FLUX AND REJECTION OF MONOETHANOLAMINE (MEA) IN WASTEWATER USING MEMBRANE TECHNOLOGY

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ABSTRACT

Treatment of wastewater containing amine solutions is very challenging since it contains very high chemical oxygen demand (COD) and degradation using existing wastewater treatment plant (WWTP) requires process extension and it potentially endangers the process performance. The present studies evaluate the flux and rejection of monoethanolamine (MEA) solutions across three different commercial reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membranes. The experimental work was carried to investigate the effect of operating pressure, feed concentration, cross-flow velocity and pH towards the flux and rejection of those membranes. At all conditions, experimental results showed that the RO membrane has the highest rejection, about 99% as compared to 75% and 35% rejection achieved by the NF and UF membranes, respectively. This work shows that the membrane separation processes, particularly RO, can be used to selectively remove MEA from an artificial wastewater.

Keywords: Monoethanolamine (MEA); Carbon Oxygen Demand (COD); Reverse Osmosis; Membrane Rejection

1. INTRODUCTION

Separation and concentration processes are key processes in industrial effluent treatment as many of the contaminant streams from industries are relatively dilute and thus needs a concentration step prior to disposal. In natural gas purification plant, various amine solutions such as monoethanolamine (MEA), methyldiethanolamine (MDEA), diisopropanolamine (DEPA) and etc are used to remove acid gases particularly carbon dioxide. During the regeneration process, a small amount of amine carries over and discharged in the wastewater. Typically it contains high carbon oxygen demand (COD) in the range of 5,000 to 25,000 ppm. Treatment of these wastewaters using wastewater treatment plant (WWTP) is very challenging since it requires plant extension and it potentially endangers the process performance.

RO and NF membranes have been applied in removing organic compounds [1], pesticides, vegetable oil and oil pollutants, [2] from water to recycle or meet environmental regulations before discharge to sewers. RO membranes were also used successfully in organic environments such as for separation of linear hydrocarbons and carboxylic acids from ethanol and hexane solutions [2]. Several recent studies have investigated the rejection of ionic and organic solutes, which possess ionizable functional groups, through RO or NF membranes. These studies have shown that for organic compounds the removal depends upon the solute size, shape, pH and polarity or hydrophobicity but the key factors that directly affect the rejection are not yet clearly known [4]. Ozaki and Li [1] found that often a high molecular weight or larger molecular width is associated with higher rejection but there is not a universal relationship for all organic compounds. It was found that the rejection of some organic compounds is almost constant in the pH range of 3–9 but for acetic acid and urea, which have the same molecular weight of 60, the rejection values are different [3, 5].

The selective layer of RO and NF membranes could be thought to be a three-dimensional network of polymer chains and therefore, these membranes do not have real pores but just free volume inside the polymer chain network. Even a minor change in this free space would have a clear impact on the membrane permeability and influence on the passage of uncharged molecules. Therefore, the separation process in RO and NF membranes is a combination of sieving and diffusion of molecules through the selective layer of the membranes [2, 6].

The present study investigated the flux and the observed rejection of artificial wastewater containing monoethanolamine (MEA) solutions across three different RO, NF and UF membranes. The effects of operating pressure, feed concentration of MEA, pH and cross-flow velocity were investigated.

2. EXPERIMENTAL WORK

The experimental study was carried out using artificial monethanolamine (MEA) solutions against commercial three tubular thin film composite polyamide RO (AFC99), polyamine NF membranes (FC40) and cellulose acetate UF (CA202) membrane. These membranes were obtained from PCI Limited, United Kingdom. The membrane has the internal diameter of 12.5 mm and length of 1.0 m.

Various concentration of artificial industrial wastewater ranging 5000 to 15,000 ppm containing MEA was prepared. The experiment was carried out using the membrane test unit, which is capable of testing four different tubular membranes simultaneously. Effect of operating pressure, MEA concentration, cross-flow velocity and also pH toward membrane flux and rejection were investigated. The wastewater pH was adjusted using 36% HCl. The volume of permeated collected versus time was recorded online simultaneously. The concentrations of feed, retentate and permeate were recorded using UV-Spectrophotometer.

The observed rejection, R_{obs} of the membrane is calculated by

$$R_{obs} = \frac{C_p - C_b}{C_b} \tag{1}$$

where c_b and c_p is the bulk and permeate concentrations, respectively.

3. RESULTS AND DISCUSSION

The flux and rejection characteristic of MEA across the RO, NF and UF membranes are given in Figures 1 to 5.

3.1 Flux Study

Figures 1(a) to (c) show the permeate flux of difference membranes versus operating pressure. These figures show that the permeate flux increases almost in linear form as the operating pressure increased. As it is expected that the RO membrane has the lowest permeate flux follow by NF and UF membranes, respectively. Due to the high rejection of MEA at RO and NF membranes which cause the concentration polarization to occur, it is clearly seen that the permeate flux at those membranes decreases as the concentration increased. Due to low rejection at UF membrane, the permeate flux at UF membrane is almost independent to the concentration.

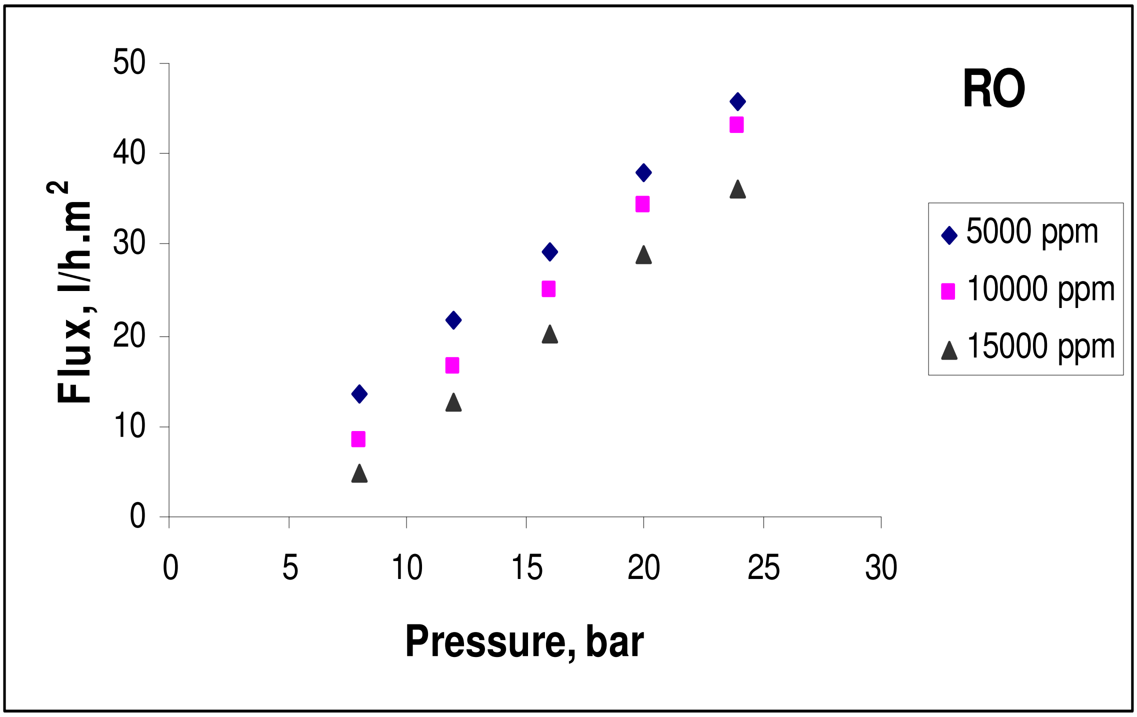

Figure 1 (a): Effect of operating pressure and feed concentration on permeate flux at RO membrane (cross-flow velocity= 6 L/min and pH =3)

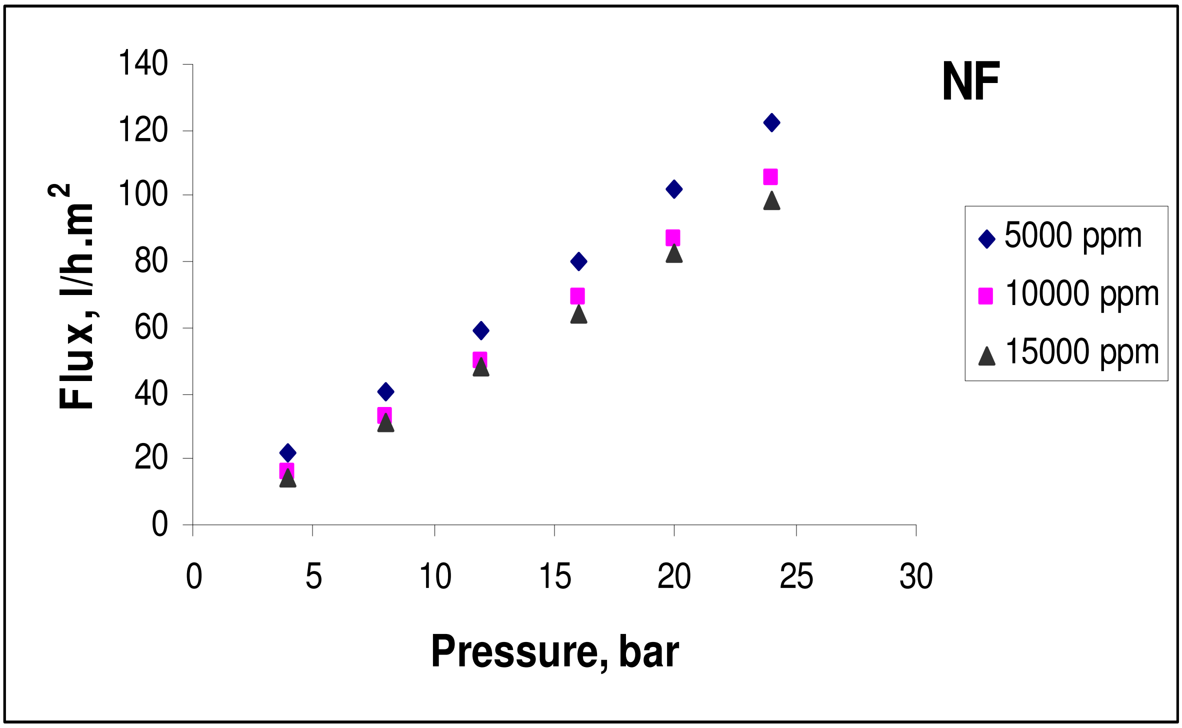

Figure 1 (b): Effect of operating pressure and feed concentration on permeate flux at NF membrane (cross-flow velocity= 6 L/min and pH =3)

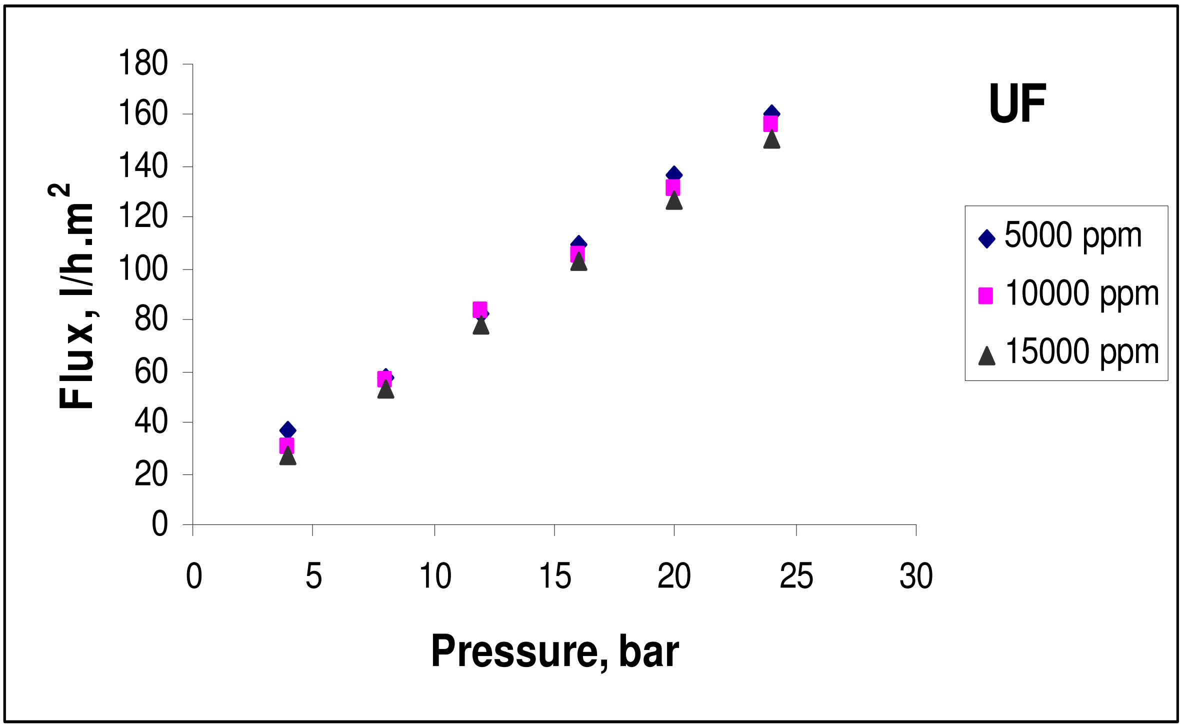

Figure 1 (c): Effect of operating pressure and feed concentration on permeate flux at UF membrane (cross-flow velocity= 6 L/min and pH =3)

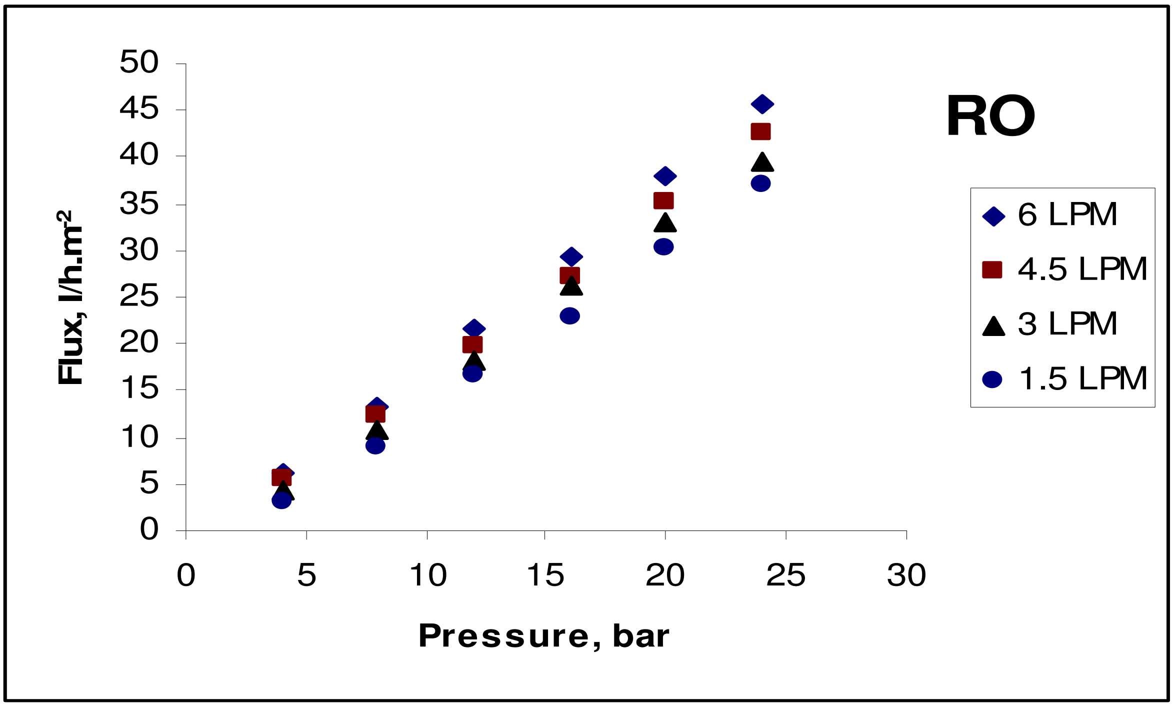

Figure 2(a). Effect of cross-flow velocity on membrane flux at RO membrane. (pH =3)

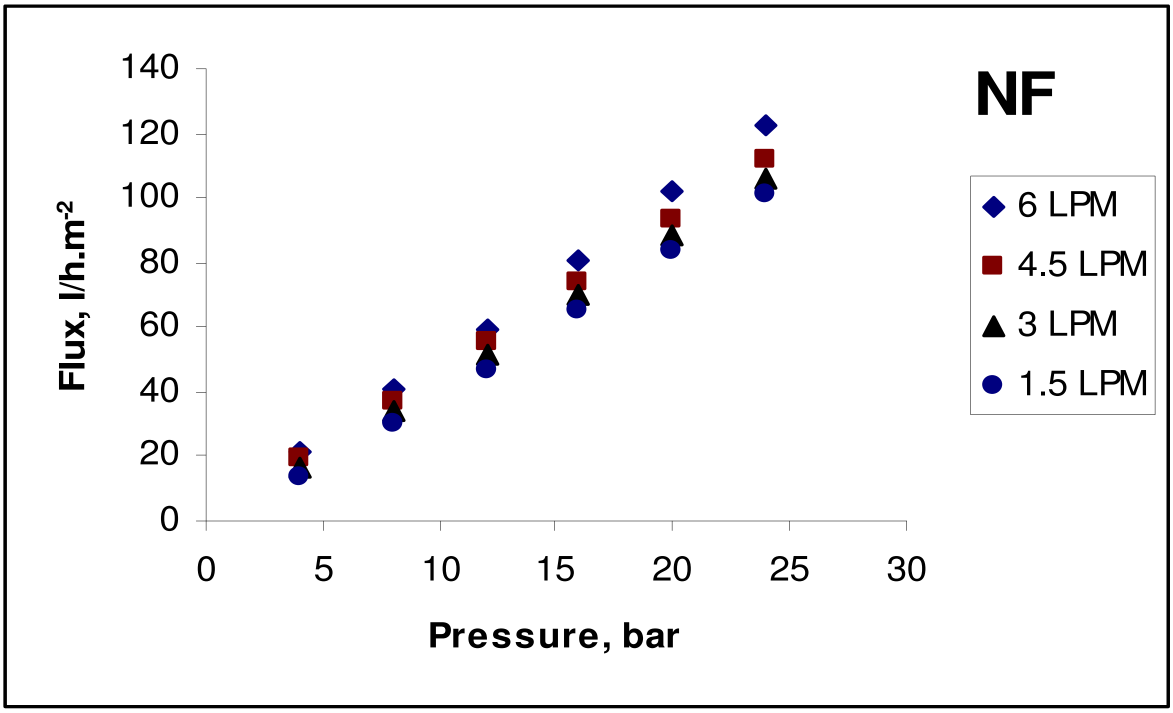

Figure 2(b). Effect of cross-flow velocity on membrane flux at NF membrane. (pH =3)

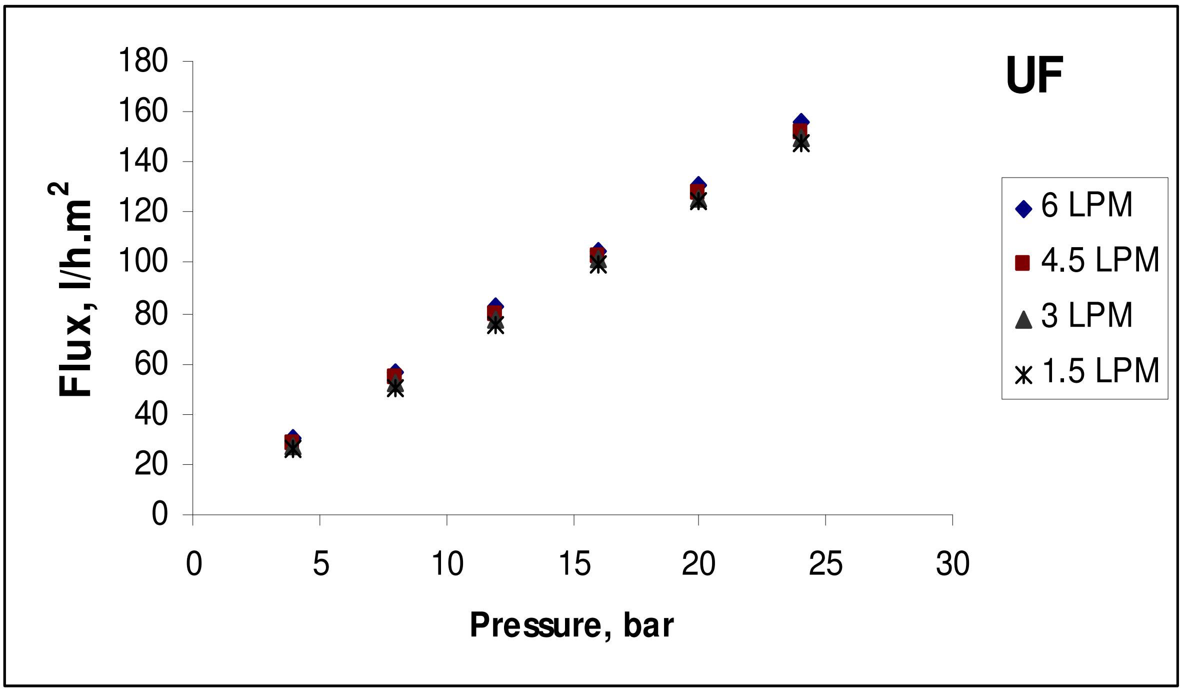

Figure 2(c). Effect of cross-flow velocity on membrane flux at UF membrane. (pH =3)

The cross-flow velocity has some effect on the flux across the RO membrane but has little effect on the NF and UF membrane as shown on Figures 2(a) to (c). Due to high rejection of MEA at RO membrane make the concentration polarization to be more significant. Increasing the cross-flow velocity would reduce the concentration polarization, hence increasing the flux, particularly for Figure 2(a).

It is also noted that increasing the pH from 3 to 8 has increased the membrane flux. This is due to the fact that, when the pH is shifted to strongly alkaline medium the carboxylic groups at the surface dissociate fully and the surface gains its strongest negative charge. However, the negative charge of the polymer chains in the three-dimensional network of the surface start to repel each other and makes the skin layer more open [6]. The free volume of the network increases and the 'pore size' of the membrane skin layer increases and this leads to the increase of flux and reduction of product quality as the solutes can easily pass through the wider free volumes of the membrane surface.

3.2 Rejection Study

3.2.1 Effect of Operating Pressure

Figures 3(a) to (c) show the observed rejection of different membranes against the operating pressure at varies MEA concentrations. These figures show that the observed rejection increases as the operating pressure increased until it reaches at the optimum value. Increasing the operating pressure reduces the shielding factor and makes the repulsion more effective, hence enhance the rejection effect. The results show that the RO membrane has the highest rejection (99%) follow by the NF (55 to 65%) and UF (30 to 35%) membranes, respectively. Due to the concentration polarization, the observed rejection decreases as the MEA concentration increased, particularly for the NF and UF membranes. As NF membrane for example, as the feed concentration of MEA increases from 5000 ppm to 15,000 ppm, the observed rejection was reduced from 70% to 65%.

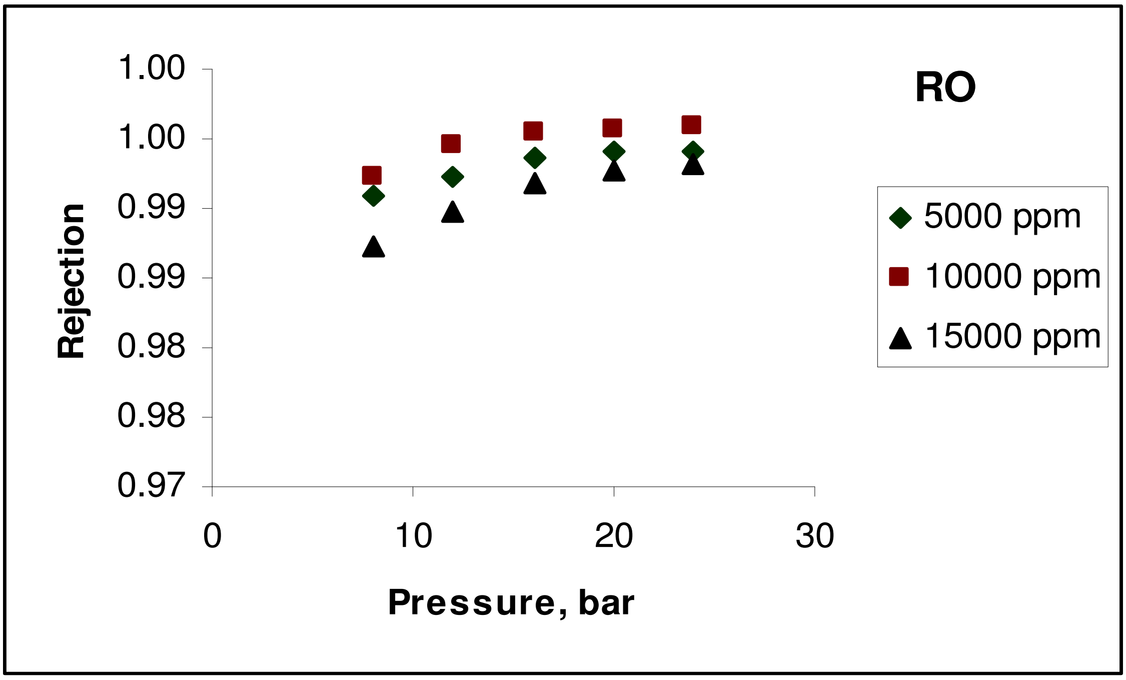

Figure 3(a): Effect of operating pressure on RO membrane rejection at different feed solute concentrations. (cross-flow velocity = 6 L/min and pH =3)

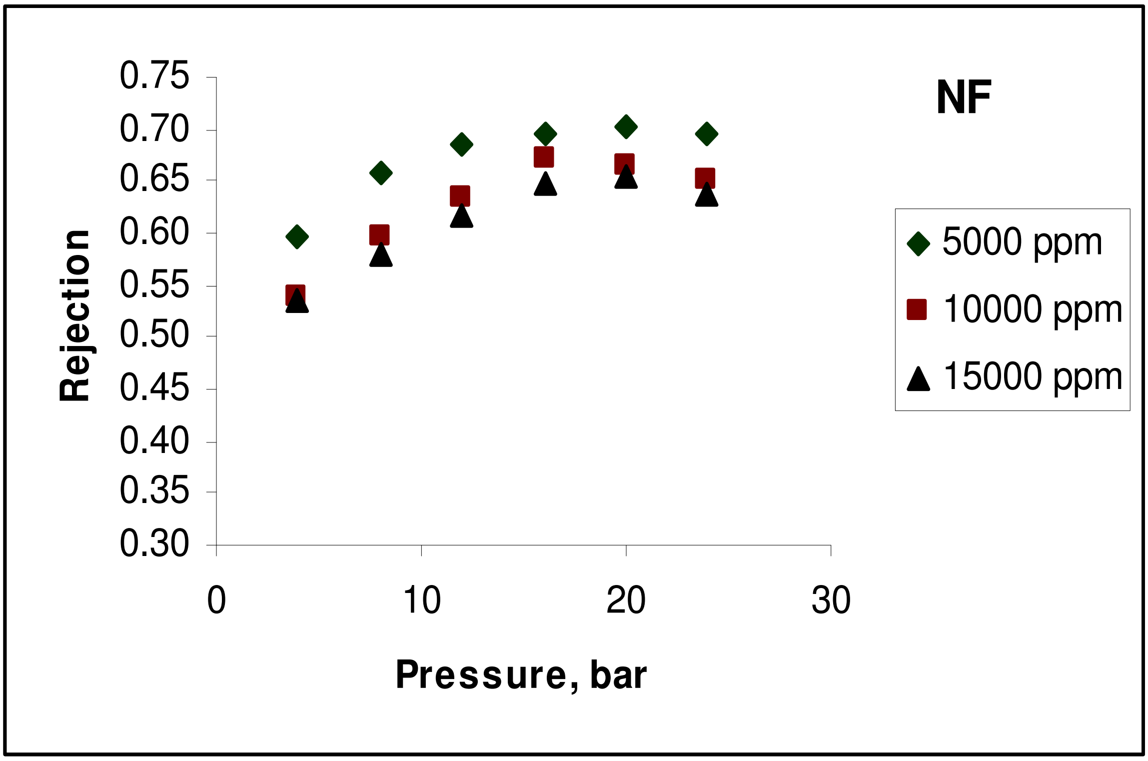

Figure 3(b): Effect of operating pressure on NF membrane rejection at different feed solute concentrations. (cross-flow velocity = 6 L/min and pH =3)

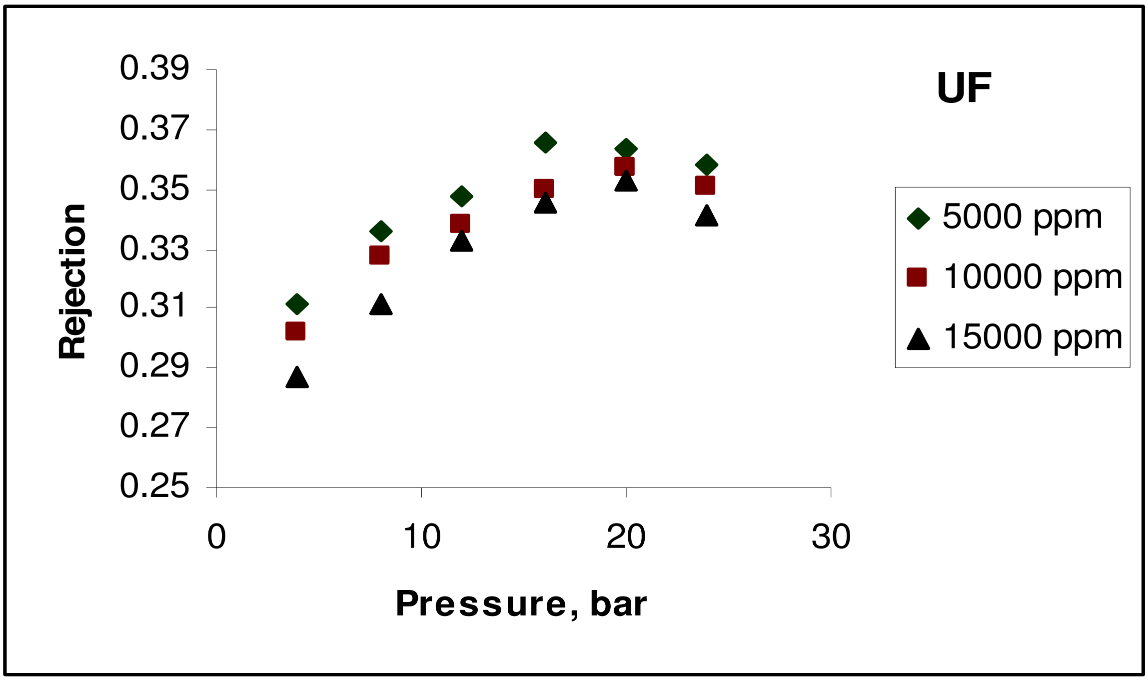

Figure 3(c): Effect of operating pressure on UF membrane rejection at different feed solute concentrations. (cross-flow velocity = 6 L/min and pH =3)

3.2.2 Effect of Cross-Flow Velocity

Figures 4(a) to (c) show the MEA observed rejection of different membranes against the operating pressure varies cross-flow velocity. These figures show that the cross-flow velocity has an effect towards the observed rejection increases. The results show that increasing the cross-flow velocities provides an increase toward the observed rejection. This is due to the reduction of the concentration polarization as the membrane surface, hence increasing the rejection value. Increasing the cross-flow velocity of NF membrane for example, from 1.5 to 6 litre per minute increases the observed rejection from 65 to 70%.

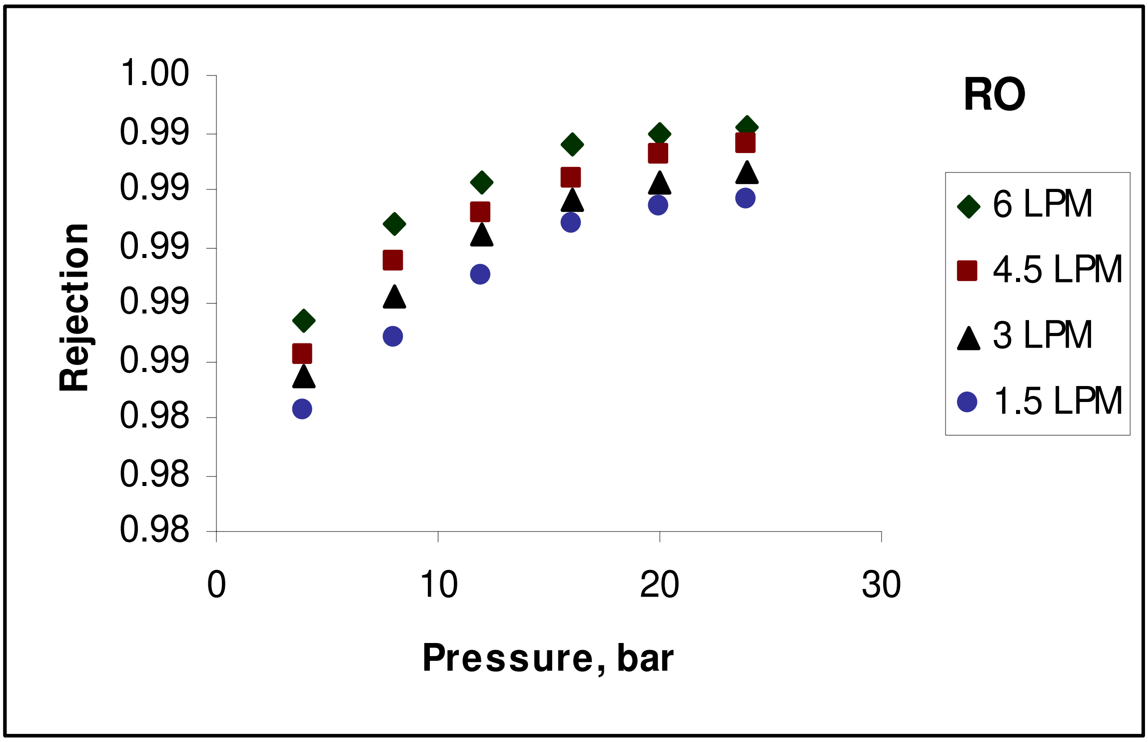

Figure 4(a): Effect of cross-flow velocity at RO membrane rejection (feed concentration =5000ppm and pH =3)

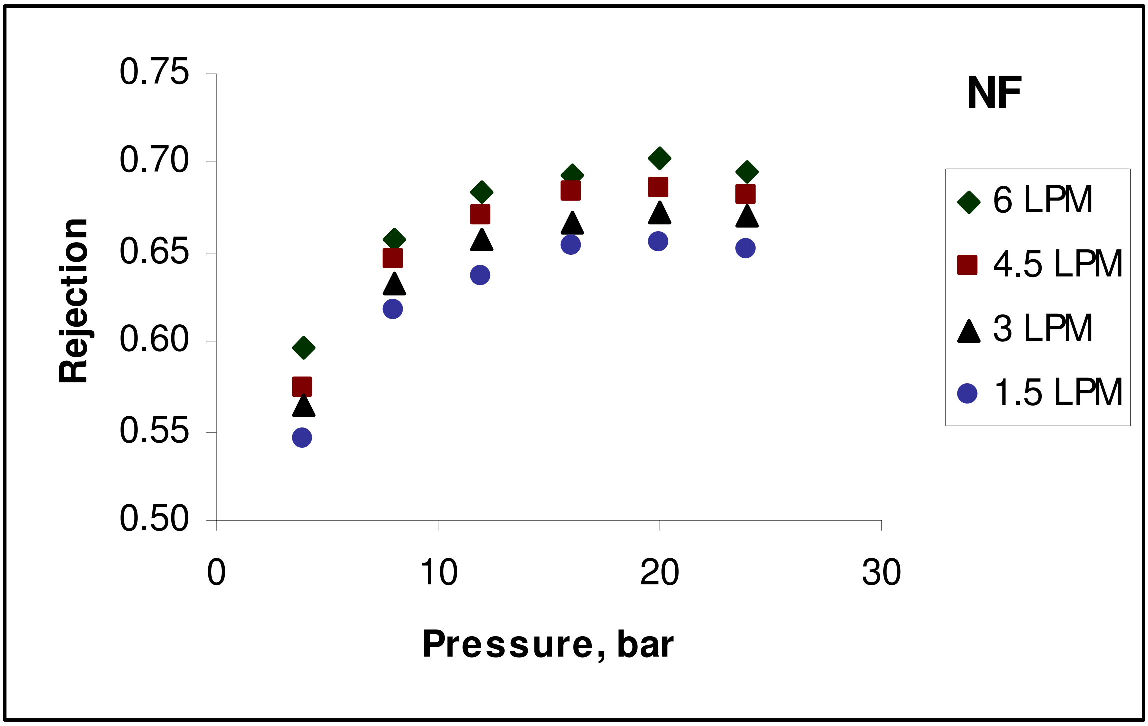

Figure 4(b): Effect of cross-flow velocity at NF membrane rejection (feed concentration =5000ppm and pH =3)

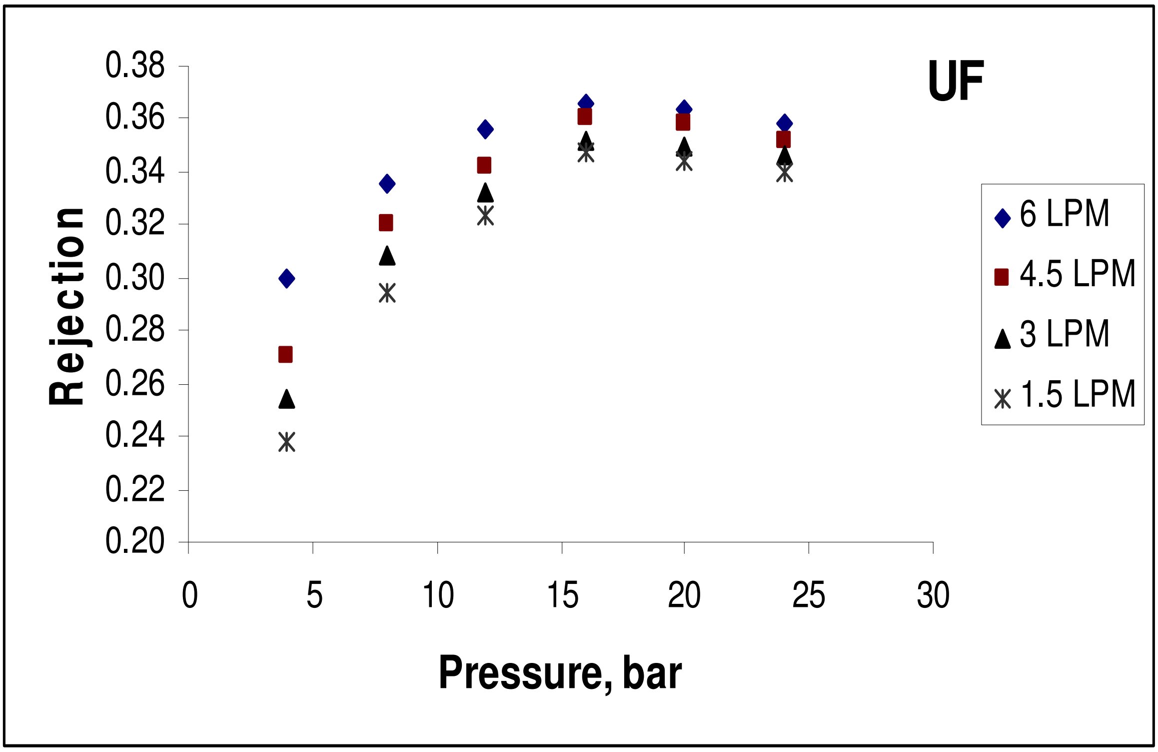

Figure 4(c): Effect of cross-flow velocity at UF membrane rejection (feed concentration =5000ppm and pH =3)

3.2.3 Effect of pH

Figures 5(a) to (c) show the MEA observed rejection of different membranes against the operating pressure at different pH. These figures show that the pH has a strong effect towards the observed rejection. The results show that increasing the pH from 3 to 8 has reduced the observed rejection. As expected the observed rejection at RO membrane has the highest value follow by the NF and UF membranes, respectively. Increasing the pH to alkaline condition has fully dissociate the carboxylic groups at the surface the surface gains its strongest negative charge. However, the negative charge of the polymer chains in the three-dimensional network of the surface start to repel each other and makes the skin layer more open [6]. The free volume of the network increases and the ‘pore size’ of the membrane skin layer increases and this leads to the increase of flux as discussed in **Section 3.1** and reduction of product quality as the solutes can easily pass through the wider free volumes of the membrane surface. When the pH is shifted to strongly acidic medium the amine groups at the surface fully dissociate and the surface gains strong positive charge. But ethanol amines are moderately basic compounds and form RH_2N^+. Unlike NH_4^+ the ionic form of amines is strong due to the electronegativity difference between nitrogen atom and the alkyl group attached to it. This leads to electrostatic repulsion between the positively charged membrane surface and amines, hence cause an increase in the observed rejection.

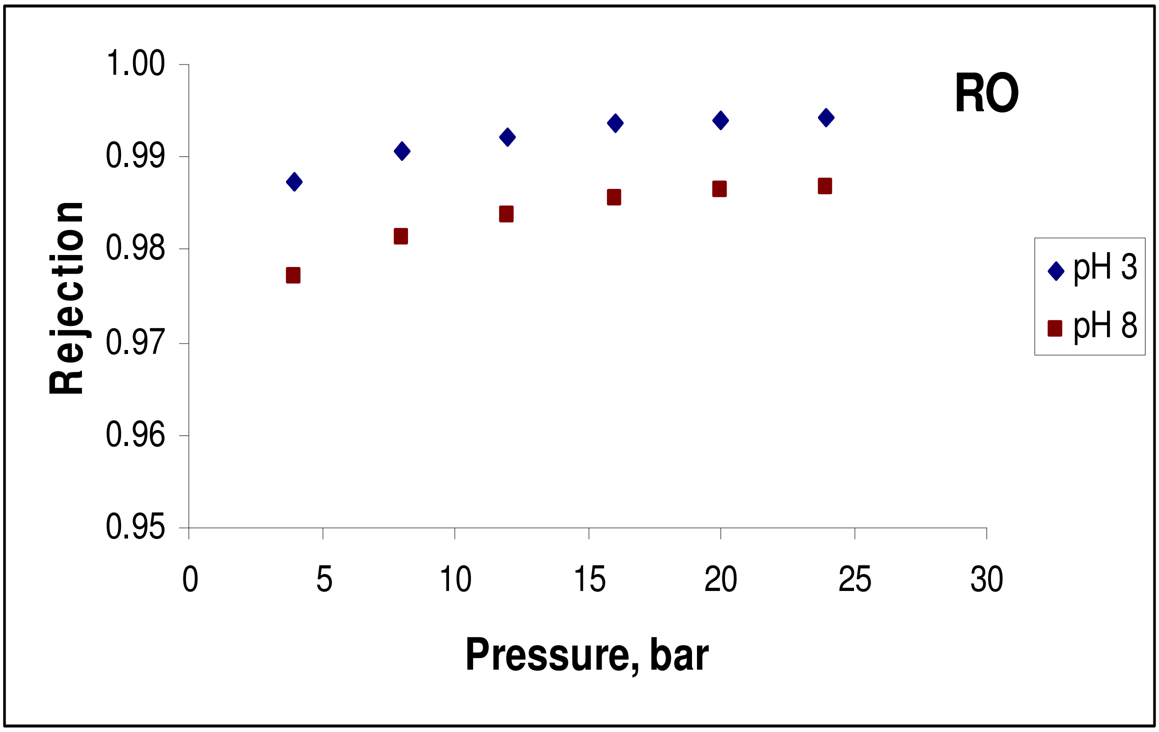

Figure 5(a): Effect of pH at RO membrane rejection (feed concentration = 5000 ppm, feed rate = 6 LPM)

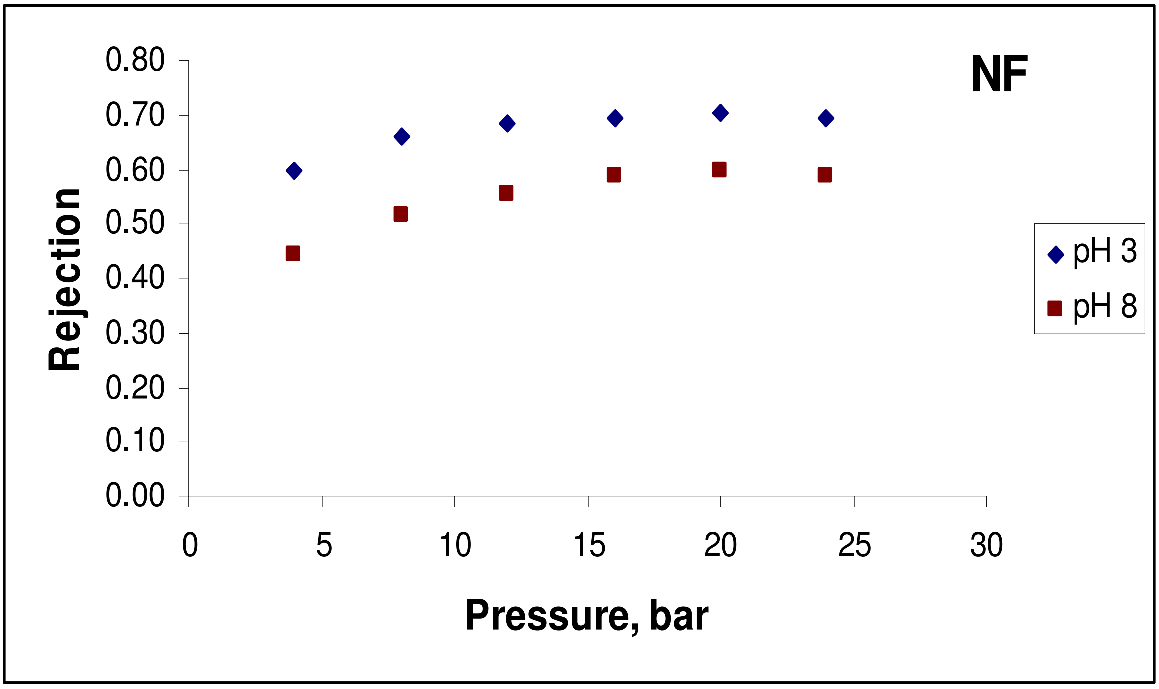

Figure 5(b): Effect of pH at NF membrane rejection (feed concentration = 5000 ppm, feed rate = 6 LPM)

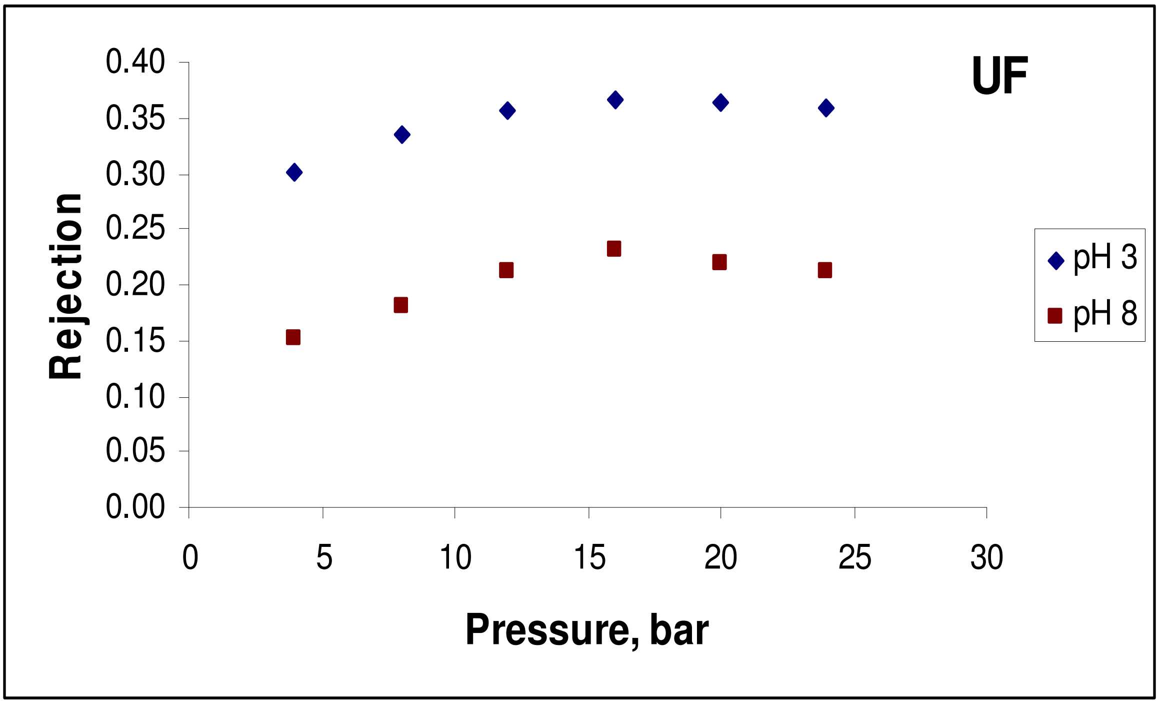

Figure 5(c): Effect of pH at UF membrane rejection (feed concentration = 5000 ppm, feed rate = 6 LPM)

4. CONCLUSIONS

This work shows that the RO, NF and UF membranes can be used to separate MEA in artificial wastewater. The rejection characteristic of these membranes is influenced by the operating pressure, feed concentration, cross-flow velocity and also pH. Generally, the rejection of MEA at RO membrane has the highest value followed by the NF and UF membranes, respectively. Increasing operating pressure has increased the observed rejection until it reaches at the optimum value. Vice-versa, increasing the feed concentration has reduced the observed rejection. Due to the reduction of concentration polarization at high cross-flow velocity has increased the observed rejection. Due to the electroneutrality of the dissociated carboxylic groups and the surface, increasing the pH has reduced the observed rejection. This work show that membrane process has the great potential to be used to separate the amine carry over in the wastewater in the natural gas processing.

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