REMOVAL OF ENDOCRINE DISRUPTING CHEMICALS USING LOW PRESSURE REVERSE OSMOSIS MEMBRANE

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ABSTRACT

Endocrine disrupting chemicals (EDCs) are one of the major focuses of contaminants in current environmental issues, as they can cause adverse health effects on animals and human, particularly to endocrine function. The objective of this study was to remove a specific group of EDCs (i.e molecular weight range 228 to 288 g/mol) using low pressure reverse osmosis membrane (LPROM). A multi-layer thin-film composite of aromatic polyamide (ES20) membrane and a C10-T cross flow module of LPROM manufactured by Nitto Denko Company was used in this study. The effects of operating parameters, i.e. pH, operating pressure, concentration and temperature were observed using a design of experiment based on MINITAB™ software. The analysis of results was conducted by factorial analysis (FA) and response surface analysis (RSA). It was found that LPROM has been effectively applied to remove pentachlorophenol (PCP) (more than 83%), 17β-estradiol (more than 87%) and bisphenol-A (BPA) (more than 87%). For permeate flux, both PCP and 17β-estradiol tests produce excellent flux rate; i.e. 23.8 $L/m^2.h$ and 22.9 $L/m^2.h$, respectively. For BPA, the permeate flux produced was slightly lower (19.1 $L/m^2.h$) due to its physical-chemical properties effect at various levels of the recovery rate. In this study, the percentage of rejection was increased with the increased of pH and concentration of compounds. The flux was observed to increase with the increase of operating pressure. This study also investigated the interaction effects between operating parameters involved. In addition, statistical models were developed to represent the performance of LPROM under two response parameters, i.e. percentage of EDCs rejection and permeate flux. Statistical models were then validated using One-Factor-At-a-Time (OFAT) design of experiments and comparisons were made to better understand the trend of EDCs rejection and permeate flux.

ABSTRAK

Bahan kimia pengganggu endokrin (EDCs) merupakan salah satu daripada bahan pencemar yang menjadi tumpuan dalam isu-isu alam sekitar pada masa kini disebabkan kesan negatif bahan tersebut terhadap kesihatan manusia dan haiwan, terutamanya berkaitan dengan fungsi endokrin. Objektif kajian ini adalah untuk menyingkirkan satu kumpulan EDCs yang spesifik (iaitu yang mempunyai berat molekul antara 228 hingga 288 g/mol) menggunakan membrane osmosis balikan bertekanan rendah (LPROM). Sejenis membran multi-lapisan filem-nipis, komposit daripada poliamida aromatik (ES20) dan modul aliran bersilang C10-T untuk LPROM yang dihasilkan oleh Syarikat Nitto Denko digunakan dalam memerhatikan kesan-kesan parameter operasi iaitu pH, tekanan operasi, kepekatan dan suhu. Rekabentuk eksperimen adalah berpandukan perisian MINITAB^{TM} dan analisis keputusan dilakukan dengan menggunakan analisis faktorial (FA) dan analisis balasan permukaan (RSA). Didapati bahawa LPROM sangat berkesan untuk digunakan dalam penyingkiran pentachlorophenol (PCP) iaitu melebihi 83%, 17β-estradiol dan bisphenol-A (BPA), masing-masing melebihi 87%. Dalam penghasilan *flux* pula, kedua-dua PCP dan 17β-estradiol mencatatkan nilai kadar *flux* yang tinggi iaitu 23.8 L/m^2.h dan 22.9 L/m^2.h. Bagi BPA, penghasilan *flux* adalah rendah sedikit iaitu 19.1 L/m^2.h disebabkan oleh kesan ciri-ciri kimia-fizik bahan tersebut pada pelbagai tahap kadar pengembalian. Peratusan penyingkiran adalah meningkat dengan peningkatan nilai pH dan kepekatan bahan. *Flux* pula didapati meningkat dengan peningkatan tekanan operasi. Kajian ini juga melibatkan kesan interaksi antara parameter-parameter operasi yang terlibat. Sebagai tambahan, model statistik turut dibangunkan untuk mewakili perlaksanaan LPROM melalui dua parameter balasan iaitu peratusan penyingkiran EDCs dan kadar *flux*. Model statistik kemudian disahkan dengan menggunakan rekabentuk eksperimen OFAT dan perbandingan dilakukan untuk lebih memahami bentuk penyingkiran EDCs dan kadar *flux.*

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

1.1 Research Background

As water resources become more limited and waste discharge becomes increasingly problematic, providing clean and sustainable water supplies is becoming important. In addition, existing water supplies may be limited in quantity or quality for meeting the increasing demands from population growth and industry expansion (Peng, 2003). Industrial, as well as human activities, produce large amount of waste materials and in chorus, the natural water system has been contaminated by various kinds of recalcitrant or hazardous substances, such as heavy metals, pesticides, toxic organics, pharmaceutical substances and endocrine disrupting chemicals (EDCs). These substances can also be classified as micropollutants.

Among these micropollutants, EDCs are among the major focus of current environmental issues, as they can cause adverse health effects in an intact organism, or its progeny, subsequent to endocrine function (Zhang and Zhou, 2005). Since the middle of last decade, a variety of adverse effects of EDCs on the endocrine systems of man and animals have been observed, and these effects may be cumulative, possibly appearing only in subsequent generations (Jiang *et* al., 2005; Coleman *et al*., 2005). In addition, Zhang and Zhou (2005) reported that advese effects have already been observed including hormone-dependent cancers, reproductive tract disorders and reduction in reproductive fitness. Reproductive abnormalities were reported in fishes living downstream of wastewater treatment plants in 1990s (Liu *et al*., 2005).

Removal of trace organics by pressure-driven membrane processes has been the subject of several recent studies. In general, the removal of these compounds by conventional wastewater and drinking water treatment processes is not effective or well understood (Comerton *et al.*, 2007). Several studies agreed that removal efficiency of hormones by conventional wastewater treatment plants varies largely, but the overall removal is generally low (Auriol *et al*., 2006; Zhang and Zhou, 2005; Coleman *et al*., 2005; Urase and Kikuta, 2005; Urase *et al*., 2005; Nghiem *et al*., 2004).

It is therefore of interest to determine the ability of advanced treatment process, such as membrane filtration, to remove these organic micropollutants. For the last few decades, the use of membrane technology has grown significantly in the water industry compared to other water treatment technologies, since membrane filtration requires minimal addition of aggressive chemicals and produces no problematic by-products (Yoon and Lueptow, 2005). Besides, membrane technologies are considered as one of the most effective processes for water and wastewater treatment with compact system, economically feasible and high rejection level of pollutants (Oh et al., 2001).

In particular, reverse osmosis (RO) including low pressure RO (LPRO) and nanofiltration (NF) are broadly used membrane processes for both potable water treatment and wastewater reuse. Ozaki and Li (2002) reported that RO is an effective technology to remove organic compounds from water bodies, especially for those that contain low concentration and low molecular weight organic compounds. Moreover, high pressure-driven membranes such as NF and RO would be powerful options to remove such organic micropollutants (Kimura *et* al., 2004). Zhang *et al*. (2006), also reported that NF and RO, as promising membrane technologies, could be alternative methods for removing low molecular weight organic micropollutants, particularly pesticides, pharmaceutically active compounds (PhACs) and EDCs.

However, the use of RO systems has a limit. Traditional RO membrane is limited due to high operational cost and maintenance as RO involves requirement of high pressure to the system and need extensive pretreatment. Recently, advancement in RO membrane has been directed towards the development of low pressure reverse osmosis membranes (LPROM). Most LPROMs are multi-layer thin film composites of polymers and the active membrane surface layer usually consists of negatively charged sulphone or carboxyl group (Ozaki and Li, 2002). Due to the active surface layers, LPROMs have improved fouling resistance against hydrophobic colloids, oils, proteins and other organic. On the other hand, some studies reported that removal of organic solutes by NF and LPROM is influenced by a lot of factors such as operating variables, sieving mechanism and electrostatic interactions with the charged membrane (Agenson *et* al., 2003; Yoon *et al*., 2005; Ozaki and Li, 2002; Nghiem *et al*., 2004; Zhang *et al*., 2006). Further explanation about LPROM are presented in Chapter II, Section 2.3.4.

1.2 Objectives of Study

The aim of this study was to remove organic micropollutants (particularly EDCs) under various operating conditions using LPROM. This can be achieved by the following specific objectives:

i. To evaluate the effectiveness of LPROM for rejection of EDCs and the permeate flux patterns under different operating parameters, i.e. pressure, temperature, pH and concentration.

ii. To analyze and optimize the operating parameters for rejection of EDCs using response surface methodology.

iii. To develop and validate statistical models for the EDCs removal efficiency of LPROM.

1.3 Scope of Study

This study is focused on the performance of LPROM, which are evaluated by response parameters, i.e. permeate flux and the percentage of EDCs removal. The study was conducted based on an experimental rig and the analytical studies include physical and chemical procedures, particularly to evaluate the performance and effectiveness in LPROM system.

The experimental design was carried out using response surface methodology (RSM). RSM is a statistical and mathematical technique which is useful for developing, improving and optimizing processes. All experiments were investigated under different operating parameters, i.e. pH, feed temperature, pressure and feed concentration.

To evaluate the effectiveness of LPROM for rejection of EDCs, three targeted compounds of EDCs were studied i.e. pentachlorophenol (PCP), 17β-estradiol (E2) and bisphenol A (BPA). These compounds were chosen to represent groups of certain molecular weights and octanol-water distribution coefficient (K_{ow}) could be examined. Compounds with larger molecular weights, i.e. more than 300 are expected to be efficiently removed by LPROM and therefore were excluded in this study.

Previous studies also showed that negatively charged compounds could be rejected by LPROM due to electrostatic repulsion between the compounds and membrane. The high rejection (more than 90%) associated with negative charge was observed even when compounds with a small molecular weight (e.g. 110) and a rather loose membrane (i.e. NF) were examined (Kimura *et* al., 2004). Therefore, charged compounds will not be considered in this study. In addition, near complete retention of low molecular weight organic compounds, particularly pesticides, by NF/RO membranes has been reported by several researches (Kimura *et* al., 2004).

1.4 Significance of Study

Many studies have been conducted on the rejection of organic solutes, such as natural hormones, estrogenic hormones, neutral EDCs and EDCs, by RO and NF membranes (Comerton *et al*., 2007; Zhang *et al*., 2006; Nghiem *et al*., 2004a, 2004b; Kimura *et al*., 2004; Ozaki and Li, 2002). Among organic micropollutants, EDCs have been receiving considerable attention recently due to insufficient studies in this area in the past, as well as availability of more sophisticated and reliable methods of EDCs characterization. It has been reported that many aquatic environments are polluted with low concentrations of EDCs (sub μg/L) (Yoon *et al*., 2006a, 2006b; Yoon and Lueptow, 2005). The removal of organic solutes, particularly EDCs using membranes, is influenced by the membrane type, permeating solutes and membrane sieving effect, and in some cases, certain membrane-solute interactions are believed to be involved. The extent of these influences is largely dependent on operating variables but yet the complete principle of organic solutes permeation through RO and NF membrane, is still unclear. Therefore, the significance of this study can be stated as follows:

i. EDCs could be removed using low energy treatment system, such as LPROM, lower than 120 psi, thus reducing the energy consumption as well as achieving high rejection levels.

ii. In establishing the best operating conditions for LPROM system to remove EDCs and producing high flux rate, the optimum range of operating parameters should be established.

iii. The optimization procedures developed in this study could be used as a basis for process enhancement of LPROM for EDCs removal.

1.5 Structure of the Thesis

There are five chapters in this thesis. Chapter I provides brief information of the whole study and the direction of research to be done. Chapter II elaborates the occurrence of EDCs in water and wastewater, as well as the mechanism of rejection by LPROM. Current models describing the retention of EDCs in the LPROM process are also presented in Chapter II. In Chapter III, the experimental set-up of this studies are explained with the analytical procedures and materials used in this study. All of the data and results of experiments are reported in Chapter IV, together with the analysis and discussions. Finally, Chapter V is devoted to the conclusions of this study. Further investigations and recommendations are also included in Chapter V.

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