

Removal of endocrine disrupting chemicals (EDCs) using low pressure reverse osmosis membrane (LPROM)

A.R.A. Razak*, Z. Ujang* and H. Ozaki**

*Institute of Environmental & Water Resource Management, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia (Email: zaini@utm.my)

**Department of Civil Engineering, Osaka Sangyo University, Osaka 574-8530, Japan (Email: ozaki@ce.osaka-sandai.ac.jp)

Abstract Endocrine disrupting chemicals (EDCs) are the focus of current environmental issues, as they can cause adverse health effects to animals and human, subsequent to endocrine function. The objective of this study was to remove a specific compound of EDCs (i.e. pentachlorophenol, C_6OCl_5Na , molecular weight of 288 g/mol) using low pressure reverse osmosis membrane (LPROM). A cross flow module of LPROM was used to observe the effects of operating parameters, i.e. pH, operating pressure and temperature. The design of the experiment was based on MINITAB™ software, and the analysis of results was conducted by factorial analysis. It was found that the rejection of pentachlorophenol was higher than 80% at a recovery rate of 60 to 70%. The rejection was subjected to increase with the increase of pH. The flux was observed to be increased with the increase of operating pressure and temperature. This study also investigated the interaction effects between operating parameters involved.

Keywords Endocrine disrupting chemicals; low pressure reverse osmosis membrane; pentachlorophenol; removal mechanism

Introduction

Endocrine disrupting compounds (EDCs) have been detected globally in surface waters. With the rapid development of analytical techniques, it has been reported that many aquatic environments are polluted with low concentrations of EDCs (sub $\mu\text{g/L}$) (Yoon and Lueptow, 2005; Yoon *et al.*, 2006a, 2006b). Some naturally occurring and man-made chemicals are widely considered to be endocrine disruptors, including certain pharmaceuticals, pesticides, insecticides, industrial chemicals, combustion byproduct, phytoestrogens and hormone excreted by animals and humans (Kim *et al.*, 2006). Steroid oestrogens, especially the endogenous 17β -estradiol and synthetic birth control pharmaceutical 17α -ethynylestradiol, have been shown to induce measurable changes in fish reproduction at concentrations as low as 2 ng/L (Liu *et al.*, 2005). EDCs have also been detected in drinking water supplies in the pg/L range (Zhang and Zhou, 2005).

Studies on EDCs in Malaysia were initiated recently (Mustafa *et al.*, 2006). Series of work to determine the concentration level of EDCs have been carried out among several states in Malaysia and the result are summarised in Table 1. It shows the level of paraquat found in Selangor and Cameron Highland do not exceed the maximum level of contaminant which is 0.02 ppm as proposed by the United States Environmental Protection Agency. However, due to the extensive usage of the particular compound, early precaution should be taken to avoid future adversity.

Table 1 Level of selected EDCs in wastewater samples in Malaysia

Types of EDCs	Compound	State/Sample	Highest level of detection
Pharmaceuticals	Chlorophenicol	Perak	264.04 ng/mL
		Melaka	176.26 ng/mL
		Selangor	221.60 ng/mL
	Sulphonamides	Perak	73% detected (of 50 samples collected)
		Melaka	51% detected (of 50 samples collected)
	Selangor	24% detected (of 50 samples collected)	
Bioactive natural waste (oestrogens)	Estrone	Perak and Melaka	228 ppt
	Estradiol	Perak and Melaka	44.55 ppt
		Klang	4.25 ppt
Toxic known compounds	Paraquat	Selangor	2.29 ng/mL
		Cameron Highland	1.83 ng/mL

(Adopted from Mustafa *et al.*, 2006)

Removal of EDCs by NF/RO membranes

Retention of organic pollutants in membrane separation processes depends on the characteristics of both membrane and the pollutants (Ozaki *et al.*, 2006). In addition, most of the papers reviewed by Bellona *et al.* (2004) show that the transport of uncharged organic compounds through reverse osmosis (RO) and nanofiltration (NF) membrane is controlled mainly by the sieving mechanism. There is a common understanding that nonionisable organic solutes of molecular molar mass ranged between 200 and 300 g/mol are efficiently rejected by the NF/RO membranes (Kimura *et al.*, 2003). However, the rejection of the uncharged organic by RO/NF membranes is often affected by physico-chemical properties of the system, and in the case of ionisable organics, the charge exclusion plays a significant role in the rejection process (Košutić *et al.*, 2006).

The sieving mechanism of solute rejection is based on the relation between the size of solute molecules and the size of the membrane pores. RO membrane has a very small molecular weight cut-off (MWCO) and it can retain a large fraction of low molecular weight compounds (e.g. amino acids or sugars). In any case, characterising an RO/NF membrane's porosity and relating it to specific solutes retentions is valuable for understanding a membrane's rejection of various organics (Košutić *et al.*, 2006). Furthermore, Kimura *et al.* (2003) reported that negatively charged compounds would be significantly rejected by NF/RO membranes due to electrostatic repulsion between the compounds and membranes, even when compounds with a small molecular weight (e.g. 110) and a rather loose membrane (i.e. NF).

The recent development of RO membrane systems, known as low pressure reverse osmosis membrane (LPROM), offers alternative technologies for producing high quality drinking water. Some authors refer to LPROM as NF, charged UF, loose RO or do not distinguish at all between NF and RO (Schäfer, 2001). The membranes operate at a low feed concentration and have high rejections for dissolved salts and organic substances (Hofman *et al.*, 1997). LPROM has been capable of removing various contaminants due to the fact that it has an RO filtration range, and low pressure is suggested for non-saline water (Hamdzah *et al.*, 2006). Besides, it can produce a specific flux of more than 60 L/m²hMPa at a lower operating pressure (0.2–0.9 MPa) (Ozaki, 2004).

It was concluded that ultra LPROM was extremely attractive for the direct treatment of surface water and the removal of pesticides and organic micropollutants (Hofman *et al.*, 1997). The water and wastewater treatment using LPROM can reject more than 90% of almost all micropollutants, depending on the operating parameters of the system (Hamdzah *et al.*, 2006). Therefore, in order to obtain high rejection of micropollutants

and high flux rate, further investigations shall be made to determine the best operating conditions for LPROM system. This paper elucidates the effect of operating parameters on the removal of pentachlorophenol (a representative of EDCs) using LPROM.

Experimental setup

A multi-layer thin-film of aromatic polyamide (ES20) membrane, manufactured by Nitto Denko was used in this study. LPROM experiments were conducted using a cross flow module C10-T. The schematic diagram of experimental set up is shown in Figure 1. Due to the membrane layer consisting of charged chemical groups (carboxyl groups and amine groups), the membrane is negatively charged at a pH above 5 as a result of dissociation of the carboxyl group present in the skin layer and it is positively charged at pH lower than 5 due to dissociation of the amine group in the skin layer.

The effective membrane surface area of the module is 60 cm². The membrane was supplied in a flat sheet form. The retentate will be circulated to increase the concentration of EDCs in the feed solution. For each experiment, permeate samples were taken every 30 min, then permeate flux and concentration were measured. The experiment was continued until permeate became stable. The rejection was evaluated based on the stable permeate. Membrane efficiency needs to be tested by sodium chloride with a concentration of 500 mg/L at the beginning and the end of every experiment.

The performance of LPROM can be expressed in terms of the overall flux and the percentage removal of specific substance or substances which are required to be removed. Percentage removal of a specific substance is more often expressed indirectly in terms of rejection. The quantity of the targeted substance in the retentate to that in the feed is called the rejection and is expressed as a percentage of the feed concentration. The concentrations of pentachlorophenol were measured using a UV-spectrophotometer, at 220 nm wavelength.

The transmembrane water flux is a function of quality of the feed stream, the degree of pretreatment, the characteristics of the membrane and the system operating parameters. The recovery rate (%) of the membrane was obtained using the formula below:

$$\text{Recovery, } r(\%) = (Q_p/Q_f) \times 100\% \quad (1)$$

where Q_p is the flow rate of the permeate (mL/min) and Q_f is the low rate of the feed (mL/min). Flow rate of the feed, Q_f , can be obtained as follows from the corresponding

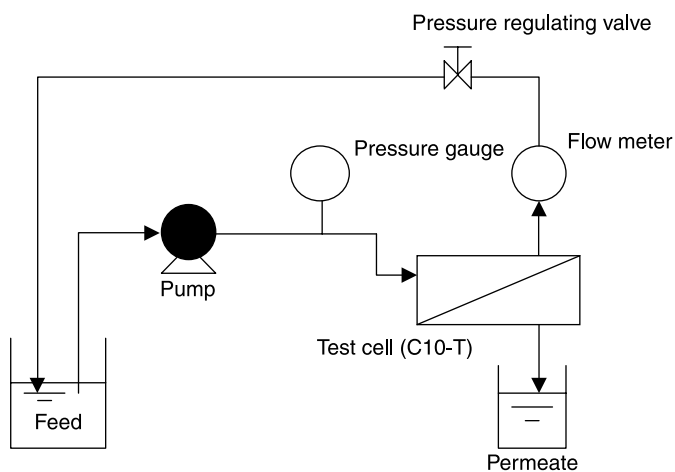


Figure 1 Schematic diagram of experimental set up

mass balance equation:

$$Q_f = Q_p + Q_c \quad (2)$$

where Q_c is the flow rate of the concentrate (mL/min). The rejection, R (%) can be termed as the percentage of solute concentration reduction of permeate stream relative to feed stream, and can be calculated as follows:

$$R(\%) = [(C_f - C_p)/C_f] \times 100\% \quad (3)$$

where R is the rejection (%), C_f is the feed concentration and C_p is the permeate concentration. Flux can be termed as mass or volume transfer through the membrane surface. It can be calculated as follows:

$$\text{Flux} = (V/A)t \quad (4)$$

where V is the volume of permeate (m^3), A is the effective area of membrane (m^2) and t is the duration (h).

Results and discussion

The results of LPRM conducted on pentachlorophenol (PCP) samples are shown in Table 2. From the results, the rejection and permeate flux of pentachlorophenol by LPRM is in the range of 83 to 98% and 13.5 to 23.8 L/m².h, respectively, at the recovery rate of 60 to 70%. The variations in the pattern of rejection and permeate flux are greatly influenced by parameters such as pH and operating pressure, which are also the determinants that governed the rejection and flux for organic compounds.

The results obtained were analysed by factorial analysis (FA), based on MINITAB™ software. FA was conducted to determine the important and significant factors and interactions between the factors that can be affected by the performance of LPRM in terms of permeate flux and the percentage of EDCs rejection. Factorial design allows for the simultaneous study of the effects that several factors may have on a process. Varying the levels of the factors simultaneously, rather than one at a time, in an experiment can

Table 2 Experimental results of LPRM conducted for pentachlorophenol

Run order	pH	Pressure (psi)	Temperature (°C)	Flux (L/m ² .h)	Rejection (%)	Recovery (%)
1	6.00	100.00	30	23.8	94.6	70.4
2	4.22	88.11	27	15.7	85.0	64.1
3	6.00	80.00	30	14.1	89.3	63.8
4	4.22	111.89	27	19.9	85.2	64.0
5	6.00	100.00	30	17.9	93.0	64.2
6	3.00	100.00	30	18.5	82.9	64.9
7	6.00	100.00	35	19.9	91.7	66.6
8	7.78	111.89	33	21.7	98.0	66.0
9	6.00	100.00	30	18.1	84.6	64.4
10	9.00	100.00	30	19.6	92.6	66.2
11	7.78	88.11	33	16.9	97.8	65.7
12	4.22	88.11	33	16.8	85.2	65.6
13	7.78	88.11	27	13.5	97.7	60.5
14	6.00	100.00	30	17.3	96.2	63.4
15	7.78	111.89	27	18.2	98.0	61.9
16	6.00	100.00	30	17.7	92.9	63.9
17	6.00	120.00	30	22.1	98.3	64.8
18	6.00	100.00	25	15.2	93.9	60.3
19	6.00	100.00	30	18.8	96.2	65.3
20	4.22	111.89	33	20.3	86.3	64.5

Initial concentration of pentachlorophenol = 10 mg/L

increase the efficiency of the experiment in terms of time and cost consumed and also allows for the study of interactions between the factors. Without the use of factorial experiments, important interactions may remain undetected.

The summary of analysis of variance (ANOVA) is shown in Table 3, which indicates the significance of the main operating parameters and their interaction effects based on the p -value (at 0.1 level of significance). With respect to the experimental conditions used in this study, the p -values show that only pH has significant effects on the rejection of PCP, as the p -value was 0.001. On the other hand, operating pressure and temperature have significant effects on the permeate flux, as the p -value was 0.001 and 0.029, respectively. All interaction effects among the operating parameters in this study were insignificant for both PCP removal and permeate flux.

The results were then illustrated by the Pareto chart and main effects plot, generated by MINITAB™ software, as shown in Figures 2–5. The effect of pH in feed solution for the rejection of pentachlorophenol was found to be significant as shown by the Pareto chart. Meanwhile, the effect of operating pressure and feed temperature was found to be significant in permeate flux production. The main effects plot for the flux and pentachlorophenol removal also indicates the similar results.

Table 3 ANOVA for permeate flux and percentage of PCP removal

Effect	PCP removal		Permeate flux	
	p-value	Significance ^a	p-value	Significance ^a
Main				
Operating pressure	0.288	No	0.001	Yes
pH	0.001	Yes	0.932	No
Temperature	0.883	No	0.029	Yes
Two-way interaction				
P × pH	0.946	No	0.726	No
P × Temp	0.946	No	0.907	No
Temp × pH	0.919	No	0.303	No
Three-way interaction				
P × pH × Temp	0.933	No	0.876	No

^aSignificant at $\alpha = 0.1$

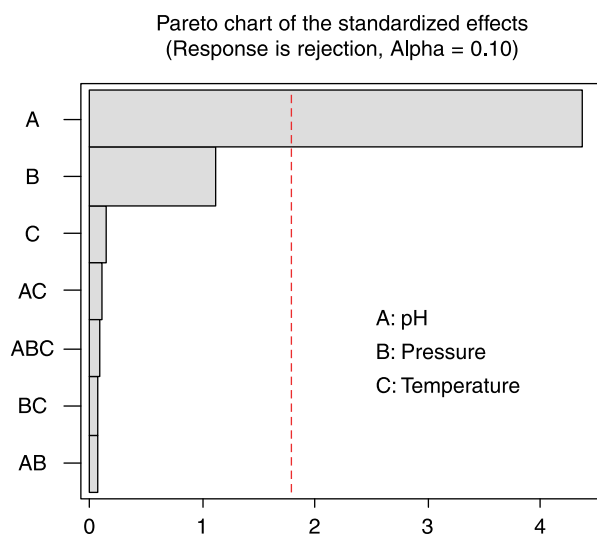


Figure 2 Pareto chart for pentachlorophenol removal

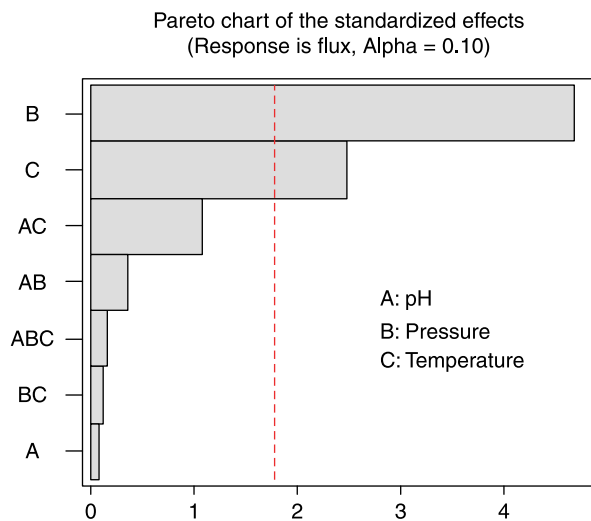


Figure 3 Pareto chart for permeate flux

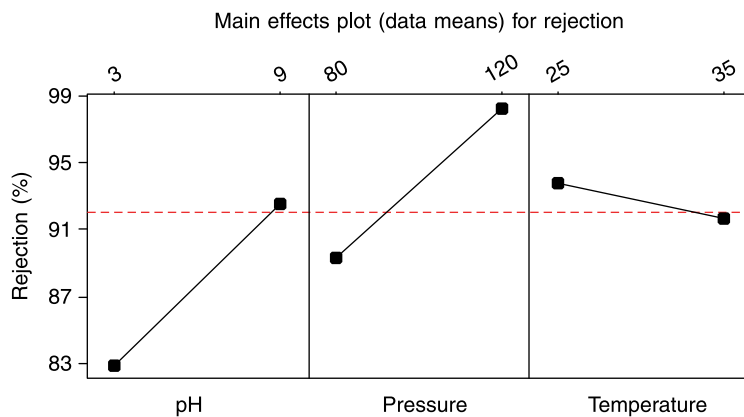


Figure 4 Main effects plot for pentachlorophenol removal

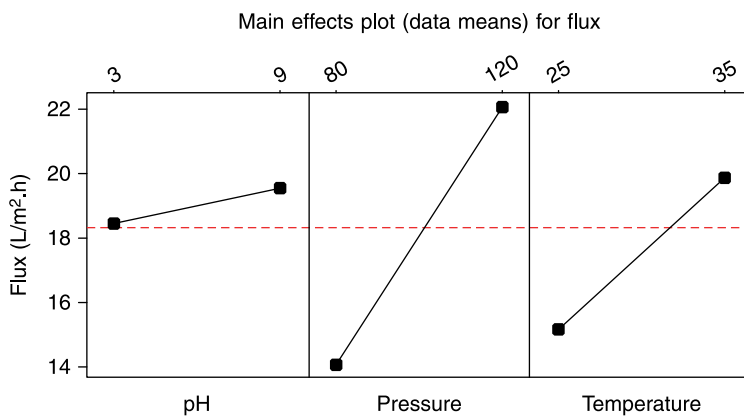


Figure 5 Main effects plot for permeate flux

Effects of operating pressure

The permeate flux increases with the increase of operating pressure as observed from the results. This finding is similar to Ujang and Anderson (1998), and this is due to the pure water passing through the membrane from the dilute solution, until the pressure from osmotic head equals the osmotic pressure of the concentrated solution. Ujang and Anderson (1998) reported that the higher the operating pressure, the greater will be the permeate flux for heavy metals from both mono- and divalent anions. Indeed, the behaviour between permeate flux and operating parameter is based on the following equation which was originally formulated by Lonsdale (1965):

$$J = A(P - \Delta\pi) \quad (5)$$

where J , A , P and π are the permeate flux, the water permeation constant, the applied pressure and the osmotic pressure, respectively. Osmotic pressure can be predicted by using the van't Hoff equation as follows (Brandt *et al.*, 1993):

$$\pi = v_i c_i RT \quad (6)$$

where v_i , c_i , R and T are the number of ions formed if the solute dissociates, the molar concentration of solute, the gas constant and the absolute temperature, respectively. It is important to increase permeate flux with operating pressure because it will dilute the solute passing through the membrane (Hamdzah *et al.*, 2006).

Effects of pH

The pH is observed to be increasing linearly with the rejection of pentachlorophenol. The phenomenon is likely due to the charged membrane and the charged solute which leads to a Donnan potential. Since pentachlorophenol possesses a relatively low pKa value, which is 4.7, it is more likely to be dissociated at low pH, therefore producing charged ions. The charged membrane attracts ions of opposite charged ion to achieve equilibrium. At the same time, the membrane will repel the same charged ions by an electrostatic force. In addition, the opposite charged ions will also be rejected due to an electro-neutrality in the solution. Because of these phenomena, the water can pass through the membrane. This mechanism enhances the rejection of pentachlorophenol due to the charges of pH which causes the membrane to be charged.

Effects of temperature

Temperature also affects water flux because increases in temperature result in increases in osmotic pressure and solute and solvent permeability; the increase in solvent permeability results in an increase in water flux. This water flux can be often described by Arrhenius temperature dependence on pure water permeability constant (Bhattacharya and Williams, 1992). Pure water flux change with temperature can also be predicted by water viscosity changes.

Conclusions

From the results obtained in this study, it is concluded that pentachlorophenol removal by LPROM is governed by pH due to the dissociation of this compound at low pH, therefore producing charge ions. The LPROM is negatively charged at a pH above 5 as a result of dissociation of the carboxyl group present in the skin layer and it is positively charged at pH lower than 5 due to dissociation of amine group in the skin layer. The charged membrane attracts ions of opposite charged ion to achieve equilibrium, and therefore enhances the rejection of pentachlorophenol. The flux is observed to be increased with

the increased of operating pressure and temperature. This is often described by the pure water passing through the membrane from the dilute solution, until the pressure from osmotic head equals the osmotic pressure of the concentrated solution. Temperature also affects water flux because increases in temperature result in increases in osmotic pressure and solute and solvent permeability; the increase in solvent permeability results in an increase in water flux. Meanwhile, the interaction among operating parameters in this study does not affect both removal of pentachlorophenol and permeate flux. Therefore, intrinsic membrane solute rejections (and hence product quality) and water flux are functions of pressure, temperature and pH (for ionisable organic solutes).

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