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Pilot Plant Studies on the Recovery of *Caprolactam* by Reverse Osmosis

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Abstract: The performance of a polyamide-based thin film composite reverse osmosis membrane (RO) in a spiral- wound element BW3025 (FilmTec) for the recovery of caprolactam from an aqueous solution have been investigated. The experimental tests of the RO membrane were carried out using pure water (permeate from a nanofiltration system), brackish water (2000 ppm NaCl) and caprolactam solution (1000 ppm) and were evaluated based on the permeate flux and rejection of the dissolved solids at different transmembrane pressures. The RO membrane provided a rejection of 99.47% for brackish water and 99.74% for caprolactam and an average permeate flux of 65 dm3/ h. It was also found that the RO membrane element has experienced no fouling during the experiments.

Keywords: Caprolactam, Composite membranes, Recovery, Reverse Osmosis, Wastewater treatment.

Introduction

Nylon forms the second most important manmade textiles after polyester. Due to vast population growth and urbanization, the production of nylon 6 fibers has dramatically increased. According to QY research reports, in 2012, global consumption of nylon filament yarn and fiber increased 3.9% against the marginal growth of 0.8% in 2011. As an important bulk chemical in Nylon Industry, caprolactam (C6H11NO, CPL) is exclusively used to manufacture Nylon-6 fiber and resins. The global production of caprolactam amounted to 4.68 million tons in 2012 and there has been an ever increasing demand in the recent years [1]. Nylon 6 fibers dominated the consumption of caprolactam and accounted for over 66% of total demand in 2012. The use of caprolactam in nylon 6 resin production employed in engineering plastics and electronic applications is anticipated to be the major growth over the next few years. Nylon 6 is formed from the hydrolytic polymerization of caprolactam. The process reaches a stage of equilibrium when about 90% of the reaction mass is the polymer. This means that the effluent of the process contains un-reacted caprolactam as it's the main constituent which causes both economic profit reduction and significant pollution to the environment and exerts toxicity to living beings.

Various processes have been employed for the elimination and recovery of caprolactam from the wastewater for reuse. Solvents used for extraction must be immiscible with water, a good solvent in impurities and oil, a non-solvent for caprolactam and economical and non-toxic. Most researchers applied benzene as the extractant. As well known, benzene is recognized as a human leukemogen [3]. Toluene is considered as a good alternative for benzene [4]. Many other extractants with less toxicity have been tested in recent years, such as ethers [5], esters [5], alcohols [6, 7] and ketones [5, 8]. However, these methods are still not ideal for recovery of caprolactam from wastewater because these solvents are usually toxic, flammable and volatile and the processes are economically unfavorable as they use additional chemicals. In addition, studies have also been made to treat such caprolactam-containing wastewater by biological degradation of caprolactam. e.g., Kulkarni (1998) reported the bioremediation of caprolactam from wastewater by use of pseudomonas aeruginosa MCM B-407, which is a microorganism isolated from activated sludge [9]. Another caprolactam-degrading bacteria, alcaligenes faecalis, used by Baxi (2002), is also an example for bioremediation of wastewater containing caprolactam [2].

Membrane technologies have become established in recent years as alternatives for environmental applications to conventional mass-exchange technology such as absorption, adsorption or extraction [10]. They are physical processes and often consume less energy with better separation efficiency than conventional separation processes and produce no problematic by-products. Membranes can be defined as semi-permeable barriers that restrict certain molecules from passing through the membrane, thereby achieving separation. Membrane separation can occur based on the size exclusion, differences in diffusivity and solubility of the permeant in the membrane or both. In particular, reverse osmosis (RO) including low pressure RO (LPRO) known as nanofiltration (NF) are broadly used membrane processes for wastewater treatment. Previous studies have shown that RO and NF are effective technologies to remove organic compounds when the solute sizes are larger than the membrane pore sizes or organic compounds have ionizable functional groups causing electrostatic repulsion [11, 12]. However, these previous studies have typically considered relatively large compounds (e.g., molecular weight (MW) > 150 g/mol) and/or relatively hydrophobic compounds (e.g., logarithm of octanol–water partition coefficient > 2.0). Only a few studies have investigated the rejection of small uncharged organic compounds by RO and NF membranes [13]. This study aims to investigate the rejection of caprolactam from nylon plant wastewater using reverse osmosis so that the caprolactam will be reused and the process will be more environmentally friendly and economically viable.

Experimental

The studies of RO were performed using the RO pilot plant (Fig. 1) equipped with a spiral wound module supplied by FilmTec. The characteristics of this module are presented in Table 1. This module is designated for raw water salt concentrations within the range of 50-10,000 ppm. However, it exhibits a good retention of organic compounds and can be used over a wider range of solutes at various operation conditions. The pilot plant as shown in Fig. 1 consists mainly of water tank, feed water pump, pulsation damper, RO membrane element assembled unit (the module), shell and tube heat exchanger, manometers, rotameters, piping and control valves.

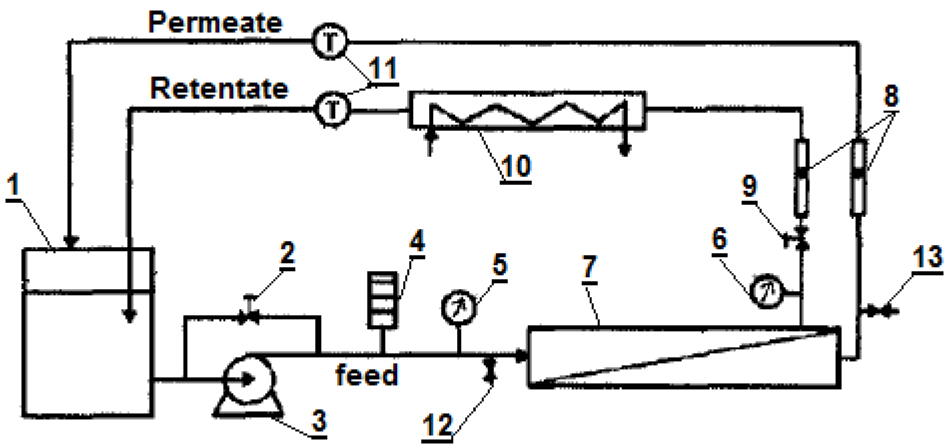

Figure 1. Schematic diagram of reverse osmosis pilot plant, 1- feed tank, 2- By-pass valve, 3- Triplex pump, 4- Damper, 5,6- Pressure gauge, 7- RO module, 8- Flowmeter, 9- Throttle valve, 10- Heat exchanger, 11- Thermometer, 12- Feed sampling valve, 13- Permeate sampling valve.

The water tank (1) which is made from polyethylene (45 cm diameter and 90 cm height) is open to the atmosphere. The tank is normally full of caprolactam solution that is used as a feed water source to the system. The pump (3) is used to supply the membrane element assembled (RO) unit (7) with high pressure feed water. A pulsation dumpener (4) is installed immediately after the pump. Pressure gauges (5,6) are used to control the pressure drop in the module. The setup is equipped with a number of valves to control the flow rate through the RO membrane unit. The permeate and the concentrate flow rates are measured with the flow meters (7) and (8) respectively. A heat exchanger (10) is installed after the flow meters to control the temperature.

Table 1. Membrane Operation Characteristics

Parameter	***Value***
Model	BW30-2540
Membrane Type	Polyamide Thin-Film Composite
Active Area, m^2	2.6
Feed Spacer Thickness, ml	28
Maximum Operating Temperature, °C	45
Maximum Operating Pressure, bar	41
Maximum Feed Flow Rate, m^3/h	1.4
Maximum Pressure Drop, bar	1.0
pH Range, Continuous Operation	2 - 11
Maximum Feed Silt Density Index	SDI 5
Free Chlorine Tolerance	<0.1 ppm
Stabilized Salt Rejection, %	99.5

Five different runs of experiments were carried out and the following feeds were used in this order: pure permeate water (electrical conductivity < 10 µS/cm), brackish water (2000 ppm NaCl), caprolactam solution (1000 ppm). For these three runs, both the concentrate and permeate were recycled to the feed tank. For the fourth run, the permeate was gradually collected in a different vessel to obtain a highly concentrated solution of caprolactam at the concentrate stream. The process was run at 25°C in the range of the transmembrane pressures from 10 to 30 bar. The permeate flux was measured and the concentration of salt and caprolactam in both the permeate and feed was determined. Samples of the feed and the permeate were collected from the valves (Fig. 1, 12, 13) directly into the cuvettes for analysis by Total Organic Carbons (TOC) analyzer (multi N/C 2000 analyzer, Analytik Jena, Germany). The degree of rejection (R, %) was calculated as follows:

$$\text{Rejection (\%)} = \frac{C_F - C_P}{C_F} \times 100\% \qquad (1)$$

where C_F and C_P are the concentration of salt in the feed and the permeate respectively.

Results and Discussion

The experimental results have demonstrated that the rejection of caprolactam for the examined solutions was significantly affected by their transmembrane pressure, concentration and temperature. Pure water was used in the first run to measure for the permeability of the membrane and stabilize the flux prior to the caprolactam experiments. The performance of the membrane was then measured using the conditions used manufacturer in their characterization studies. As BW3025 membrane is designated for ionic compounds rejection and specifically for desalination, a brackish water of 2000 ppm NaCl was used in the experiment. Fig. 2 shows the values of water flux and NaCl rejection. When the pressure is increased from 10 bars to 30 bars, the flux is almost doubled and NaCl rejection increased by 0.33%. The recovery also increased from 13.19% at 10 bars to 22.75% at 30 bars.

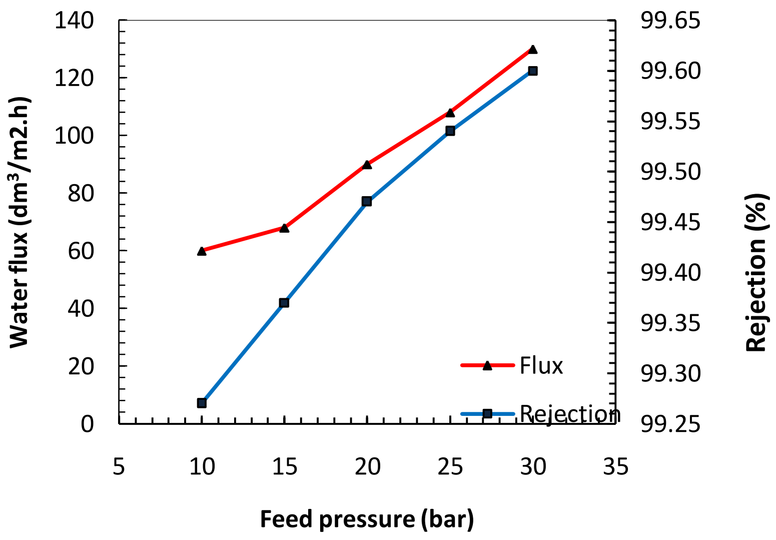

Figure 2. Effect of pressure on the properties of brackish water desalination membrane (BW30

Table 2 shows a comparison of the flux and rejection values in the FilmTec product specification sheet and the values obtained experimentally. The results precisely match the specifications of the membrane given by manufacturer. However, there is a slight reduction in the flux which may be due to limitations and errors in the experimental measurements. It is also necessary to take into account that the flux given in the product specification sheet is based on an element in a multi stage membrane configuration which, for some reasons, flow distribution is necessary i.e. equilibrate permeate flow between stages. For individual elements, the permeate flow rate may vary +/-20%. The experimental value of the flux is in the range of -20% of that given in the product sheet.

A preliminary experiment of caprolactam solution was carried out to determine the optimum operation conditions (feed concentration, pressure and temperature) that give the best flux and rejection. It is important to remind here that the permeate was not removed from the system but was again collected at the same vessel as the feed.

Table 2. Comparison of product sheet and experimental values

Parameters	Membrane Model BW30-2540	
	Product Sheet Values	Experimental values
Permeate Flow Rate(m^3/d)	3.2	1.2
Stabilized Salt rejection (%)	99.5	99.47
Recovery (%)	15	14.51

As shown in Fig. 3, the RO membrane displays good performance with caprolactam solution in terms of flux and caprolactam rejection. It is observed in the figure that permeate flux increases linearly with pressure while the rejection is almost constant at 99.75%. The permeate flux is relatively high since caprolactam is completely soluble in water (4560 g/l) and the effect of concentration polarization is negligible or not exists. On the other hand, the high rejection of caprolactam may be returned to the molecular shape that has a radius of 0.28 nm. Generally, higher molecular weight compounds have better rejection than low molecular weight compounds. However, the rejection is not purely a function of molecular weight.

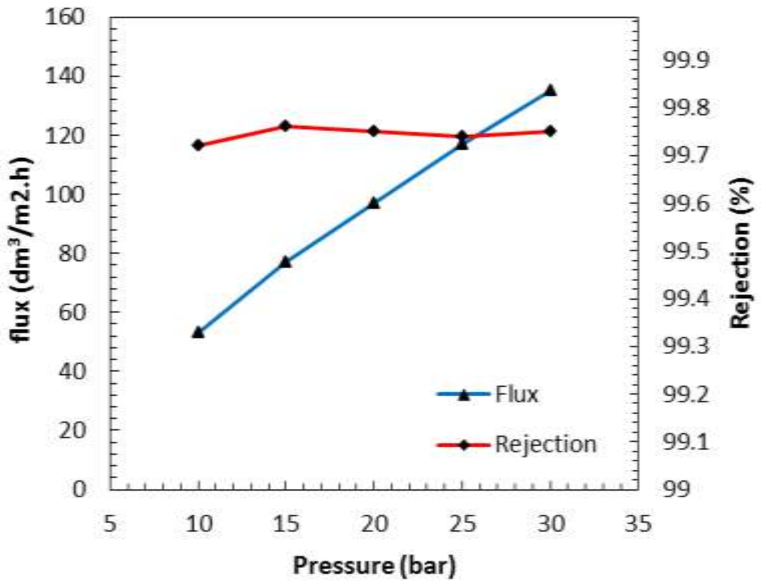

Figure 3. Flux and rejection of caprolactam at different pressures

Although the caprolactam solution concentration used is lower than the concentration of NaCl solution discussed in the previous section, a little comparison between the fluxes will be important. The fluxes of the three experiments conducted follow the order: pure water > caprolactam > NaCl solution. The highest flux is observed when RO permeate was used as a feed. This is because no plugging of the membrane occurs due to the composition of the feed stream. The permeate flux of the brackish water (2000 ppm) decreases by 12% compared to that of the pure deionized water at 30 bar. This was caused by the higher concentration of ions and the enhanced influence of concentration polarization. When caprolactam solution of 1000 ppm is used as a feed, the flux is little bit higher than that of brackish water. This also returns to the concentration driver and that caprolactam is completely soluble in water and causes no significant concentration polarization.

The caprolactam concentration experiment was conducted taking into account the optimum operation conditions shown in Fig.3. Practically, Evaporation is used to recover the 10% unreacted caprolactam in the effluent of a nylon production process. However, the stream that leaves the evaporation contains approximately 0.1 wt% of caprolactam that cannot be removed by the evaporation. RO membrane is used to concentrate this 0.1 wt% caprolactam stream to at least 1 wt% so that it can fed back to the evaporation. The concentration process is performed in several steps at a pressure of 15 bars and temperature of 25 °C. Lower pressure is used to control the flux as the experiment involves in collection of relatively small volumes. The process is started with a 200 liters caprolactam solution of 1000 ppm. In the first step, 100 liters was collected as a permeate. A rejection of 99.7% was achieved in this step. This makes the concentration of the remaining 100 liters almost double i.e. the volume concentration ratio is 2 and the recovery is 50%. In the second step, 50 liters was collected making the recovery up to 75% and the volume concentration ratio is 4. The process goes on until the volume concentration ratio is 20 and the recovery is 95%. The process ends up with a 10 liters solution of caprolactam that is 20 times more concentrated than the feed i.e. 2 wt% of caprolactam.

Fig. 4 shows the effect of concentration change on each of the permeate flux and the rejection of caprolactam. At the beginning of the process, the flux is 65 l/m2.h. It shows a little increase at the first two stages. However, it starts to decreases at the third stage and keeps declining. At the end of the process, a decrease 31% of the flux is observed. This is because the osmotic pressure increases with the increase of concentration and the driving force of the water declines according to the flux equation. On the other hand, the rejection of caprolactam is constant at 99.74% during most of the process. However, a slight increase is observed at elevated concentrations of caprolactam.

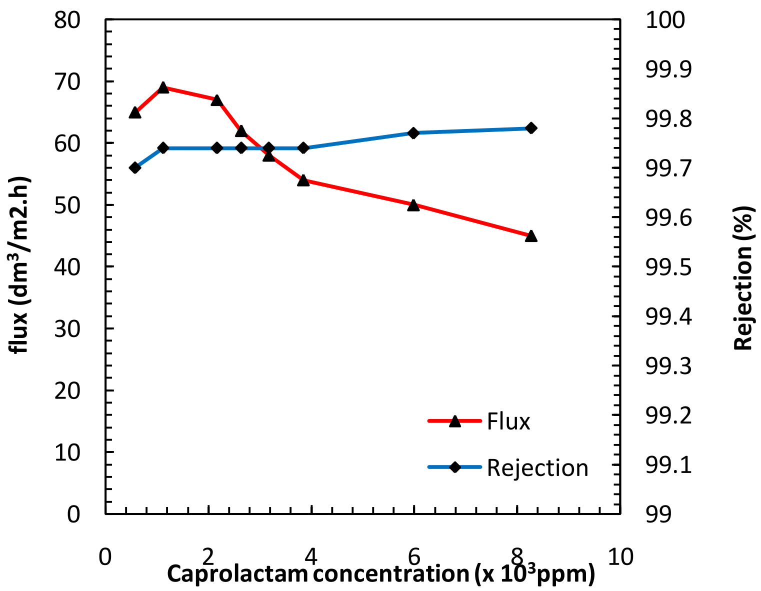

Figure 4. Effect of concentration on flux and rejection of caprolactam

The relationship between volume concentration ratio and water recovery rate is shown in Fig. 5. The more permeate is collected from the process, the more the concentrate is more concentrated as almost the same amount of caprolactam remains in less volume of water.

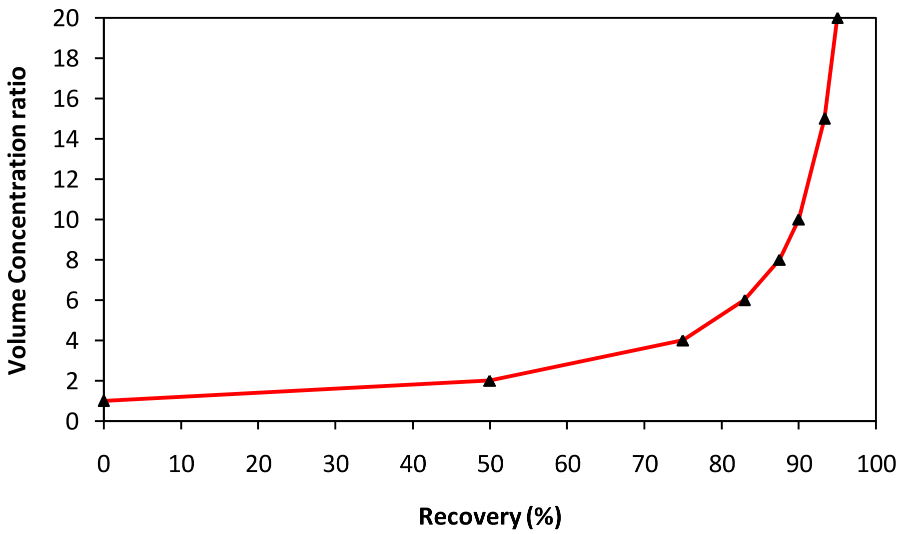

Figure 5. The effect of water recovery rate on the concentrate solution concentration factor

After conducting the caprolactam recovery experiment, the fouling of the membrane element was tested. This is done by measuring the permeability of the membrane with pure water flux. Fig. 6 shows a comparison of the pure water fluxes before and after the caprolactam experiment. It can be seen that the two fluxes overlay on each other and this shows that there is no fouling happened during the experiment. This result was expected since the most important factors that cause fouling were absent in this experiment. First, there is no buildup of material on the membrane that may cause pore blockage or gel formation. Second, there is no concentration polarization which is an accumulation of particles or solutes in a mass transfer boundary layer adjacent to the membrane surface. These two factors were not applicable to the caprolactam experiment since the caprolactam has a very high solubility in water and formation of gels or concentration polarization is too far to happen. At higher pressures, the flux of the pure water after the caprolactam experiment is higher than that before the caprolactam. This can be explained that the organic solutes cause the membrane to swell which makes the membrane pores bigger and the water flux higher.

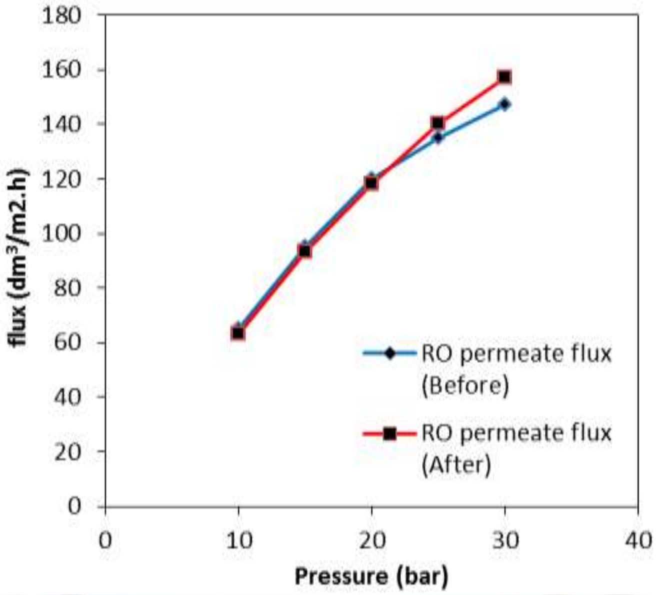

Figure 6. Comparison of pure water fluxes before and after caprolactam experiment

Conclusion

Caprolactam, important bulk chemical in Nylon Industry, is produced in huge amounts worldwide and most of it is used for the production of nylon 6. The effluent of the process contains un-reacted caprolactam which causes both economic loss and significant pollution to the environment. The objective of this research was to perform feasibility study to evaluate the application of Reverse Osmosis (RO) for the recovery of caprolactam from aqueous solutions. RO pilot plant that uses BW30-2540 (Filmtec) spiral wound element was used. The operating parameters for the recovery of caprolactam were optimized experimentally as follows: transmembrane pressure of 20 bars and temperature of 25 °C. A caprolactam rejection of 99.7% and pure water recovery of 95% was achieved at volume concentration ratio (VCR) of 20. The fouling phenomenon during the treatment of caprolactam solutions by spiral wound RO membrane element was negligible as proved by measurements of permeate flux after the caprolactam concentrations experiments. It can be concluded that reverse osmosis technology exhibits great potential in recovering the caprolactam from the effluents of nylon factory and, at the same time, providing pure water that can be using for washing and rinsing other products.

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