_o)/R_o) and J_v can be obtained from the experiment. Hence, the model parameters, namely solute transport parameter, P_m, the mass transfer coefficient at the boundary layer, k and the reflection coefficient, σ can be estimated by curve fitting method using R_o and J_v.

Methods: The experimental study was carried out using artificial MDEA wastewater against commercial tubular thin film composite polyamide reverse osmosis membrane (AFC99). The membrane was obtained from PCI Limited, United Kingdom and has an internal diameter of 12.5 mm, length 1.2 m and effective surface are of 0.05 m^2.

The experimental study was carried out using a membrane test unit, which is capable of testing four different tubular membranes simultaneously. Before conducting the actual experimental study, the membrane was subjected to stabilization at 25 bar overnight to avoid possible membrane compaction during the experiment. The experimental studies were carried out at different operating conditions: (1) feed concentrations of MDEA (5000, 10000 and 15000 mg L^{-1}); (2) cross flow velocity (1.5, 3, 4.5 and 6 L min^{-1}); (3) feed pH (3 and 8) and (4) operating pressures (4, 8, 12, 16, 20 and 24 bar). The feed temperature was maintained constant at 25±1°C throughout the experiment. The pH of the wastewater was adjusted using 36% HCl. Experiments were performed in batch circulation mode and the permeate samples were collected every hour for data analysis. The volume of permeate collected versus time was recorded simultaneously using a computer. The concentrations of feed, retentate and permeate were analyzed using UV-Spectrophotometer. Both permeate and retentate were returned to the feed vessel in order to maintain constant bulk concentration. Effect of operating pressure, cross-flow velocity, feed concentration and pH towards membrane permeate flux and observed rejection was investigated.

RESULTS AND DISCUSSION

Effect of pressure on permeate flux and observed rejection: Figure 1 shows the permeate flux and observed rejection for AFC99 membrane under different operating pressure conditions for MDEA solution. The findings show that the permeate flux increases with increases in operating pressure. Studies show that for pressure driven membrane separation process, the permeate flux depends on the net pressure across the membrane (Baker, 2004). Thus, increasing the operating pressure increases the net pressure as well and consequently the permeate flux.

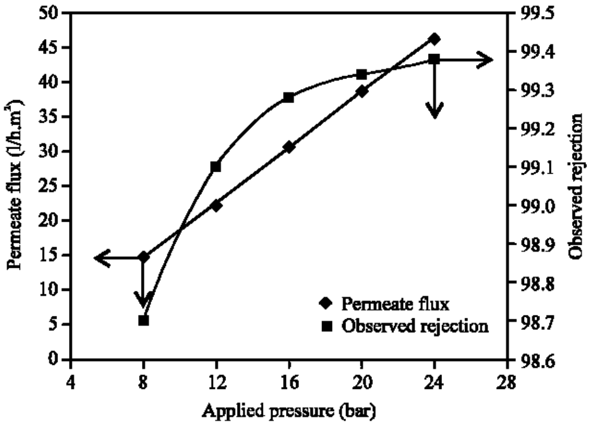

Fig. 1: Effects of pressure on permeate flux and observed rejection (u =6.0 L min^{-1}, C_b = 5000 mg L^{-1}, pH = 8)

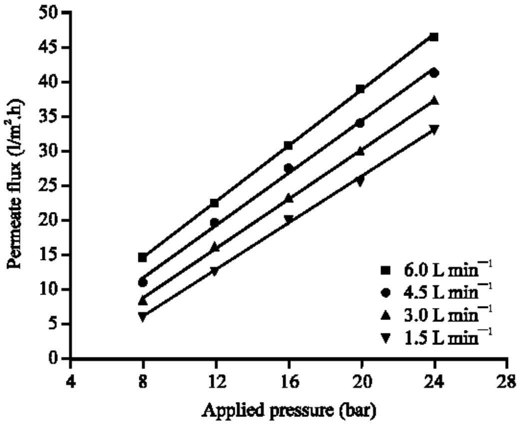

Fig. 2: Effect of cross flow velocity on permeate flux of MDEA solution across AFC99 membrane (C_b = 5000 mg L^{-1} and pH = 8)

The findings also show that the observed rejection of the MDEA solution across the AFC99 membrane was found to increase as the operating pressure increases. The investigation shows that the observed rejection of MDEA increases from 98.0 to 99.4% for the range of operating pressure under the study. Studies show that the solute flux depends on concentration gradient across the membrane. Thus, when the operating pressure increases, the solute passage is increasingly overcome as waster is pushed through the membrane at a faster rate than solute can be transported (Baker, 2004). Hence, the observed rejection increases with increasing pressure.

Effect of cross-flow velocity on permeate flux and observed rejection: Figure 2 shows the effects of cross-flow velocity on permeate flux of methyldiethanolamine solution across AFC99 membrane. The findings show that the permeate flux increases with increasing in cross-flow velocity for the range of operating conditions. This is attributed to the effect of concentration polarization, which occurs due to the accumulation of retained solutes at the membrane-solution interface (Damak *et al*., 2005). Thus, the increase in cross-flow velocity can increases the boundary layer mass transfer coefficient and hence improves the performance of the membranes (Van der Bruggen *et al*., 2002).

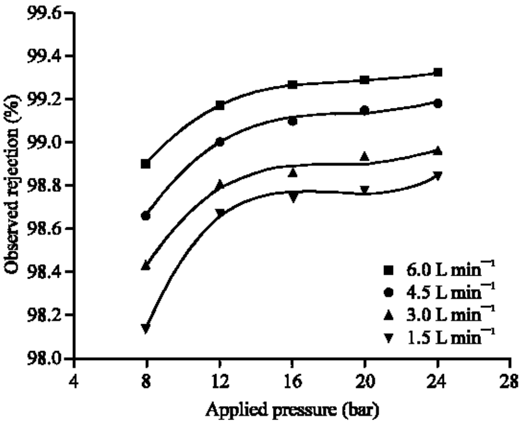

Fig. 3: Effect of cross flow velocity on observed rejection of MDEA across AFC99 membrane (C_b=5000 mg L^{-1} and pH = 8)

Figure 3 shows the effects of cross-flow velocity on observed rejection of MDEA across AFC99 membrane. The findings show that the observed rejection increases from 98.84 to 99.32% when the cross-flow velocity increases from 1.5 to 6.0 L min^{-1}.

The solute flux through the membrane increases due to the increase in concentration gradient at the membrane solution interface during the separation process. However, as discussed above, the increment in cross-flow velocity increases the shear force at the membrane interface and sweeps away the retained solutes and subsequently minimizes the concentration gradient across the membrane. Therefore, this phenomenon reduces the driving force of the solute flux and subsequently increases the observed rejection of the solutes (Baker, 2004).

Effect of feed concentration on permeate flux and observed rejection: Figure 4 shows the effect of feed concentration on MDEA permeate flux at different operating pressure across AFC99 membrane. Results show that the permeate flux decreases as the concentration of the feed increases. This is because increasing feed concentration can effectively increases the osmotic pressure in the solution and the overall

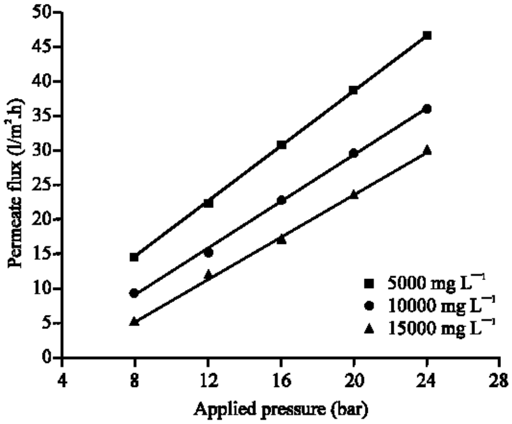

Fig. 4: Effect of concentration on permeate flux of MDEA solution across AFC99 membrane ($u = 6$ L min^{-1} and pH = 8)

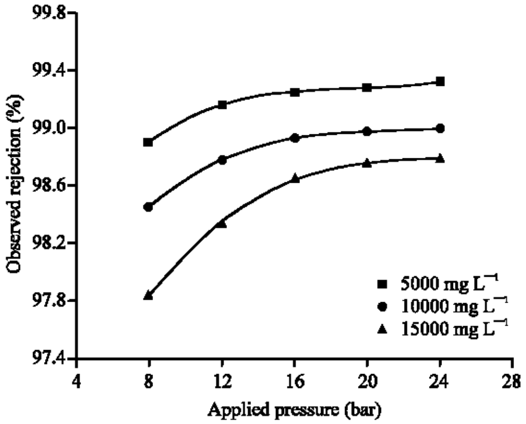

Fig. 5: Effect of concentration on observed rejection of MDEA across AFC99 membrane (u=6 L min^{-1} and pH = 8)

membrane resistance as well. As the result, it reduces the net driving pressure which causes reduction in the permeate flux of the amine (Murthy and Gupta, 1997).

Figure 5 shows the effect of feed concentration on the observed rejection of MDEA solutions across AFC99 membrane. The findings show that the observed rejection of the amine decreases as the feed concentration increases. This is because solute flux across the membrane increases with increases in feed concentration due to the higher effect of concentration polarization and sorption of solutes on the membrane's surface (Ozaki and Li, 2002). Thus, these phenomenon can reduce the effectiveness of the membrane's surface to reject solutes and consequently results in an increase in solute concentration into the permeate flux. Hence, the net effect would be a decrease in solute rejection when the feed concentration increases.

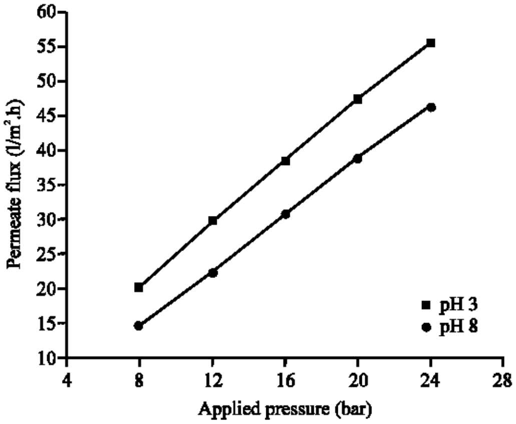

Fig. 6: Effect of pH on permeate of MDEA across AFC99 membrane (C_b = 5000 mg L^{-1}, u = 6 L min^{-1} and pH = 8)

Effect of pH on permeate flux and observed rejection: Figure 6 shows the effect of pH on permeate flux across AFC99 membrane for methyldiethanolamine solution. The finding shows that the permeate flux increased with decreases in feed pH.

Studies show that, the effect of pH on the membrane performance is due to the chemistry of the membrane surface material and the feed solution (Zeman and Zydney, 1996). Due to the presence of dissociable functional groups in polyamide, the surface of the AFC99 membrane can have positive charge when the pH of the feed is strongly acidic and negative surface charge when the feed pH is in alkaline medium (Van der Bruggen *et al*., 1999; Manttari *et al*., 2006). The membrane become more hydrophilic (polar) and will attain wider void space between the polymer matrix due to the repulsion of the functional groups resulting an increase in the permeate flux.

Figure 7 shows the effect of pH on observed rejection of MDEA across AFC99 membrane. The finding shows that the observed rejection increases when the pH decreases from 8 to 3.

MDEA solution is alkaline and forms a positive ion (R_3NH^+) due to protonation of the amine. Thus, when the operating pressure increases, more solutes would be brought closer to the membrane surface and subsequently the electrostatic repulsion between the positively charged membranes and the protonated amines increases and gives higher rejection (Manttari *et al*., 2006).

Estimation of model parameters: The membrane transport parameters were estimated by curve fitting using Eq. 6 is given in Table 1. It can be seen from the table that the values of the solute transport parameter, reflection

Table 1: Estimated parameters for AFC99 membrane using CFSK model

			k*106	Pm*10^8	
C_b (mg L^{-1})	u (L min^{-1})	σ	------ (m sec^{-1})	------	R^2
5000	1.5	0.9921	22.09	2.248	0.946
	3.0	0.9922	34.04	2.467	0.968
	4.5	0.9935	59.08	2.866	0.983
	6.0	0.9949	75.64	3.062	0.992
10000	1.5	0.9904	21.70	1.347	0.943
	3.0	0.9906	31.94	1.536	0.906
	4.5	0.9909	56.97	2.330	0.991
	6.0	0.9916	71.45	2.683	0.994
15000	1.5	0.9890	14.74	2.400	0.989
	3.0	0.9892	25.08	2.958	0.996
	4.5	0.9868	50.87	1.508	0.887
	6.0	0.9890	65.03	2.356	0.924

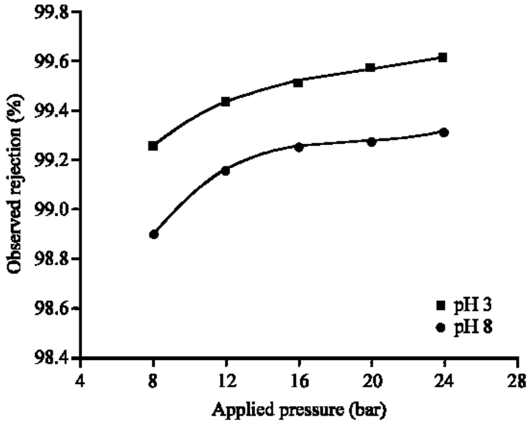

Fig. 7: Effect of pH on permeate of MDEA across AFC99 membrane (C_b = 5000 mg L^{-1}, u = 6 L min^{-1} and pH = 8)

coefficient and mass transfer coefficients are dependent on the cross-flow velocity.

The findings show that the solute transport parameter and mass transfer coefficient increase with increases in cross-flow velocity. This is due to the effect of concentration polarization. The table also shows that the reflection coefficient increases with cross-flow velocity due to the increase in solute rejection.

Modeling results: Figure 8 shows the comparison between the experimental and calculated observed rejection values of AFC99 membrane.

The observed rejection values of the membrane were calculated using Eq. 6 and the estimated transport parameters from Table 1 for a given permeate flux from the experiment. Figure 8 compares the experimental and predicted observed rejection of AFC99 membrane calculated using CFSK model. The findings show that the model predictions of the observed rejection values are in good agreement with the experimental results and the errors are below 3%.

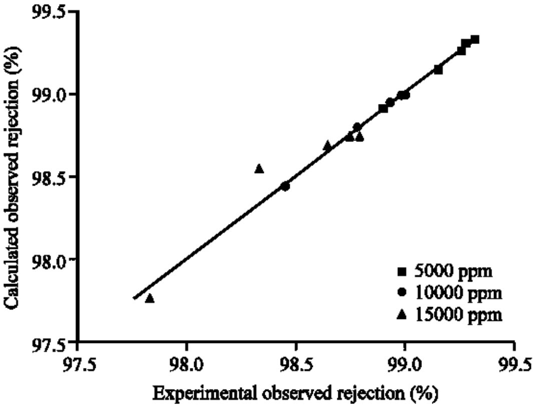

Fig. 8: Comparison of experimental and calculated observed rejection for AFC99 membrane using CFSD model (u = 6 L min^{-1} and pH = 8)

CONCLUSIONS

The removal of Methyldiethanolamine (MDEA) from artificial wastewater was studied using composite polyamide reverse osmosis membrane (AFC99). The operating parameters that affect membrane performance, including operating pressure, cross-flow velocity, concentration and pH were discussed systemically. Increasing operating pressure has increased the observed rejection until it reaches an optimum value. The observed rejection has also increased with increase in cross-flow velocity due to the reduction of concentration polarization. The findings also show that the observed rejection increased with decrease in pH due to the electrostatic repulsion between the positively charged membrane surface and the protonated MDEA. The study of the model parameters showed that the solute transport parameter, the mass transfer coefficient and reflection coefficient has generally increased with cross-flow velocity, but the values decreased with increasing in feed concentration. The calculated observed rejections were also in good agreement with the experimental values.

The overall results show that AFC99 membrane has excellent rejection behavior for removal of MDEA from artificial wastewater. Generally, the study shows that AFC99 membrane can be used as a standalone treatment plant to selectively remove methyldiethanolamine from wastewater.

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