APPLICATION OF REVERSE OSMOSIS TO REMOVE ANILINE FROM WASTEWATER

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ABSTRACT

The presence of organic toxic solutes in industrial wastewater is a common environmental problem. Aniline is known to be a harmful and persistent pollutant and its presence in wastewater requires treatment before disposal. The performance of reverse osmosis to remove aniline from aqueous solutions is studied in this paper. The study has been carried out in a flat membrane test module using three thin layer composite membranes, two of polyamide, HR98PP and SEPA-MS05, and one of polyether sulphone, DESAL-3B. Recycling of both concentrate and permeate has been carried out in order to keep the feed concentration practically constant and so simulate a continuous process in a quasi-stationary state. The influence of different operational variables (pressure, feed volumetric flow rate, feed concentration and pH) on the performance of the aniline removal process is analyzed.

Keywords: Membrane processes; Aniline; Reverse osmosis; Wastewater

1. INTRODUCTION

Aniline is widely used as raw material in many industrial processes including the manufacture of dyes and pigments, herbicides and pesticides, pharmaceuticals and explosives, and as a solvent in perfumes, varnish and resins [1,2]. Aniline is released to the environment directly in industrial wastewater and indirectly through the degradation of some the above mentioned organic compound (herbicides, pesticides, dyes, etc.) [3,4].

Great care should be taken concerning the contamination of groundwater because aniline is known to be a toxic and persistent pollutant that is harmful not only to aquatic life but also to humans [5,6]. Indeed, aniline is toxic through ingestion, inhalation and contact with the skin. The short-term effects of aniline in humans are mainly connected with the lung, and include upper respiratory tract irritation and congestion. Repeated exposure may have effects on the liver, kidneys, blood (methaemoglobinaemia, resulting in cyanosis) and spleen. It goes without saying, then, that industrial wastewater containing significant levels of aniline should be treated to avoid pollution.

Several processes to remove aniline from wastewater have been described, including biodegradation [7,8], adsorption [9-10], oxidation [11,12] and different membrane processes such as pervaporation [13], liquid membranes [14,15], nanofiltration [16] and reverse osmosis [17].

In this paper, aniline removal from aqueous solutions by reverse osmosis using different membranes and different operational variables (pressure, feed volumetric flow rate, feed concentration and pH) is studied.

2. THEORY

The performance of a given membrane process is determined by two parameters, the selectivity and the flow through it [18]. For dilute aqueous mixtures consisting of water and a solute, the selectivity of a membrane towards the mixture is usually expressed in terms of the solute rejection coefficient. This parameter, R, is a measure of the ability of the membrane to separate the solute from the feed solution, and is defined, as a percentage, by the equation

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

where C_f and C_p are the solute concentration in the feed and in the permeate, respectively. The flow or permeation rate, J, is defined as the volume flowing through the membrane per unit area and time.

The solution-diffusion model [19] assumes that both the solute and the solvent dissolve in the non-porous homogeneous surface layers of the membranes and each diffusing across it in an uncoupled manner due to its chemical potential gradient, which is result of concentration and pressure differences across the membrane. The effect of concentration polarization and fouling are not considered in this study because model dilute feed solutions and high feed velocities were used to minimize deviations from ideal mass transfer.

The solvent flux depends on the hydraulic pressure applied across the membrane, ΔP, minus the difference in the osmotic pressures of the solutions on the feed and permeate side of the membrane, Δπ

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

where A_w is the water permeability constant, which depends on the structure of the membrane, ΔP is the membrane pressure gradient and π is the osmotic pressure. The solute flux depends on the solute concentration gradient across the membrane

$$J_s = B_s(C_f - C_p) \quad (3)$$

where B_s is the solute permeability constant, which is a function of the solute composition and the membrane structure, with the following value

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

D_s being the solute diffusion coefficient, K_s the solute distribution coefficient and *l* the membrane thickness. Expressing permeate concentration as $C_p = J_s/J_w$ [18] and combining equations (2), (3) and (4), the rejection coefficient can be written as:

$$R = \frac{A_w(\Delta P - \Delta\pi)}{A_w(\Delta P - \Delta\pi) + B_s} \qquad (5)$$

3. EXPERIMENTAL EQUIPMENT AND PROCEDURE

Experimental tests were performed in an INDEVEN flat membrane test module, which consists of a unit that provides data on the behaviour of the membranes in cross flow conditions with a reduced surface area, low feed and short times. Aniline aqueous solutions were treated in the test module, recycling both concentrate and permeate in order to keep the feed concentration practically constant and to simulate a continuous process in a quasi-stationary state (Fig.1).

Three membranes were used, HR98PP from Dow/Filmtec, SEPA-MS05 from Osmonics and DESAL-3B from Desalination Systems. Those membranes are thin layer composite membranes, with a high selectivity towards salts, which can be used in a relatively wide range of temperatures, pressures and pH values. The characteristics of the membranes are described in Table 1.

Typical experimental conditions were operating pressure of $40 \cdot 10^5$ N/m^2, feed aniline concentration of 0.1 kg/m^3, feed volumetric flow rate of $2.78 \cdot 10^{-5}$ m^3/s, pH=7 and temperature of 25ºC.

To study the influence of the different operational variables on the performance of the aniline removal process, the following experimental series were carried out: operational pressure variation ($30 \cdot 10^5$, $35 \cdot 10^5$, $40 \cdot 10^5$, and $45 \cdot 10^5$ N/m^2), feed volumetric flow rate variation ($2.78 \cdot 10^{-5}$, $4.17 \cdot 10^{-5}$ and $5.56 \cdot 10^{-5}$ m^3/s) feed aniline concentration variation (0.02, 0.05, 0.1 and 0.2 kg/m^3) and pH variation (6, 7, 8, 9 and 10).

The aniline concentrations in feed and permeate solutions were determined spectrophotometrically at 280 nm, after dilution with 1 M NaOH, using an UV spectrophotometer Shimazdu UV-160A.

4. RESULTS AND DISCUSSION

The influence of the different operational variables on aniline rejection is shown in Fig. 2. The rejection percentage slightly increases with pressure for all three tested membranes, the highest rejections being obtained with HR98PP membrane (91.8%) and the poorest with MS05 membrane (79.0%) (Fig. 2a). These results agree with equation (5), where ΔP is the only variable, assuming that the constants A_w and B_s are independent of pressure. So, an increase in ΔP leads to an increase in R. In the same way, an increase in feed aniline concentration produces slight increments in aniline rejection in the three tested membranes (Fig. 2b). When the feed concentration increases, the permeation concentration increases, but as the increase of permeate concentration is lower than the increase in feed concentration, rejection increases according to equation (1).

Variations in rejection at different pH values are not very important (Fig. 2c) in the experimental range of pH used in this work (the surroundings of the typical values of aqueous aniline solutions pH). A slightly increase of rejection between pH 6 and 7, followed by a slight decrease at pH values higher that 7, is observed for the HR98PP and for MS05 membranes, while no significant variations is observed for the DESAL-3B membranes.

Rejection changes with pH are presumably related to the presence of ionizable groups in the membrane structure and to the net charge of the aniline molecule as a result of its dissociation equilibrium [20]. Polyamide membranes have free carboxylic acids in their structure, which become negatively charged at pH values in the order of 5. This means that in the experimental pH range the membrane surface has negative charge. On the other hand, the aniline pKa is 4.6 and so, at pH values higher than 4.6, the anilinium proportion will decrease because of the formation of neutral aniline.

The initial slight increase in rejection between pH 6 and 7 could be related with the retention of the remaining anilinium cations by the negative carboxylate groups of the membrane. At pH values higher than 7, rejection decreases because the proportion of anilinium cations decreases significantly at a higher pH, and neutral aniline is not so retained by the negative charge of the membrane. At a pH higher that 8, no variations in rejection are observed with pH.

Since the DESAL-3B membrane does not possess these ionizable groups, no significant variations in rejection with pH are observed.
The increase of volumetric feed flow rate increases the rejection in the case of the HR98PP and DESAL-3B membranes and decreases the rejection when MS05 is used.

The influence of the different operational variables on permeation rate is shown in Fig. 3. Polyamide membranes (HR98PP and MS05) show higher permeation rates than polyether sulphone membrane (DESAL-3B) in the whole range of conditions studied.
Permeation rate increases with operation pressure, this increase being higher with HR98PP and MS05 membranes than with DESAL-3B membrane (Fig. 3a). According

to equation (1) J_w increases with operation pressure, but J_s is not affected and is only determined by the concentration difference across the membrane. So, a permeation rate increase is only due to water flux increase. The lower permeation rate increase for DESAL-3B membrane would be related to its lower water permeability.

No significant influence of aniline feed concentration on permeation rate is observed (fig. 3b). As mentioned above, when feed concentration increases, the permeate concentration increases, but the increase of permeate concentration is lower that the increase of feed concentration. So, J_w should decrease, as a consequence of the increase in $\Delta\pi$, and J_s should increase as a consequence of the ΔC (C_f-C_p) increase. No influence of pH on the permeation rate is observed (Fig. 3c). This agrees with other results described in the bibliography [21].

Finally, the permeation rate is not affected by the volumetric feed flow rate in the case of MS05 and DESAL-3B membranes, but decreases with the HR98PP membrane.

5. CONCLUSIONS

The performance of reverse osmosis to remove aniline from aqueous solutions is studied in this paper. Three thin layer composite membranes, two of polyamide, HR98PP and SEPA-MS05, and one of polyether sulphone, DESAL-3B, has been used. The influence of operational variables such as pressure, feed volumetric flow rate, feed concentration and pH on the rejection and permeate flow rate has been analyzed. The highest rejections are obtained with HR98PP membrane (91.8%) and the lowest rejections with MS05 membrane (79.0%). Aniline rejection slightly increases with pressure and feed aniline concentration for the three tested membranes. The observed changes in aniline rejection with pH are related to the charge of ionizables groups in the membrane structure and to the net charge of aniline molecule as a result of its dissociation equilibrium**.** Permeation rate increases with operation pressure, but no significant variations with feed aniline concentration and pH are observed. No discernable trend of feed volumetric flow rate on performance is obtained for all three membranes tested.

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Table 1. Main characteristics of the membranes used in the experimental test module.

	Membrane		
Manufacturer	Dow/Filmtec	Osmonics Inc.	Desalination Systems Inc.
Product denomination	HR98PP	SEPA MS05	DESAL-3B
Type	Thin film composite	Thin film composite	Thin film composite
Composition	Polyamide	Polyamide	Polyether-sulphone
Effective membrane surface area (m^2)	0.003	0.003	0.003
Maximum pressure (N/m$^{2)}$	$60 \cdot 10^5$	$70 \cdot 10^5$	$45 \cdot 10^5$
Maximum temperature (ºC)	60	80	50
NaCl rejection	> 97.5	> 98	> 98.5
pH range	2 - 11	3 - 11	4 - 11
Chlorine tolerance	Low	Low	Low

Figure captions

Fig. 1. Flow diagram of reverse osmosis test unit flat membrane module: (A) feed tank, (B) membrane module, (C) high pressure pump.

Fig. 2. Influence of different operating conditions in rejection percentages: a) pressure, b) feed aniline concentration, c) pH, d) volumetric feed flow rate.

Fig. 3. Influence of different operating conditions on permeation rate: a) pressure, b) feed aniline concentration, c) feed pH, d) volumetric feed flow rate.

Figure 1

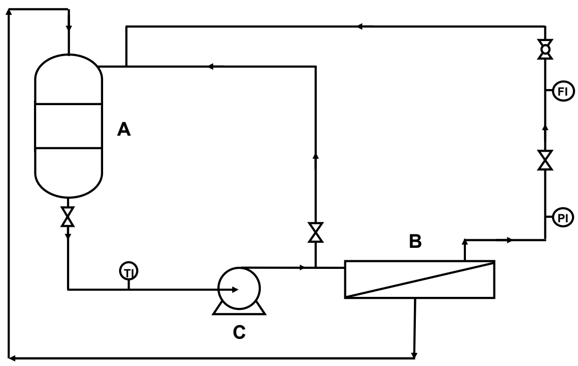


Figure 2

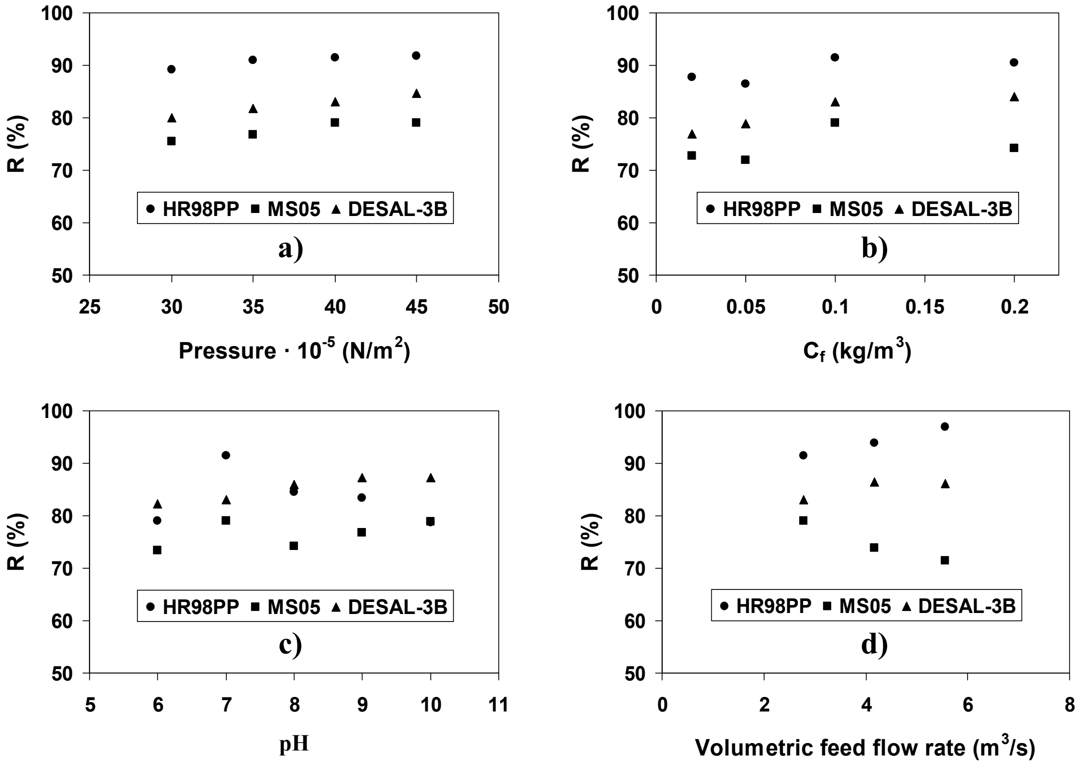
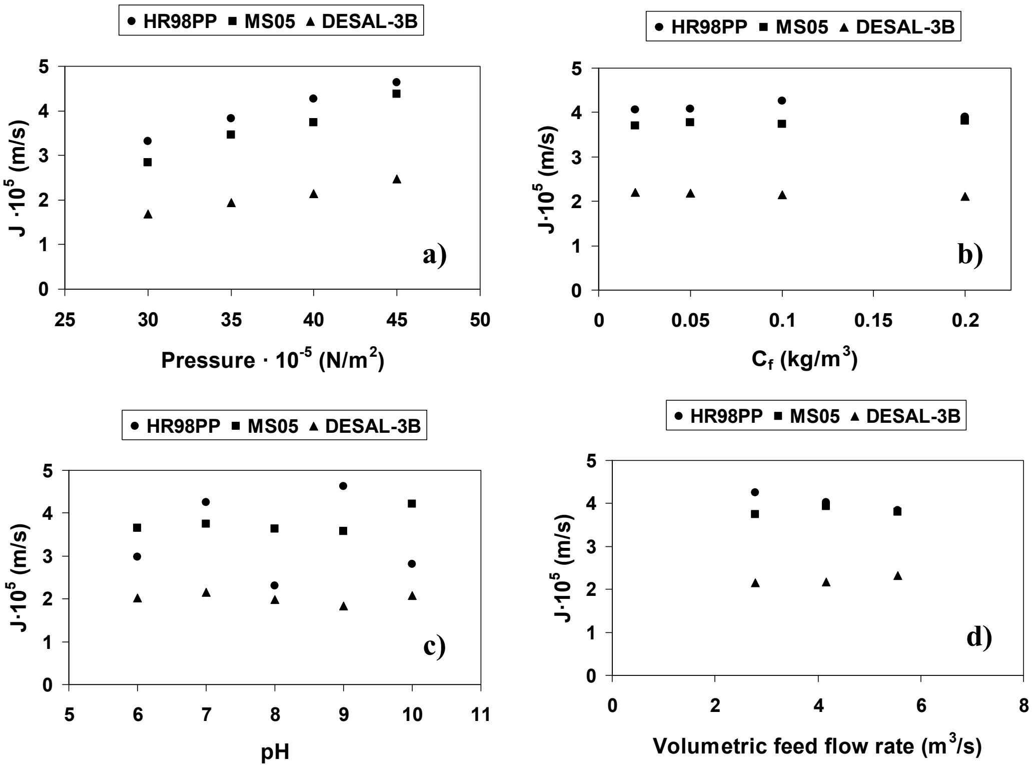

a)
b)
c)
d)
HR98PP
MS05
DESAL-3B
R (%)
Pressure · 10-5 (N/m2)
Cf (kg/m3)
pH
Volumetric feed flow rate (m3/s)

Figure 3



HR98PP MS05 DESAL-3B
J ·10^5 (m/s)
Pressure · 10^-5 (N/m^2)
a)
J·10^5 (m/s)
C_f (kg/m^3)
b)
J·10^5 (m/s)
pH
c)
J·10^5 (m/s)
Volumetric feed flow rate (m^3/s)
d)