Research Paper

Treatment of Phenolic Wastewaters by a Domestic Low-Pressure Reverse Osmosis System

Fatemeh Khazaali¹, Ali Kargari¹,²*

¹ Department of Petrochemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Mahshahr Campus, Mahshahr, Iran
² Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

ARTICLE INFO

Received 2014-09-03
Revised 2015-12-15
Accepted 2015-12-15
Available online 2015-12-15

GRAPHICAL ABSTRACT

KEYWORDS

Phenol
Wastewater
Reverse osmosis
Rejection

HIGHLIGHTS

• Removal of phenol by using aqueous solution in a low pressure reverse osmosis membrane
• Investigating the effect of feed pressure, feed concentration, feed flow rate and feed pH on phenol rejection
• Feed pH is the most affective parameter on the phenol rejection
• The maximum rejection equal to 71% at 200 mg/L, 408.1 kPa, pH =10 and 1.172 L/min feed flow rate

ABSTRACT

In this paper, the removal of phenol by using aqueous solution in a low pressure reverse osmosis membrane was investigated. The effect of feed pressure, feed concentration, feed flow rate and feed pH on phenol rejection was investigated. The results showed that feed pH is the most affective parameter on the phenol rejection. Rejection of phenol increased with increasing pH from 2 to 10 under the best conditions. According to the results, there was a critical pressure in this separation and for pressures higher than this pressure, phenol rejection decreased. Feed flow rate had a positive effect on the phenol rejection but the effect of feed concentration was similar to the effect of feed pressure. The results showed that the maximum rejection was measured equal to 71% at 200 mg/L, 408.1 kPa, pH =10 and 1.172 L/min feed flow rate.

1. Introduction

In recent years, water contamination with dangerous compounds has attracted much attention in the entire world [1-4]. Phenol compounds are among the main pollutants in industrial wastewaters that are hardly removed using common biological treatment methods [5]. Phenolic compounds have created an extreme concern because of their toxicity, low biodegradability and adverse effects on the environment and aquatic ecosystem [6,7].

Industrial processes including oil refineries, ceramic plants, steel plants, coal conversion, phenolic resins, dyes, textile, rubber manufacturing, pesticides and pharmaceutical industries are among the industries that produce phenolic wastewaters [8-10]. The presence of phenolic compounds in...
water at concentrations as low as 1μg/L could cause nasty odor and taste in water and make it unpleasant [11]. Due to toxicity and environmental problems caused from the existence of phenolic compounds in water even at low concentrations, it is necessary to employ developed and advanced methods for their removal [12-14]. Different methods including steam distillation, solvent extraction, liquid-liquid extraction, adsorption, chemical or enzymatic oxidation, ozonation, bacterial decomposition, incineration and hybrid processes for elimination or destruction of phenolic compounds from wastewaters have been used [12, 17, 15-19]. Membrane processes are new and effective processes that have been recently developed for the removal of organic pollutants from wastewaters [20, 21]. The most important membrane processes which have been used for phenol removal from wastewaters are liquid membranes [22-27], pervaporation and reverse osmosis/nanofiltration [9, 20, 28-30]. Although early applications of reverse osmosis (RO) were limited to sea water desalination, today reverse osmosis has found applications in other fields such as organic compound removal and wastewater treatment [31-33]. The reverse osmosis process has some advantages such as low volume of reject stream, low occupied space, easy work-up, lower energy consumption compared to other technologies and, modular structure that facilitates the development of a system and increases its flexibility [34, 35]. Organic compound rejection by the RO membrane is affected by different factors including operating conditions, adsorption of solute onto the membrane surface, electrostatic interactions between the solute and membrane, hydrophobicity interactions and properties of solute and membrane [16, 36, 37].

In liquid separation processes such as RO, rejection is defined as:

\[ R = (1 - \frac{C_p}{C_f}) \times 100 \]  

(1)

where, \( C_p \) and \( C_f \) are permeate and feed concentration (mg/L), respectively [17].

Due to the ability of reverse osmosis in organic compound removal, different studies were done on phenol removal from aqueous solutions by the RO process. Arsuaga et al. [20] studied phenol removal from aqueous solution using two commercial reverse osmosis (TFC-HR, BW-30) membranes and one nanofiltration (NF-90) membrane. Their investigation was carried out at constant pressure, feed concentration and natural pH of the solution, and maximum rejection with two RO and NF membranes was 70% and 29%, respectively. In another study that was performed by Lopez-Munoz et al., phenol removal from aqueous solution was examined using two NF (NF-90) and RO (TFC-HR) membranes. In this case, feed concentration, feed pH and pressure were also constant and maximum rejection was obtained at approximately 80% with the RO membrane [16]. In a work that was conducted by Koseoglu et al., phenol removal using different nanofiltration membranes has been investigated. In their work, the feed pH was the most effective parameter and also the effect of feed concentration was investigated [6]. Bodalo et al., studied phenol removal from aqueous solution by nanofiltration and reverse osmosis membranes and investigated the effect of pressure, feed concentration and pH where the feed flow rate was remained constant [9, 17]. It should be noted that the type of the membranes applied in these studies are quite different with the membrane applied in the present work. They applied high pressure NF and RO membranes at the pressure range of 10-25 bar [9] and 30-45 bar [17] while the current study is performed at the pressure range of 1.36-4.76 bar (20-70 psig) which are very lower pressures. It is well known that the increase in feed pressure increases the permeation flux and consequently the rejection percent of the solutes. On the other hand, the reported results in Refs [9] and [17] have been limited to the feed concentrations of 50-200 ppm where in the current study the effect of higher feed concentrations (up to 500 ppm) is investigated and the presence of a critical pressure is reported for the first time.

Therefore, in the current work, phenol removal from aqueous solution using a low pressure RO membrane is investigated. The effect of feed pressure, feed concentration, feed flow rate and feed pH on the rejection of phenol is studied. Because feed flow rate has an important effect on the RO system performance then we also investigate the effect of feed flow rate on phenol rejection.

2. Experimental

2.1. Chemicals

Phenol with 99% purity was obtained from Merck. Table 1 indicates the physico-chemical properties of phenol. 5 M sodium hydroxide solution and 25% HCl were used for pH adjustment at the desired level and purchased from Merck and Dr. Mojallali laboratory chemicals Co. 4-aminoantipyrine and potassium ferricyanide were purchased from Alfa Aesar and Merck, respectively. Chloroform and ammonium hydroxide were purchased from Dr. Mojallali laboratory chemicals Co. and Merck, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₆H₅OH</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>94.11</td>
<td>g/mol</td>
<td>[16]</td>
</tr>
<tr>
<td>Density</td>
<td>1.07</td>
<td>g/cm³</td>
<td>[28]</td>
</tr>
<tr>
<td>Vapor pressure (at 25 °C)</td>
<td>0.35</td>
<td>mmHg</td>
<td>[28]</td>
</tr>
<tr>
<td>Melting point</td>
<td>40.91</td>
<td>°C</td>
<td>[28]</td>
</tr>
<tr>
<td>Boiling point (at 101.3 kPa)</td>
<td>181.75</td>
<td>°C</td>
<td>[28]</td>
</tr>
<tr>
<td>Water solubility (at 20 °C)</td>
<td>8.3</td>
<td>g phenol/100 mLH₂O</td>
<td>[28]</td>
</tr>
<tr>
<td>Water solubility (at 25 °C)</td>
<td>8</td>
<td>g (wt/%)</td>
<td>[16]</td>
</tr>
<tr>
<td>pKₐ</td>
<td>9.86</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Log Kₐ</td>
<td>1.46</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>1.49</td>
<td>Debye</td>
<td>[16]</td>
</tr>
</tbody>
</table>

Table 1. The physico-chemical properties of phenol.

2.2. Experimental set-up

The experimental RO system is shown in Figure 1. In this set-up, we used a TFC polyamide low pressure reverse osmosis membrane (TW30-1812-100) supplied from Dow Filmtec Company. Properties of the membrane have been shown in Table 2. The apparatus that we used in this work are a pump (model HF-8367) with maximum working pressure of 125 psi and flow rate of 1.2 LPM, a flow meter (model 10A1227) manufactured by Bailey-Fischer & Porter, a pressure gauge (model Marsh), two manual needle valves (model AISI 316L) manufactured by Fujikin, a diaphragm valve (model SS-4DAL) manufactured by Nupro, all of which are stainless steel and a glassy feed tank with 2 liters capacity.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>4.8</td>
<td>ft²</td>
</tr>
<tr>
<td>Diameter</td>
<td>1.75</td>
<td>In</td>
</tr>
<tr>
<td>Length</td>
<td>10</td>
<td>In</td>
</tr>
<tr>
<td>Max. Working Pressure</td>
<td>300</td>
<td>Psi</td>
</tr>
<tr>
<td>Max Flow Rate</td>
<td>7.6</td>
<td>L/min</td>
</tr>
<tr>
<td>Max. Feed water Temperature</td>
<td>45</td>
<td>°C</td>
</tr>
<tr>
<td>pH Range</td>
<td>2-11</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. The specifications of TW30-1812-100 reverse osmosis membrane [29].
According to Figure 1, at first the aqueous solution containing phenol was sent to the membrane module by a diaphragm pump. For indicating feed pressure, the pressure gauge is monitored at feed stream. The flow meter is placed at feed stream before the membrane, for showing the flow rate of the feed. One of the high prescience needle valves has been placed at the feed line for regulating feed flow rate. The influent stream to the membrane produces two effluent streams that are permeate and reject. Permeate and reject streams have been returned to the feed tank so that feed concentration remained relatively constant and quasi steady state conditions are established.

At the reject line the second needle valve was located for pressure regulation. The diaphragm valve was placed at the permeate line for sampling from the permeate stream.

2.3. Experimental procedure

For preparing feed solution for this work, at first a stock solution with 1000 mg/L concentration was prepared by dissolving 1g phenol in 1 liter of distilled water. Then with diluting this stock solution, desired feed concentrations were made. Before using the solution with adjusted concentration, feed pH was set at acidic or alkaline range by HCl and NaOH dilute solutions.

Phenol aqueous solutions in 100, 200, 300 and 500 mg/L concentrations were prepared in order to investigate the effect of feed concentration. For analyzing the effect of pH, a pH range of 2-10 was chosen. Operational pressure in the range of 136-544.2 kPa and feed flow rate in the range of 0.25-1.172 L/min were selected for investigating the effect of pressure and flow rate. All of the experiments were carried out at room temperature.

Before and after each test the membrane was washed with distilled water for ensuring that the previous test could not affect the new test. Every 15 minutes, samples from the feed, reject and permeate stream were taken, and it was clear that after 1 hour permeate, feed and reject fluxes were steady. Sampling from the permeate stream after one hour was performed. The phenol rejection percentage was calculated using equation 1.

2.4. Analytical method

The concentration of phenol in the feed and permeate streams were determined by "sensitive 4-aminoantipyrine method" using a spectrophotometric method at 460 nm [40]. A Cecil spectrophotometer (model CE1010) was used for measuring the absorbance of the samples.

3. Results and Discussion

3.1. Effect of pressure

Figure 2 (A to D) shows the effect of feed pressure on phenol removal using the reverse osmosis system at room temperature and 1.172 L/min feed flow rate at different feed concentrations. Almost at four different concentrations, phenol rejection increased with increasing pressure until reaching a maximum value at a critical pressure. By increasing the feed pressure beyond the critical pressure, phenol rejection decreased. This critical pressure depends mainly upon the feed concentration and varies between 408-476 kPa. The reason for this behavior is that pressure is the driving force in the reverse osmosis system, and since water flux is directly proportional to pressure difference, an increase of pressure causes an increase of water flux which, in turn, aggravates the concentration polarization because the solute that was rejected through the membrane accumulates at the membrane surface. Due to concentration polarization, phenol concentration at the membrane surface increased and consequently phenol concentration in the
permeate stream was increased. At lower feed concentration, concentration polarization was low and consequently critical pressure was larger. At pressures lower than critical pressure, feed flow can decrease the effect of concentration polarization, but at higher pressures feed flow cannot decrease the effect of this phenomenon and thus rejection is decreased. It was reported that feed pressure should not be more than a certain limitation because high permeate fluxes cause an increase of concentration polarization [41].

3.2. Effect of feed pH

According to Figure 3, with an increase in pH, rejection is increased. As it is clear, the maximum phenol rejection occurred at pH=10. For every four concentrations, this trend is observed. Phenol is a weak acid and has a tendency to maintain its molecular structure. Phenol rejection is low at low pH values, and this can be attributed to maintaining the molecular structure of phenol. In its molecular state, phenol is easily adsorbed onto the membrane and diffuses in it, through hydrogen bonding or hydrophobic–hydrophobic adsorption between the phenol molecule and the membrane. With an increase in pH, phenol loses its proton and gives negative charge according to the dissociation reaction:

\[
\text{C}_6\text{H}_5\text{O}^+ + \text{H}^+ \rightarrow \text{C}_6\text{H}_5\text{O}^2- 
\]

With a further increase in pH, the amount of phenolate ions with negative charge increases. Equation 2 shows the relationship between pH and phenolate concentration.

\[
\frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}]} = \frac{K}{K + 10^{-p\text{H}}} 
\]

Phenol in its ionic form (phenolate) has low solubility in the membrane, and thus rejection increases. At highly alkaline solutions, the selective layer of the RO membrane is hydrolyzed and results the products with negative charges which increase the repulsion between the membrane surface and phenol in solution. In this condition, adsorption of phenol onto the membrane decreases and causes higher rejection. At pH =10 almost all of the phenol molecules dissociate and have negative charge, therefore maximum rejection is obtained at this pH. At lower pH, dissociation of phenol is low and phenol molecules can be easily adsorbed onto the membrane.

3.3. Effect of concentration

The effect of feed concentration on phenol rejection is shown in Figure 4. Results show that maximum rejection at 200 mg/L concentration is obtained. According to results, an increase of feed concentration causes a decrease in rejection.
Fig. 4. Effect of feed concentration and feed pressure on the rejection percent of phenol at 1.172 L/min feed flow rate and different feed pH: (A) pH=2, (B) pH=5, (C) pH=7, (D) pH=8, and (E) pH=10.

When feed concentration is increased, the competition between phenol molecules and water molecules for passing through the membrane becomes strong. An increase in the feed concentration is caused with more passage of phenol through the membrane; thus phenol rejection is reduced. In addition to increasing the feed concentration, the concentration polarization and concentration of phenol at the membrane surface is increased. Due to concentration polarization enhancement, phenol adsorption onto the membrane surface is high and consequently the rejection decreases. Also by
increasing feed concentration, osmotic pressure enhances and thus the driving force decreases, which causes reduction in water flux and rejection.

Among the tested phenol concentrations, maximum phenol rejection was obtained at a phenol concentration of 200 mg/L. When phenol concentration is low (100 mg/L), water flux is high and this aids the phenol molecule to bringing neighbor phenol molecules; thus decreasing phenol rejection. At 200 mg/L, flux falls and the passage of the phenol molecule and thus neighbor molecules are reduced. Also feed flow up to 200 mg/L can eliminate the effect of concentration polarization, but for a concentration beyond 200 mg/L, feed flow cannot remove concentration polarization. Therefore, at 200 mg/L maximum rejection occurs.

3.4. Effect of feed flow rate

Figure 5 indicates the effect of feed flow rate on phenol rejection at different concentrations (100-500 mg/L) and optimum pH (pH=10). The results indicated that by increasing feed flow for all concentrations, phenol rejection is enhanced and maximum rejection is obtained at 1.172 L/min. This trend is due to the fact that increasing feed flow rate can decrease concentration polarization and thus increase phenol rejection. An increase of feed flow rate is most important at high phenol concentration because it can increase rejection and also efficiency of this separating technique.

4. Conclusions

Phenol removal from aqueous solution was successfully investigated with a low pressure RO membrane. The effect of feed concentration, feed pressure, pH and feed flow were investigated. Conclusions that were obtained in this study are as follow:

- Increase of pressure up to a critical pressure enhanced the rejection almost linearly, for pressures higher than that phenol the rejection was decreased.
- Increase of feed concentration up to 200 mg/L increased the rejection, but for concentrations higher than 200 mg/L the rejection was decreased.
- Increase of feed pH in the range of 2-10 increased the rejection.
- Increase of feed flow rate caused a rejection increase.

Also, optimum conditions for phenol removal using this RO membrane were found to be 200 mg/L feed concentration at pH=10, 408.1 kPa feed pressure and 1.172 L/min feed flow rate and the obtained phenol rejection was 71.7%.

Although the current studies are focused on the MBRs and enzymatic digestion of phenolic compound, the use of an inexpensive simple membrane filtration system as the pretreatment is quite useful especially for the cases in which the recovery of phenol is the final goal.

5. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_p</td>
<td>solute concentration in the permeate stream (mg/L)</td>
</tr>
<tr>
<td>C_f</td>
<td>solute concentration in the feed stream (mg/L)</td>
</tr>
<tr>
<td>R</td>
<td>rejection (dimensionless)</td>
</tr>
<tr>
<td>K</td>
<td>Reaction constant</td>
</tr>
</tbody>
</table>

![Fig. 5](image-url) Effect of feed flow rate and feed pressure on the rejection percent of phenol at pH=10 and different feed concentration: (A) 100 mg/L, (B) 200 mg/L, (C) 300 mg/L, and (D) 500 mg/L.
6. References


