Bulgarian Chemical Communications, Volume 50, Issue 1, (pp. 21 – 26) 2018

Employing reverse osmosis for the removal of *ortho*-toluidine from wastewater

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Received September 6, 2017; Accepted December 23, 2017

Ortho-Toluidine (OT) is a dangerous and persistent organic pollutant in the industrial wastewater and needs treatment before disposal. In this project, the performance of reverse osmosis membrane system (RO 90) for the removal of OT from aqueous solutions is investigated. The influence of different operational variables such as pressure, concentration, pH and the volumetric flow rate of feed was considered in the removal performance of the OT. The influence of feed flow rate on the rejection percentage and the permeate flux was not the same. The results showed that at the optimum conditions obtained for rejection, (feed concentration at 80 mg/l, the pressure of feed at $50 \times 10^5 N/m^2$, pH at 7, and feed flow rate at $8 \times 10^{-5} m^3/s$), the rejection percentage and the permeate flux were 97.8%, and $38.5 \times 10^4\ m^3/m^2.s$, respectively.

Keywords: rejection percentage; ortho-toluidine; reverse osmosis; permeate flux; industrial wastewater.

INTRODUCTION

Ortho-Toluidine (OT) is an aromatic amine employed as an intermediate in the dyeing and petrochemical industries with numerous uses in rubber handling, chemical production, pesticides, pharmaceuticals, etc. [1]. *O-Toluidine* can also be absorbed in living organisms and convert to a number of compounds which are active endotoxins. According to its many environmental concerns and opposing effects on human health, it has received growing attention in recent decades [2].

Membrane technologies are valuable approaches for wastewater treatment because of the many benefits such as low power consumption, high quality of water and low area requisite [3]. The reverse osmosis (RO) is one of membrane technologies that can remove organic pollutants [4]. RO processes can significantly decrease the volume of waste streams and the pollutants are concentrated into a small volume compared to the total waste size. Both organic and inorganic contaminants can be removed instantaneously by RO membrane processes. Additional gains of RO process are: energy saving, simple design and easy work, in comparison with customary processes. But fouling, scaling, and concentration polarization can decrease the efficiency of the RO process [5, 6]. The RO system cannot degrade toxic pollutants, but it can transfer the pollutants from one phase to another and this subject is one of the main limitations of RO techniques. In the separation and reuse of pollutants it can be considered as a useful method for wastewater treatment.

Several processes have been used to remove OT from wastewater, including Fenton [7] and photo Fenton [8] processes, catalytic ozonation [9], electrochemical [10], UV/H_2O_2 [11] and other AOPs [12]. In this paper the removal of OT from aqueous solution by reverse osmosis using a RO90 polyamide membrane, and the effect of different experimental conditions such as pressure, volumetric flow rate, pH and concentration of feed was studied.

EXPERIMENTAL

*Materials***.** *O-Toluidine* (99.5%) was of reagent grade, obtained from Merck. The features of *o*-toluidine are shown in Table 1. The pK_a is the acid dissociation constant at which the organic molecule loses a hydrogen atom and becomes negatively charged; log K_{ow} displays the hydrophobicity of the organic molecule. A thin film composite polymeric membrane (RO 90) produced by Alfa Laval (Manufacturer Dow chemical) was employed. Other analytical grade reagents used in this work were sodium hydroxide and sulfuric acid, supplied from Merck. Distilled water was used throughout.

Experimental setup. The schematic of the experimental setup is presented in Fig. 1. The feed tank was a 2 L glass vessel. The set up was equipped with an RO membrane, diaphragm pump (HEADON model HF-8367) with maximum flow rate of $10^{-4} m^3/s$, membrane module, pressure gauge, and a diaphragm valve. The maximum pressure of the membrane was 55×10^5 N/m^2. The regulation of the feed flow rate was performed by a flow meter combined with needle valve on the feed stream. A second globe valve was used for pressure tuning. A pressure gauge was installed for monitoring the inlet feed pressure.

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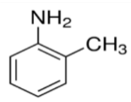
Table1. Some physico-chemical properties of *o*-toluidine.

Molecular formula	Structural formula	Molecular weight (g/mol)	Water solubility (g/L) (25ºC)	Log $K_{o/w}$	pK_a	Density at 20/4 ºC (water = 1)
C_7H_9N		107.15	15	1.32	4.44	1.004

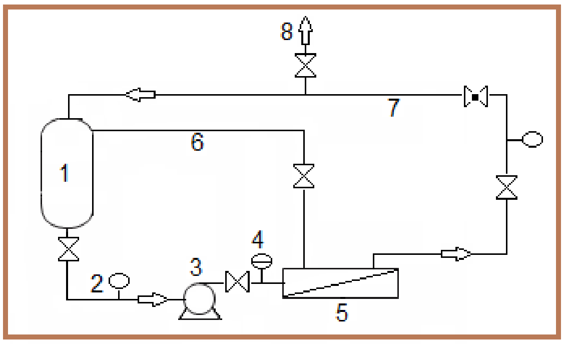


Fig. 1. The schematic diagram of the RO setup; (1) Feed tank, (2) Instrumentation device, (3) Diaphragm pump, (4) Pressure indicator, (5) Membrane module, (6) Reject line, (7) Permeate line, (8) Sampling valve.

Procedure. A stock solution was prepared by dissolving the required amount of OT in distilled water. The solubility of OT in water in alkaline medium is more than under acidic and neutral conditions. Concentrations of 40, 80, 120 and 160 mg/l of OT were prepared by diluting the stock solution for exploring the effect of feed concentration. For considering the effect of pH, different pH at 5, 7, 9 and 11 were adjusted by adding sodium hydroxide and sulfuric acid. The effect of feed flow rate at 2, 4, 6, and $8 \times 10^{-5} m^3/s$ and the influence of feed pressure at 20 to 50 kPa was investigated. All experiments were performed at 25°C. The feed solution was pumped into the membrane module with the chosen pressure and flow rate. The rejected and permeated streams were spilled back to the feed reservoir. Samples from permeate and rejected lines were withdrawn until finding the steady state condition. The steady state condition was achieved after 70 min of recirculation. The rejection of Solute was estimated as:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (1)$$

Where C_F and C_P are the feed and permeate concentration, respectively [13]. The permeate flux (J_p) can be defined as the volume flowing *via* the membrane per unit area and time (m^3/m^2s). In this study, the feed solution was diluted and the velocity of the feed was high, therefore the concentration polarization and fouling were insignificant and minor deviations from ideal mass transfer were observed. As it can be seen from the following equation, the solvent flow (J_w) depends on the hydraulic pressure used across the membrane (ΔP), minus the difference in the osmotic pressures of the solutions on the permeate and feed side of the membrane ($\Delta\pi$):

$$J_w = A_w(\Delta P - \Delta\pi) \qquad (2)$$

Where A_w is the water permeability constant, which can be influenced by the properties of the membrane and $\Delta\pi$ signifies the osmotic pressure difference across the active layer of the membrane [14]. The solute flux (J_s) depends on the differences in solute concentration across the membrane:

$$J_s = B_s\,(C_s - C_p) \qquad (3)$$

B_s is the solute permeability constant, which depends on the solute composition and the membrane structure, with the following value:

$$B_s = \frac{K_s D_s}{l} \qquad (4)$$

Where K_s is the solute distribution coefficient, D_s is the solute diffusion coefficient, and l is the membrane width. The permeate concentration can be introduced as $C_p = J_s/J_w$ [15].

The OT concentrations in feed and permeate solutions were determined by spectrophotometry at 281 nm, using a UV–Vis spectrophotometer (Agilent, 5453, U.S.A.).

RESULTS AND DISCUSSION

Effect of feed pressure. The effect of feed pressure on OT rejection and permeation at pH 7, feed concentration of 40 mg/l and volumetric flow rate of $2 \times 10^{-5} m^3/s$ in the range of 20–50 kPa was tested and showed in Figs. 2 A and B. As can be seen, the rejection of OT increased from 73.2 to 80% with the increase in pressure from 20 to 50 kPa. Based on the Spiegler–Kedem–Katchalsky model, the driving force for solvent and solute transport is pressure and concentration, respectively. In addition, the solute flux is less pressure-dependent than water flux [14]. Therefore, the water flux (J_w) is enhanced directly with pressure and the solute flux is due to the concentration difference and water flux. Concentration polarization increases the osmotic pressure [16], but in this project, it was not considerable because of high feed velocity. The increase in rejection with practical pressure is expected from equation 2, where ΔP is the only variable, supposing that the constants A_w and B_s are not relying on pressure. Higher fluxes derived from higher trans-membrane pressures result in lower permeate concentrations, which leads to higher rejections. Similar results were achieved by other researchers for the removal of organic pollutants by nano filtration and reverse osmosis membranes [17].

The effect of pressure on the permeate flux is presented in Fig. 2B. The permeate flux was increased from 33.5 to $39.0 \times 10^4\ m^3/m^2.s$ with an increase in operating pressure from 20 to 50 kPa. Based on Eqs. 2 and 3, J_w was increased with operating pressure, but J_s is not influenced and is only determined by the concentration difference across the membrane. So, an increase in permeation rate is only owing to the enhancement in water flux.

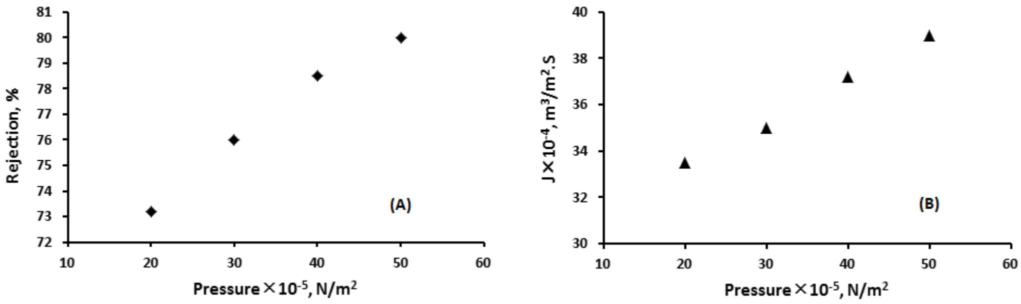


Fig.2. Effect of feed pressure on rejection percentages (A) and permeate flux (B); (feed concentration 40 mg/l, pH 7, and feed flow rate at $2 \times 10^{-5} m^3/s$).

Effect of feed concentration. The effect of initial feed concentration on rejection and permeate flux of the OT is shown in Figs. 3 A and B. The osmotic pressure was increased with increase in feed concentration and according to Eq. (2) the water flux was reduced. By rising in the feed concentration, the accumulation of OT and concentration polarization are increased, therefore the rejection of the OT was decreased. The results showed that at 80 and 40 mg/l, maximum and minimum rejections of the OT were observed at 89.2 and 80%, respectively. At low concentration (40 mg/l), the osmotic pressure difference was low, so based on Eq. (2), water flux was considerable and the concentration of OT on the membrane surface was low, so the flux of OT was low. But at a concentration of 40 mg/l, the water flux is so high that can transport the dissolved OT in the membrane surface to the permeate side. When feed concentration increases, the slight variation in the rejection was occurred as it has been described by other researchers with other organic compounds [18].

As it can be observed, there were no noteworthy variations in permeate flux with increases in feed concentration, which can be clarified by the sum of two contrary effects: the reduction in the water flux as a consequence of the increase in $\Delta\Pi$ and the enhancement in solute flux according to the increase in feed concentration.

Effect of feed pH. As it can be seen from Figs. 4 A and B, the effect of feed pH on rejection and permeation flux was investigated in the range of 5–11. The maximum rejection was obtained at pH 7 and the minimum rejection at pH 10. In alkaline solutions, ionization of the polyamide membrane occurred and the membrane surface was negatively charged because of the free carboxylic acid groups in the structure [19]. Rejection changes with pH are seemingly related to the existence of ionizable groups in the membrane structure and to the net charge of the OT molecule as a result of its dissociation equilibrium [20]. The pK_a of OT is 4.44 and thus, at pH values higher than 4.44, the toluidinium amount will decrease because of the formation of neutral toluidine.

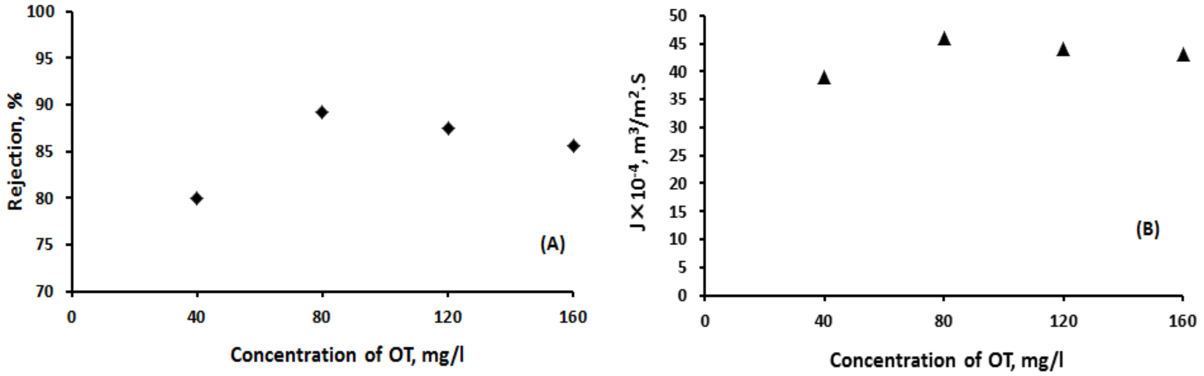


Fig.3. Influence of feed concentration in rejection percentages (A) and permeate flux (B); (feed pressure $50 \times 10^5 N/m^2$, pH 7, and feed flow rate at $2 \times 10^{-5} m^3/s$).

The increase in rejection between pH 5 and 7 can originate from the retention of the remaining toluidinium cations by the negative carboxylate groups in the membrane. At pH values higher than 7, rejection decreases because the amounts of toluidinium cations considerably decrease and neutral OT is not taken in by the negative charge of the membrane. Similar results, that pK_a value had a very significant role in the rejection of 4NP, were obtained by Ozaki and Li [21].

The pH has a strong effect on the permeation behavior of polyamide membranes owing to the superficial charge of the membrane and the net charge of the organic pollutant. Minimum permeate flux is obtained at pH of 5.

At pH 5, both membrane surface and the OT molecules are positively charged, which leads to an increase of pore size, originated from the electrostatic repulsion between functional groups with the same charge, causing lower OT transport, so that there is a minor solute flux, which is accompanied with the increase of water flux. According to all this, at pH 7–11, the OT has no net charge, but the membrane will have a negative charge, which will lead to improve the water flux, originated from the increase of pore size, and consequently, a decrease in permeate concentration.

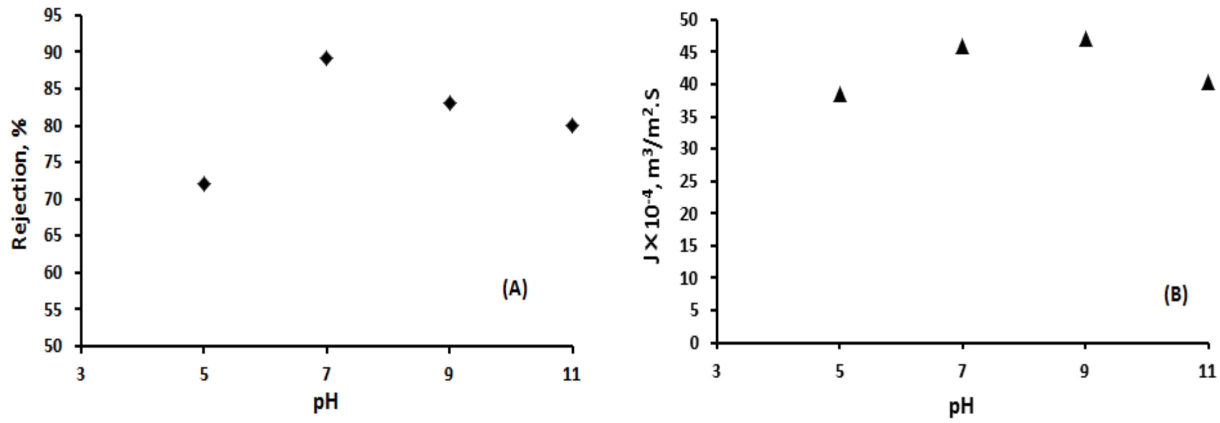


Fig.4. Influence of feed pH in rejection percentages (A) and permeate flux (B); (feed pressure $50 \times 10^5 N/m^2$, 80 mg/l OT, and feed flow rate at $2 \times 10^{-5} m^3/s$).

Effect of feed flow rate. The influence of feed flow rate on OT rejection and permeation is presented in Figs. 5 A and B. As it is obvious, the rejection is enhanced by increasing the flow rate and the permeation flux is in contrast. The influence of feed flow rate on the rejection percentage and the permeate flux was not the same. By increasing the feed flow rate from 2×10^{-5} to $8 \times 10^{-5} m^3/s$, the rejection percentage was increased from 89.2 to 98.7% and the permeation flux decreased from $46 \times 10^4\ m^3/m^2.s$ to $38.5 \times 10^4\ m^3/m^2.s$. This effect can be described as concentration polarization. The width of the concentration polarization layer was reduced at high feed flow rates and therefore the osmotic pressure decreased. Based on Eq. (2), by reducing the osmotic pressure difference the water flux increases and the rejection of OT is improved. The maximum rejection was obtained at $8 \times 10^{-5} m^3/s$ of feed flow rate and feed concentration at 80 mg/l.

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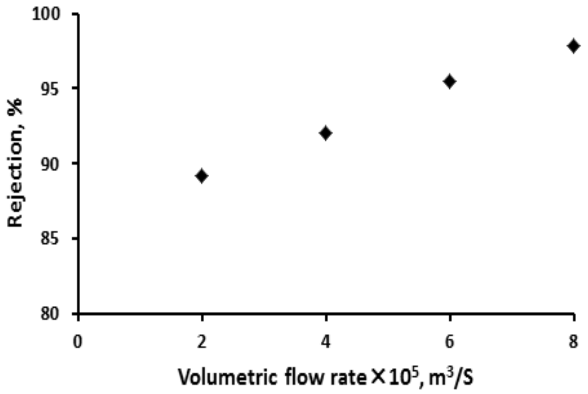

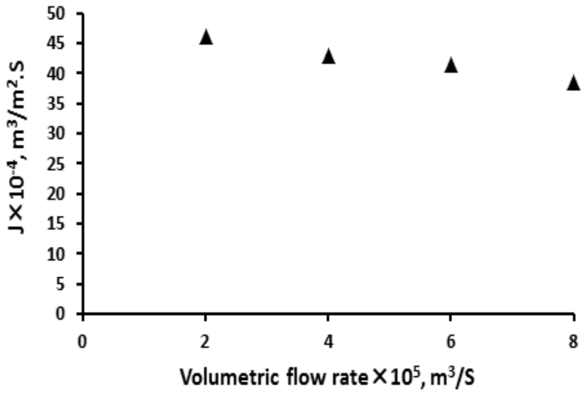

Fig.5. Influence of feed flow rate in rejection percentages (A) and permeate flux (B); (feed pressure $50 \times 10^5 N/m^2$, 80 mg/l OT, and pH at 7).

CONCLUSIONS

The performance of reverse osmosis for the removal of OT from aqueous solutions was explored and the effect of operational variables such as pressure, feed volumetric flow rate, feed concentration and pH on the rejection and permeate flow rate was investigated. The highest rejection (97.8%) was achieved at 80 mg/l of OT, feed pressure of $50 \times 10^5 N/m^2$, pH 7, and feed flow rate at $8 \times 10^{-5} m^3/s$. The rejection percentage was increased with an increase in pressure and feed volumetric flow rate. The permeate flux was improved with increase in pressure and decrease in volumetric flow rate of the feed. The observed changes in OT rejection with pH were related to the charge of ionizable groups in the membrane structure and the net charge of OT molecule. The maximum permeation flux ($46 \times 10^4\ m^3/m^2.s$) was achieved at optimum conditions obtained for rejection except the volumetric flow rate of feed which was $2 \times 10^{-5} m^3/s$. The influence of feed flow rate on rejection percentage and the permeate flux was not the same.

Acknowledgments: *The author wishes to thank the HSE department of the national petrochemical company of Iran for scientific guidance.*

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ИЗПОЛЗВАНЕ НА ОБРАТНА ОСМОЗА ЗА ОТСТРАНЯВАНЕ НА *ОРТО*-ТОЛУИДИН ОТ ОТПАДНА ВОДА

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Получена на 6 септември, 2017 г.; приета на 23 декември, 2017 г.

(Резюме)

орто-Толуидин (ОТ) е опасен и устойчив органичен замърсител в промишлена отпадна вода и трябва да се отстрани преди изхвърлянето й. В настоящата статия е изследвано действието на мембранна система за обратна осмоза (RO 90) за отстраняване на ОТ от водни разтвори. Изследвано е влиянието на оперативни променливи като налягане, концентрация, pH и обемна скорост на захранващия поток върху отстраняването на ОТ. Влиянието на обемната скорост на захранващия поток върху процента на очистване и преминаващия поток е различно. Установено е, че при оптималните условия (концентрация на захранване 80 mg/l, налягане на захранване $50 \times 10^5 N/m^2$, pH 7 и скорост на захранващия поток $8 \times 10^{-5} m^3/s$), процентът на очистване и преминаващият поток са съответно 97.8% и $38.5 \times 10^4\ m^3/m^2.s$.