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Removal of Monoethanolamine from Wastewater by Composite Reverse Osmosis Membrane

Azry Borhan*, Muhammad Muhibbudin Mat Johari

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

*Corresponding author: azrybo@petronas.com.my

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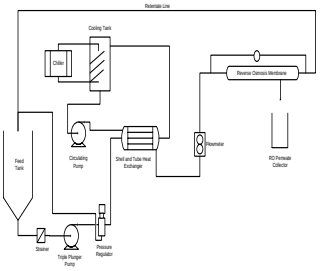
Graphical abstract



Abstract

Monoethanolamine (MEA) has been vastly used for the removal of carbon dioxide (CO_2) in natural gas processing plant. However, during the absorption-desorption process and maintenance activities, a small amount of amine get carries over and discharged into the effluent wastewater stream. Due to its high Chemical Oxygen Demand (COD) and require large volume of water for dilution, therefore treatment of MEA contaminated wastewater is a major concern in most amine sweetening plants. In this research, MEA wastewater generated from PETRONAS Fertilizer Kedah Sdn. Bhd (PFK) was treated via AFC99 tubular thin film composite polyamide Reverse Osmosis (RO) membrane. The effect of operating parameter (transmembrane pressure (TMP), feed concentration and pH) towards permeate flux and MEA rejection were studied to obtain the optimum operating conditions. Experimental results showed that AFC99 membrane is able to reject MEA up to 98% when operated at TMP of 20 bars, feed concentration of 300 ppm and pH of 4. This work shows that the RO membrane was feasible and desirable to be used for removal of MEA contaminants from wastewater. Besides, the treated water fulfills the watering standards.

Keywords: MEA; reverse osmosis; polyamide membrane; TMP; feed concentration

1.0 INTRODUCTION

Carbon dioxide (CO_2) removal is one of the important steps used in petrochemical industry, especially in natural gas processing plant. Prior to further processing activities, the gas stream needs to undergo treatment to remove significant amount of CO_2 to meet specifications for successful liquefaction LNG process [1]. In this step, an absorbent will be used to remove this hazardous gas. One of the absorbent that has been utilized vastly in CO_2 removal is monoethanolamine (MEA), which is used in most acid gas recovery system as it provides sufficient alkalinity to absorb CO_2 [2]. After this MEA solution has been used to absorb CO_2, the solvent will be regenerated and recycled back to the absorber unit to be reused again. However, during the process of absorption–desorption, maintenance and transportation activities, a small amount of MEA may be carried over and channeled into the wastewater stream. Amines are known as toxic material and can affect human health as well as environment depending on the concentration and duration of the exposure [3]. Since MEA is an organic matter, there is a risk that MEA will upset the water stream by increasing the Chemical Oxygen Demand (COD). A high COD value signifies oxygen deficiency in water. Decomposition of organic matter will consume the amount of water-dissolved oxygen, which in turns leads to lack of oxygen and ultimately destroy the aquatic ecosystem. Although the existing technology and facilities are capable of treating all kinds of wastewater contaminated by anthropogenic industrial activities, but the entire system seems to be complex and costly [4]. Prior to effluent release or reuse, the conventional treatment system often involves an array of processes ranging from chemical to mechanical treatment methods [5, 6].

The application of membrane technology in wastewater treatment has been reported since the 1970s [7] and it has become a modern choice of separation technique due to their potential to minimize additional costs and disposal issues associated with current technologies. In many cases, one membrane process is followed by another with the purpose of producing water of increasing purity and quantity for various purposes. The use of the reverse osmosis (RO) technology is the result of the introduction of thin-film composite membranes for their performances of high flux and high selectivity unmatched by other types of membranes [8]. The applications of RO membranes are diverse and can be found in seawater and brackish water desalination, drinking and industrial water production, water softening, removal of natural organic matter from water, food and chemical processing and wastewater treatment [9]. It has been reported that the performance of RO has improved so much in recent years, that the removal efficiency became nearly 100% [10]. Due to this reason it is decided that MEA

removal is crucial and there is no proven technology from literatures that reported work involving the use of RO membrane to treat MEA in wastewater.

The purpose of this paper is to investigate the performance of composite RO membrane separation process towards MEA rejection. Studies on the effect of several operating parameters such as transmembrane pressure (TMP), feed concentration and pH have been selected in order to determine flux and rejection characteristics of MEA across composite reverse osmosis membrane.

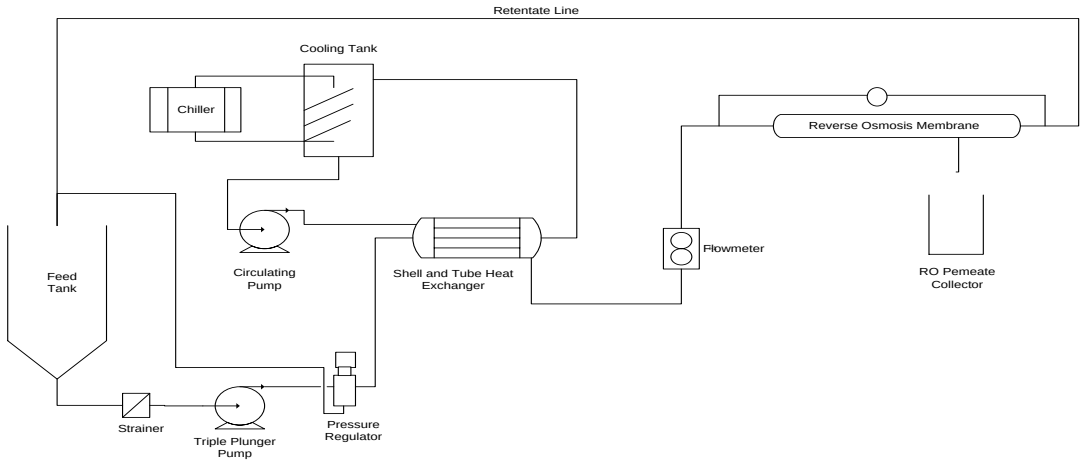


Figure 1 Schematic diagram of membrane test unit

2.0 EXPERIMENTAL

2.1 Theory

The TMP is defined as the average pressure applied across the membrane minus the pressure on the permeate side and can be calculated using the following equation [11, 12]:

$$\text{TMP (bar)} = \frac{(Pf+PR)}{2} - \text{Pp} \quad (1)$$

where *Pf* and *PR* are feed and retentate pressures, respectively and *Pp* is the atmospheric permeate pressure. Permeate flux (*PF*) is defined as volume of permeate obtained per unit area (*A*) per unit time (*t*). It can be expressed as [12, 13]:

$$\text{PF (Lh}^{-1}\text{m}^{-2}) = \frac{1}{A}\frac{dV}{dt} \quad (2)$$

where *dV/dt* is the permeate flowrate and *A* is the membrane effective area. MEA rejection (*R*) on the other hand is referring as the percentage of the amount of MEA that has been removed or rejected by the membrane from its initial concentration. MEA rejection can be calculated using equation below [14]:

$$\text{R (\%)} = 100 \text{ x } (1 - \frac{Cf}{Ci}) \quad (3)$$

where *Ci* and *Cf* represents initial and final MEA concentration, respectively.

According to Interim National Water Quality Standard provided by Department of Environment (DOE), Malaysia, no disposal limit has been defined for specific compound of MEA. The closest reference to determine the disposal limit of MEA in wastewater will be Chemical Oxygen Demand (COD) and can be estimated from the concentration of oxidizable compound in the sample based on its reaction with oxygen to produce water, carbon dioxide and ammonia. COD can be calculated based on chemical equation below [15]:

$$C_2H_7NO + 5/2\ O_2 \longrightarrow 2CO_2 + 2H_2O + NH_3$$

$$\text{COD (ppm)} = (\frac{C}{FW})(\text{RMO}) \ (32) \quad (4)$$

where *C* represents concentration of MEA in the sample, *FW* is the formula weight of MEA (61.08 g/mol) and *RMO* represents ratio of mole of oxygen to MEA to produce CO_2, H_2O and NH_3.

In a two-component gel, it is easy to modify the molecular structure of either of the two components.

2.2 Sample of MEA

Wastewater containing MEA during maintenance activity of an absorbent unit was taken from PETRONAS Fertilizer Kedah Sdn. Bhd., located in Gurun, Kedah, Malaysia. About 30 litre of this solution was collected from the effluent stream before entering wastewater treatment facility. This original MEA solution was first pre-treated using Vacuum Filtration. A Whatman Glass Microfibre filters disc (934-AH) having pore size of 1.5 µm was utilized to filter oil, grease, and suspended solids from the original solution. The filtered MEA is then been used as feed for RO membrane.

2.3 Design of Experiment

The experimental study was carried out using a SOLTEQ® membrane test unit model TR08. A commercial tubular thin film composite polyamide reverse osmosis membrane (AFC 99) produced by PCI Limited, United Kingdom was used because its stability under different operating conditions. It has an internal diameter of 13 mm, length of 1.2 m and effective surface area of 0.05 m^2. A schematic of the RO pilot system is shown in Figure 1 and is used in all experiments. The permeate from RO membrane was collected in a 2000 mL polypropylene beaker and weighed using electronic balance. The process of this treatment is continuous where both retentate and permeate were returned to the

feed tank to maintain constant bulk concentration and feed level. The unit is equipped with cooling system to keep the membrane feed temperature within the operating temperature limit. Three different operating parameters were carried out in this experimental work: (1) TMP of 8, 12, 16 and 20 bars; (2) Feed concentration of 300, 500 and 700 mg/L; and (3) Feed pH of 4, 7 and 10. Both the effect of different feed concentration and pH was performed at four different TMP (8, 12, 16 and 20 bars) for every different parameters. The feed temperature was maintained constant at 25 ± 2ºC throughout the experiment. The pH of MEA feedwater was modified using 38% hydrochloric acid (HCL) and 2M sodium hydroxide (NaOH) solution. MEA standard solution is prepared first by diluting pure MEA into distilled water and obtained its rate of absorbance using different concentration ranging from 20 to 800 ppm. The COD and pH of feed and permeate was measured using HACH UV-vis Spectrophotometer (DR-5000) and EUTECH pH meter (model 510) respectively. All results obtained were than compared with the standards to verify the results.

3.0 RESULTS AND DISCUSSION

3.1 Effect of TMP on Permeate Flux and MEA Rejection

Figure 2 shows the effects of MEA permeate flux for AFC 99 membrane under different TMP conditions. From the figure, the highest value of permeate flux observed at 8, 12, 16 and 20 bars are 3.53, 3.91, 4.18 and 4.28 L/m^{2}h, respectively. The findings show that the permeate flux increases proportionally with increase in TMP within the pressure range studied and become constant after 65 minutes for every runs of the experiment. This phenomenon can be explained from the Darcy's law stating that increase in pressure will consequently increase the permeate flux [8]. Higher TMP indicates that higher driving force was applied across the membrane to push the water molecules to pass through its semi permeable membrane which could result in higher permeates flux [16]. The amount of permeate obtained with increasing TMP can also be explained by the effect of concentration polarization in the system. Concentration polarization occurred due to increase in osmotic pressure that exist due to tendency of water to move from low solute concentration to high solute concentration. The effect of concentration polarization will result in reduced flux and increased the probability of scale development on the surface of the membrane [17]. From the figure, it can be concluded that the effect of concentration polarization is reduced when higher TMP applied to the system. As the effect is reduced, it will result to the increase on permeate flux obtained throughout the system.

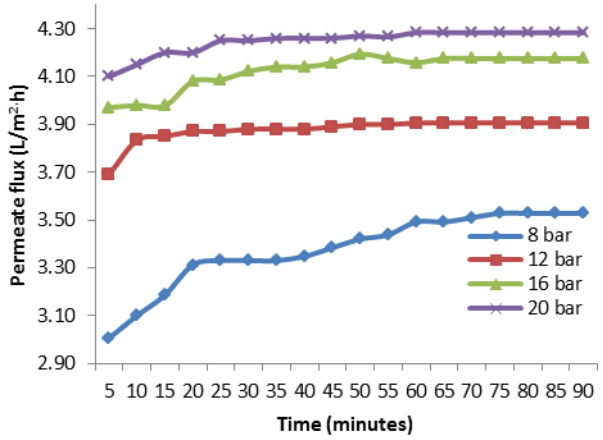


Figure 2 Effect of TMP on permeate flux

Figure 3 shows the relationship between TMP towards the percentage of MEA rejection. From the graph, the trends show that increasing the TMP will result in increase in MEA rejection throughout the membrane separation process. As the TMP is increased from 8 to 20 bars, the percent of MEA removal is increased from 93.7 % to 97.7 %. The graph also shows that the percent of MEA removal becomes constant after 45 minutes for every runs in the experiment. This relationship has been agreed by previous researchers that studied the effect of TMP on ion rejection through membrane separation process. It is said that higher TMP will leads to a denser and compacted membrane structure [18]. As the membrane becomes more compact, molecules other than water will have difficulties to pass through the membrane, hence increasing the rejection of molecules other than water in the treatment process. Higher TMP will also reduce the solute passage and increase water flux throughout the system [19]. This solute passage can be related with earlier scenario where the membrane structure become more compact to allows only water to pass through the membrane. Therefore, increasing TMP to the system will give better MEA removal during membrane separation process.

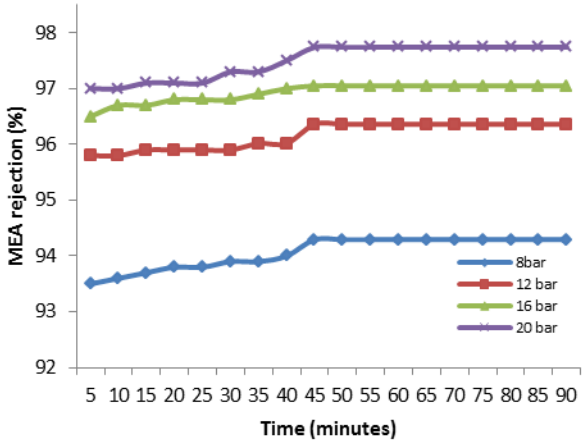


Figure 3 Effect of TMP on MEA rejection

3.2 Effect of Feed Concentration on Permeate Flux and MEA Rejection

Figure 4 show the effect of feed concentration on MEA permeates flux at different TMP across AFC99 membrane. Results show that the permeate flux decreases as the concentration of the feed increases. The highest permeate flux obtained at 300, 500 and 700 ppm are 4.28, 4.14 and 4.01 L/m^{2}h respectively. As seen from the graph, the permeate flux increased with increasing TMP for every feed concentration. This trend has been explained in earlier section. At high feed concentration, the surface become crowded with surfactant molecules hence increasing the concentration polarization effect. As mentioned in earlier, the concentration polarization refer to the pressure gradient resulted from the accumulation of molecules near the membrane. Higher effect of concentration polarization will decrease the permeate flux in the process. At high concentration, the pore blocking is severe due to effect of concentration polarization; hence increase the resistance over membrane surface [16]. Therefore, the permeate flux is decrease. At low concentration, the process will favor the membrane arrangement and the membrane's pore will be unblocked due to less accumulation of molecules over membrane's

surface. Due to that reason, the permeate flux is higher at lower feed concentration throughout the separation process.

Figure 5 shows the effect of feed concentration towards MEA rejection. The findings show that observed rejection of MEA decreases as the feed concentration increases. The percentage removal of MEA has been reduced from 97.3 to 95.4% for feed concentration at 300 and 700 ppm respectively. However, the percent of MEA removal is still increase with increasing TMP. This phenomenon can be explained as at higher feed concentration, the mass transfer coeficient will decrease resulting in low MEA rejection (due to concentration polarization effect). Plus, the solvent (water) flux will be increased more than solute flux at low feed concentration [20]. More water molecules can pass through across the membrane due to high flux leaving the solute from passing together with the solvent through the membrane. Due to that reason, the percent of MEA removal increases at low concentration. This relationship between feed concentration and MEA rejection can also be explained by referring to Donnan exclusion. The presence of charged groups at the membrane will influences the equilibrium of ion distribution in the process. For co-ions, its concentration in the membrane will be lower than in MEA solution while for counter ions, the concentration in the membrane is higher than in MEA solution. In the separation system, co-ion and counter ion will be repulsed and attracted by Donnan potential respectively. This Donnan potential refers to potential difference exists to control the equilibrium between electrochemical of the membrane and the MEA solution. At low concentration, the Donnan exclusion becomes more effective, hence increasing MEA removal throughout the membrane separation process [21].

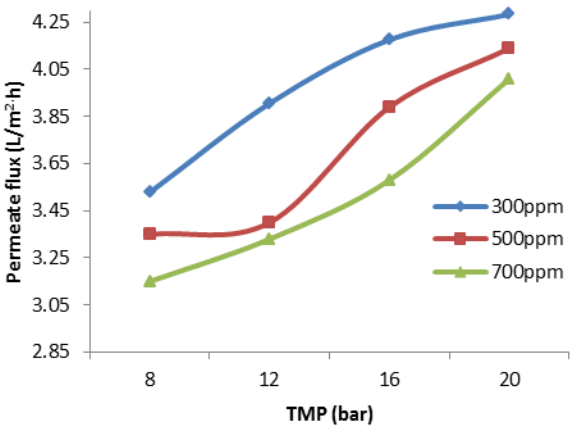


Figure 4 Effect of feed concentration on permeate flux

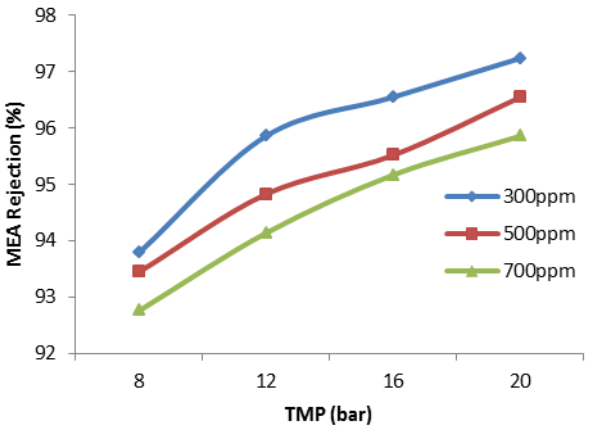


Figure 5 Effect of feed concentration on MEA rejection SEM

3.3 Effect of Feed pH on Permeate Flux and MEA Rejection

Figure 6 below shows the effect of feed pH on permeate flux. Result shows a decreasing in permeate flux when the feed pH was increased from 4 to 10. However, the permeate flux is still increasing with increasing TMP, proving once again earlier relationship between TMP and permeate flux. The relationship between feed pH and permeate flux can be explained by the influence of the pH on the dissociation of the functional groups of the membranes. The membrane will have positively charged below the isoelectric point and will be negatively charged above the isoelectric point. Here, the isoelectric point is at pH 7 [12]. The effect of feed pH can be further explained by referring to the surface chemistry of membrane such as presence of dissociable functional group, degree of their dissociability, and orientation of the functional groups. It was found that, at the surface of composite polyamide membrane, AFC99, there was an excess of carboxylic and amine functional group resides there. This membrane will become positively charged due to protonation of amine functional group in the presence of strong acid. The membrane will become negatively charged with the presence of alkaline due to deprotonation of carboxylic group in the membrane. The electrostatic repulsion between membrane and MEA solute is increase when the membrane is positively charged; results in increase of permeate flux [22].

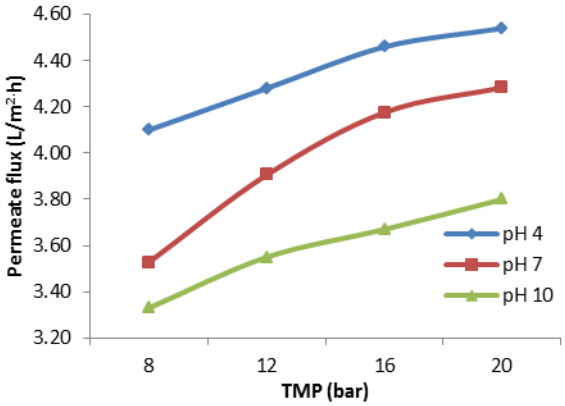


Figure 6 Effect of feed pH on permeate flux

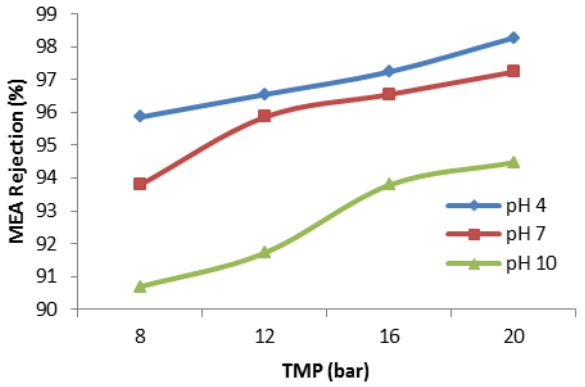


Figure 7 Effect of feed pH on MEA rejection

Figure 7 shows the effect of feed pH towards MEA rejection. It was observed that the percentage removal of MEA decreases with increase of feed pH. The percentage removal of MEA reduces from 98.7% to 94.5 % for feed pH of 4 and 10 respectively. This phenomenon can be explained through electrostatic repulsion between solute and the membrane. The chemistry of amine in MEA was dominated by lone pair electrons on nitrogen atoms. Due to the domination of the lone pair, amine are basic and easily protonated by strong acids, therefore the solute will have positively charged. As mentioned in earlier section, the amine functional groups will be protonated on the surface of the membrane which leads to the membrane also having positively charged with strong acid. Due to the repulsion of positively charged membrane with positively charged solute, the percent of MEA removal increases at low feed pH or when the feed solution is acidic. For high feed pH or when the solution is alkaline, the membrane will become negatively charged due to deprotonation of carboxyl groups in alkaline solution. However, the solute at that condition has no charge because MEA is a weak base. Therefore, lack in repulsion between solute and the membrane cause the percent removal of MEA to be reduced at higher feed pH [22].

3.4 Treated Water Analysis

Table 1 shows the comparison of MEA concentration and pH in the wastewater before and after treatment using the AFC 99 RO membrane. Results were obtained from the process at TMP of 20 bars, feed concentration of 300 ppm and pH of 4.

Table 1 Treated water quality

Parameter	Feed wastewater	Treated water condition	Allowable limit by DOE [12]	Separation
COD (ppm)	300	5	10	98.7
pH	9.5	7.3	6.5 – 8.5	-

The COD content and pH of treated wastewater sample was found to be 5 ppm and 7.3, respectively which is below than allowable limit set by the Interim National Water Quality Standards for Malaysia 2012 [23]. From the comparison, it can be concluded that the treated MEA wastewater by AFC 99 RO membrane is safe to be discharged to the environment as the values comply with the standards.

4.0 CONCLUSION

This study showed that the RO operation using composite polyamide membrane AFC 99 could effectively remove the MEA from wastewater. The removal efficiency of MEA from the wastewater sample is up to 98.7% under the experimental conditions at TMP of 20 bar, feed solution concentration of 300 ppm and pH of 4. It was observed that the permeate flux increase with increasing TMP while increase in feed concentration and pH causes permeate flux and rejection of MEA to decrease. Overall for permeate flux, TMP gave the most impact on it followed by feed concentration and pH. Meanwhile for the percentage of MEA rejection, different feed pH affected the most followed by feed concentration and TMP. The treated wastewater from RO separation met the limitation on MEA treatment provided by the government. Based on that, it is concluded that the product from composite RO membrane separation is safe to people and environment and can be considered as a clean water.

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