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Effect of pH on Flux and Rejection for Diglycolamine and Triethanolamine

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One of the solutions to reduce global warming is controlling carbon dioxide (CO_2) emission to the atmosphere. Therefore, CO_2 that contains in raw natural gas should be removed. Practically, alkanolamine solvent is used to capture CO_2 in raw natural gas. During that process a volume of amines losses in some unit operations caused amines discharged into wastewater having higher chemical oxygen demand (COD). Due to that reason, amines wastewater must be treated prior discharge into the water body. Thus membrane was used to treat the wastewater with different adjusted pH to identify which pH gives better performance for nanofiltration membrane especially. The objectives of this study are to investigate the flux and rejection of two different types of amines called diglycolamine (DGA) and triethanolamine (TEA) across AFC40 membrane, and to evaluate the effect of feed pH on flux and rejection performance for this membrane against various types of amines. The experimental study was conducted to evaluate permeate flux and rejection of amines wastewater using nanofiltration AFC40 membrane at constant feed concentration (5000 mg/L) yet different pH (pH 3 and pH 8) solution. Samples taken from permeate flux study was used for rejection study where the samples was analysed using Standard Method 5220D closed reflux (colorimetric) method. The COD of those samples was measured by HACH DR5000 spectrophotometer at 620 nm. Experimental study showed that DGA obtained higher flux than TEA. This is because lower molecular weight of DGA gave it an advantage to diffuse faster through the membrane due to lesser resistant. Conversely, TEA achieved higher rejected amine compared to DGA. This can be clarified by molecular weight of amines. As TEA (149.19 g/mol) has higher molecular weight than DGA (105.14 g/mol), therefore TEA experienced greater sieving effect that maximised the surface resistant. Hence, higher rejection of TEA produced. Besides that, this study also found that DGA and TEA able to obtain higher flux at pH 8 compared to pH 3. This is because, AFC40 was made from polyamide which contains carboxyl and amine group at the surface which induced positive surface charged due to amine protonation in acidic solution and negative surface charged owing to deprotonation of carboxyl group in alkaline solution. The result showed that the membrane surface rich in carboxyl group at high pH. Therefore deprotonation of carboxyl group caused membrane surface become hydrophilic and looser skin thus higher flux can be gained. On the other hand, pH 3 amines solutions obtained higher rejection than pH 8 solutions. Due to the lone pair electron on nitrogen atom conquered by DGA and TEA, both solutions are actually basic and easily protonated by strong acid thus these solutions turned into positively charged solutes. As membrane surface also induced positive charged at that condition, electrostatic repulsion interaction between solute and membrane resulted in higher rejection for acidic solution. It can be conclude that AFC40 membrane exhibited positive charged at pH 8 and negative charged at pH 3. The result showed that pH variation plays significant role on membrane performance. Overall of this study, pH 3 of TEA showed good observed rejection behaviour towards AFC40 membrane.

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1. Introduction

Producing electricity in power stations, generating heat for homes and industries, and fuel for transportations are some of the natural gas applications. Raw natural gas comprises of a mixture, where methane as the main component, higher hydrocarbons gases (ethane, ethylene, propane, butane etc.), unwanted acid gases (carbon dioxide, hydrogen sulfide etc.) and water. Due to safety and pipeline requirement, as well as to meeting customer's contract provisions and reduce carbon dioxide (CO_2) emission to the atmosphere, CO_2 and hydrogen sulphide (H_2S) that are contained in raw natural gas must be removed (Erayanmen, 2010). Utilization of alkanolamine is the most efficient absorbent and widely been used in natural gas acid gases removal (Ramli et al., 2014). During the process, an amount of amine transported into the effluent and caused the increment of chemical oxygen demand (COD) of the discharged wastewater (Md Isa et al., 2004). Typically, amines wastewater generate about 50,000 mg/L of COD (Luo and Wan, 2013). Whereas, allowable limit stated by local authorities to discharge wastewater into water bodies is 100 mg/L of COD as stated in Environment Quality Act 1974. As such, separation of amine from wastewater is an essential duty prior it can be discharged into water bodies. Therefore, this paper study the membrane specifically nanofiltration membrane to treat amine wastewater.

NF membranes are normally polymeric, asymmetric and consist of a functionally active porous top layer (Pérez-González et al., 2014). According to Mänttäri et al. (2006), surface charges play more important role in NF than other pressure driven membrane processes. Besides that, NF is able to give more flux than reverse osmosis and higher rejection than ultrafiltration. Therefore this advantage made NF popular amongst water and wastewater treatment due to its less fouling designed. However, acidic or basic feed solution introduced to NF may affect its performance. Here, there are some previous studies which showed the role of pH in nanofiltration. Dalwani et al. (2011), studied the effect of pH on performance of thin film composite (TFC) nanofiltration using salt and glucose, found that molecular weight cut off (MWCO) of the membrane increased and reduction in flux when the pH rose more than 11, while Mänttäri et al. (2006), experimented the effect of pH on the filtration performance of commercial nanofiltration membrane using mixture of glucose and natrium chloride (NaCl), reported that membranes was more opens at high pH due to the repulsion of polymer chains. In this present study, diglycolamine (DGA) and triethanolamine (TEA) with different pH are used as artificial wastewater. To be exact, pH of DGA and TEA wastewater will be adjusted to pH 3 and pH 8 using hydrochloric acid. These solutions were fed into membrane system to examine their flux and rejection behaviour. Thus, the objectives of this study are to investigate the flux and rejection of two different types of amines called DGA and TEA across AFC40 membrane, and to evaluate the effect of feed pH on flux and rejection performance for this membrane against various types of amines.

2. Methodology

2.1 Permeate Flux Study

AFC40 membrane was purchased from PCI Limited, United Kingdom. The AFC40 membrane has 0.0125 m internal diameter with 1.2 m length and 0.05 m^2 membrane surface area. AFC40 membrane module was inserted into TR08 membrane test unit. Membrane test unit TR08 was equipped with 20 L of feed and product tanks, tube heat exchanger as temperature controller of fluids, triple plunger pump to pump the feed solution from the feed tank into the turbular membrane module, pressure regulator to regulate the operating pressure and flow meter for cross-flow velocity adjustment. The system also supplied with electronic balance to weight the permeate automatically using a computer with respect to time.

The experiment was carried out as per stated condition. Cross-flow velocity of the system was set at 6.0 L/min and the feed temperature was maintained at 278 ± 1 ^oC. The artificial wastewater was made using DGA and TEA were purchased from Merck and R&M Chemicals respectively. The solutions was made for 5000 mg/L of concentration and the pH of those solutions was adjusted using hydrochloric acid to attained pH 3 and pH 8. The flux was observed at 3, 6, 9,12,15 and 18 bar for each different parameters.

The wastewater from feed tank was pumped into the membrane module for flux observation. Let the system ran for 20 min to reach its steady state. Then, the permeate sample was collected for every change in operating condition. The data such as volume of permeate collected versus time must be recorded for flux calculation.

2.2 Rejection Study

Rejection was studied in terms of feed pH (pH 3 and pH 8) and types of amines (DGA and TEA). Permeate of DGA and TEA that obtained from flux study, and the bulk concentration were determined using HACH Spectrophotometer. Standard Method 5220D closed reflux (colorimetric) method was used for COD measurement. COD of both permeate and bulk solution of DGA and TEA was measured by HACH DR5000 spectrophotometer at 620 nm.

Observed rejection (R_o) can be calculated by the equation :

$$R_o = 1 - \frac{C_p}{C_b} \quad (1)$$

where C_p of concentration of permeate and C_b is bulk concentration

3. Result and Discussion

3.1 Effect of Amines Solution on Permeate Flux

Figure 1 shows the graph of permeate flux of amines solutions against operating pressure across AFC40 membrane. From the trend shown below, DGA achieved higher flux compared to TEA. This behaviour can be explained by difference of the molecular weight (MW) of amines. DGA has smallest MW with 105.14 g/mol that gave it the ability to move faster and achieved the highest flux compared to TEA which has MW 149.19 g/mol. Smaller molecular weight diffused faster than larger ones due to the minimum resistance between the solute and the membrane surface which subsequently increased the permeate flux. In addition, higher molecular weight was identified as having larger impact on membrane fouling and resulted in lower flux (Ozaki and Li, 2002).

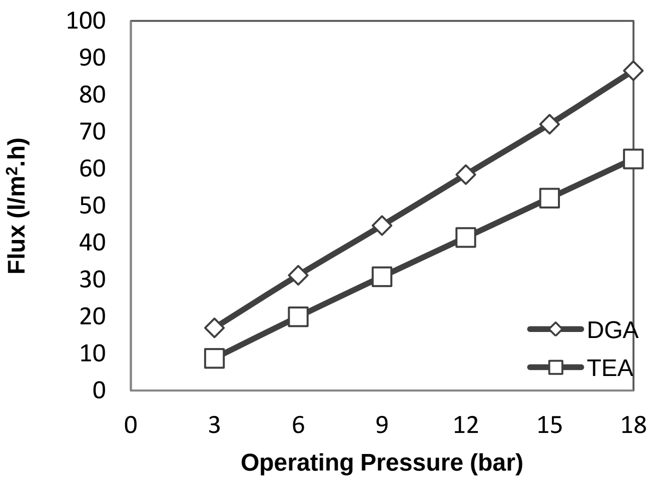

Figure. 1: Effect of DGA and TEA on permeate flux across AFC40 membranes (C_b= 5000 mg/L, u= 6.0 L/min and pH=8)

3.2 Effect of Feed pH on Permeate Flux

Figure 2 shows the effect of feed pH on permeate of DGA and TEA fluxes across AFC40 membrane. From observation, both fluxes of DGA and TEA decreased at pH 3 and increased at pH 8. The effect of the pH can be explained by the dissociable groups on the membrane surface and the degree of dissociable of functional group. When the membrane surface interacted with high or lower pH, it caused the surface become more or less hydrophilic (Mänttäri et al., 2006). Selective layer of AFC40 membrane was prepared from hydrophilic polymeric materials polyamide (PA). The surface has carboxyl (-COOH) and amine ($-NH_2$) groups which induced positive or negative surface charge depending on the pH of the solvent (Bandini et al., 2005). From previously reported work by Luo and Wan (2013), the outer surface of the thin polyamide layer was richer in carboxylic groups at high pH (alkaline) where streaming potential of membrane is from positive to negative. The positive surface charge is due to the protonation of the amine functional group ($-NH_2 \rightarrow NH_3^+$) in strongly acidic medium, whereas the negative charge consequences of deprotonation of the carboxyl groups ($-COOH \rightarrow COO^-$) in alkaline medium (Childress and Elimelech, 2000). This statement is supported with (Dalwani et al., 2011) which mentioned the same behaviour of functional groups. Membrane pore was more open at high pH that caused the flux increased. This was proved by dissociating groups that has been discussed above, the charge of polymer chain started to repel at elevated pH, produced more hydrophilic and looser membrane surface (Mänttäri et al., 2006). Hence, the permeate flux increased. In addition, Nilsson et al. (2008) discovered an increment in water flux after an alkaline cleaning. As well as Al-Amoudi et al. (2008) who found that the calculated pore size of nanofiltration membrane was slightly larger compared to virgin membrane after alkaline cleaning. Therefore, higher permeate flux was obtained at pH 8 compared to pH3.

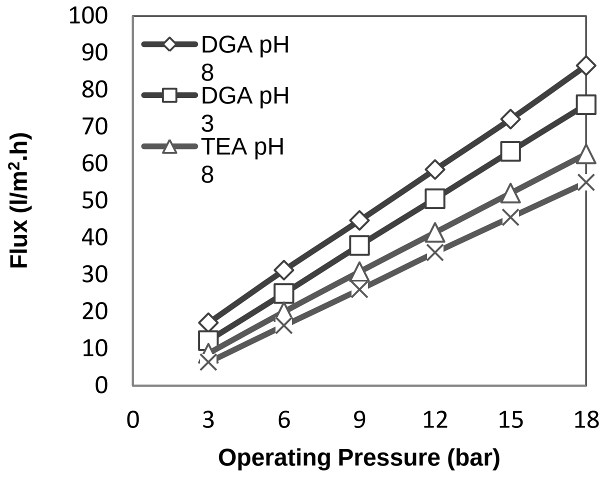

Figure 2: Effect of feed pH on DGA and TEA permeate flux across AFC40 membrane (C_b= 5,000 mg/L and u= 6.0 L/min)

3.3 Effect of Amines Types on Observed Rejection

Figure 3 shows the effect of amine types on observed rejection across AFC40 membrane. The finding showed that TEA achieved the highest rejected amine with 76.50 % followed by DGA with 62.45 % across AFC40 membrane.

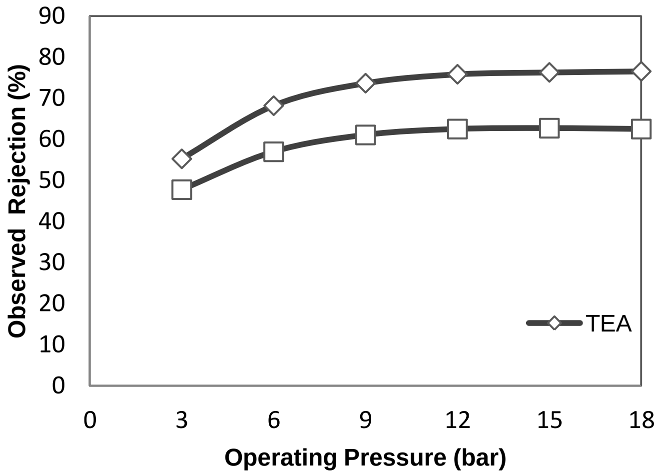

Figure 3: Effect of DGA and TEA on observed rejection across AFC40 membrane (C_b=5,000 mg/L, u=6.0 L/min and pH=8).

The result showed that the rejection behaviour increased due to the MW of amine where MW of TEA is 149.19 g/mol which was higher than DGA with 105.14 g/mol of MW. According to Plakas and Karabelas (2012), larger molecule has greater sieving effect that caused bigger surface resistance for permeate to flow through the membrane. Therefore, this result suggested that the highest the MW, the greater be the rejection.

3.4 Effect of Feed pH on Observed Rejection

Figure 4 shows the effect of feed pH of amines solution on observed rejection across AFC40 membrane. Based on the finding, it showed that the observed rejection increased as the feed pH decreased. From the experiment data, it showed that pH3 experienced greater rejection compared to pH 8. The removal of TEA decreased from 83.79 % to 76.50 % when pH of feed solution increased from pH 3 to pH 8. On the other side, rejection of DGA also reduced from 68.04 % to 62.45 % as the feed pH rose from pH 3 to pH 8. As the pressure increased, it was easier to bring more solute closer to the membrane surface due to the sweeping effect that minimised the cake formation on the membrane surface. In addition, AFC40 was made from polyamide material, therefore it possesses dissociable carboxylic-rich and amine groups, which can exhibit either negative or positive surface charge depending on pH of solution (Mänttäri et al., 2006). In addition, both DGA and TEA have dominated lone pair electron on nitrogen atom which made these amines are basic and easily protonated by strong acid and the solute become positively charged (Borhan and Johari, 2014). As discussed at section 3.2, membrane surface become positively charged in alkaline solution. When positive surface charged of membrane encountered with positive charged of solute, there are electrostatic repulsion experienced between membrane and solutes. Due to that electrostatic repulsion interaction, alkaline solution of amine gave higher rejection compared to acidic solution.

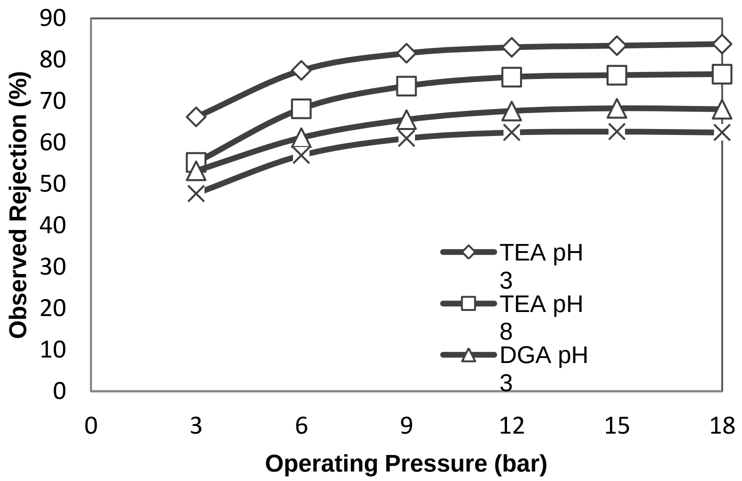

Figure 4: Effect of feed pH on observed rejection of DGA and TEA across AFC40 membrane (C_b=5,000 mg/L, u=6.0 L/min)

4. Conclusion

Types of amines and different feed pH through AFC40 membrane successfully been studied in terms of flux and observed rejection. From the findings, it was found that DGA achieved higher flux compared to TEA and TEA obtained higher rejection than DGA. Different molecular weight of DGA and TEA made this happened. Smaller MW of DGA made it easier to diffuse through the membrane while larger MW contributed bigger resistant to TEA that made it gave higher rejection. Likewise, membrane performance toward different feed pH solutions was also investigated. DGA and TEA was able to obtain higher flux at pH 8 compared to pH 3 as well as higher rejection achieved by pH 3 than pH 8. This is due to the carboxyl and amine groups attached to the AFC40 polyamide support membrane. The membrane triggered positive charged when acidic solution was introduced to the membrane. Vice-versa, the membrane act negatively charged when alkaline solution presented to the membrane. Lone pair electron dominated on nitrogen atom of amine structure made it easier to protonate at acidic medium caused the solution converted to positively charged solutes. As AFC40 membrane induced positive charged at acidic medium, therefore positive charge membrane interacted with positive charge solutes. At this moment, electrostatic repulsion between them become resistant for solutes to come near the membrane surface, thus contributed to lower flux obtained yet higher rejection. In case of negatively charged membrane at alkaline medium introduced with positively charge solutes, electrostatic attraction between them minimized the resistant for permeate to flow to the membrane surface thus produced higher flux and lower rejection. Based on the findings, rejection of TEA decreased from 83.79 % to 76.50 % when pH of feed solution increased from pH 3 to pH 8 and rejection of DGA also reduced from 68.04 % to 62.45 % as the feed pH rose from pH 3 to pH 8.The result shows that pH variation plays significant role on membrane performance. Overall of study, pH 3 of TEA exhibited as the best observed rejection behaviour for AFC40 membrane. In addition, rejection mechanism of AFC40 showed the combination of charge interaction and molecular sieving able to reject up to 83 %.

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