LOW PRESSURE REVERSE OSMOSIS MEMBRANE FOR REJECTION OF HEAVY METALS

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This thesis is dedicated to my beloved husband, Mohd Amri Yahaya, mama, Hafizah Jaaffar, abah, Hamdzah Md Daly, atuk, Hj Jaaffar Hj Asri, nenek, Hjh Hasnah Tohirang, my brother, Mohd Eezan, my sister, Mazeeha Hamdzah and particularly to my little princess, Kayra Humaira Mohd Amri.

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ABSTRACT

Low Pressure Reverse Osmosis Membrane (LPROM) has been introduced to water and wastewater industries in the past few years due to the high cost of operational and maintenance of conventional high-pressure RO membrane system. LPROM may remove more than 90% of heavy metals depending on the operating conditions of the system. LPROM with operating pressure less than 100 psi is commercially available to make treatment system more affordable and cost effective. Therefore, the aim of this study was to produce high-quality drinking water using LPROM system by removing heavy metals and other contaminants. The main objective of this study was to evaluate the effectiveness of LPROM for rejection of heavy metals, under different operating parameters (i.e. pressure, feed concentrations and pH). A commercially available LPROM (ES20) system manufactured by Nitto Denko Company was used in this study. The experimental design was carried out using Response Surface Methodology (RSM). Two types of wastewater containing heavy metals (i.e. synthetic polluted water containing copper and magnesium from copper chloride and magnesium sulphate solutions, and raw water from ex-mining pool from Tasik Biru, Sarawak) were studied. The experimental study for copper showed that higher operating pressure increased permeate flux and higher feed concentration and pH values increased the percentage of removal. However, the two-way interaction parameter (i.e. pressure vs. pH, pressure vs. feed concentration and pH vs. feed concentration) showed insignificant effects in determining permeate flux and copper removal. For magnesium, all parameters and all two-way interaction were significant in determining the percentage of magnesium removal. The higher the operating pressure resulted in a higher permeate flux and percentage of magnesium removal. A higher the value of pH has caused a lower permeate flux. However, it will increase the percentage of magnesium removal. Besides, the higher the feed concentration of magnesium was also resulted the higher percentage of magnesium removal. The optimum range of operating pressure for both copper and magnesium removal was between 90 to 120 psi and at pH between 5.5 and 7.5. The optimum statistical model for these processes based on the experimental conditions of this study indicates that operating pressure was the most significant parameter in determining the permeate flux. However, the statistical analysis of heavy metals removal was statistically insignificant and showed that the range of parameters in the study appears to be less significant to develop a sensitive and comprehensive model. This was due to the transport or separation mechanism between micropollutants and membrane surface, effect of chemical characteristics as well as effect of metal complexation. As a conclusion, operating conditions such as operating pressure and pH must be taken into account when designing the LPROM system for an optimum process in order to achieve a better heavy metals removal with higher permeate flux.

ABSTRAK

Sistem membran osmosis balikan bertekanan rendah telah diperkenalkan dalam proses olahan air dan airsisa industri berikutan daripada kos operasi dan penyelenggaraan yang tinggi oleh sistem konvensional osmosis balikan bertekanan tinggi. Sistem ini dapat menyingkirkan lebih dari 90% bahan cemar bersaiz mikro bergantung kepada keadaan operasi sistem. Kini, ia telah dikomersialkan dengan tekanan kurang daripada 100 psi bagi menjadikan sistem ini lebih berkemampuan dan kos efektif. Matlamat utama kajian ini adalah untuk menghasilkan air minum berkualiti tinggi menggunakan osmosis balikan bertekanan rendah di samping menyingkirkan bahan cemar bersaiz mikro. Objektif kajian ini adalah untuk menilai keberkesanan membran osmosis balikan bertekanan rendah dalam menyingkirkan bahan cemar bersaiz mikro bergantung kepada parameter operasi yang berbeza seperti tekanan, pH dan kepekatan larutan. Membran komersial (ES20) diperbuat oleh *Nitto Denko Company* digunakan dalam kajian ini. Rekabentuk ujikaji dilaksanakan dengan menggunakan *Response Surface Methodology* (RSM). Dua jenis airsisa telah diuji, iaitu airsisa sintetik daripada larutan kuprum klorida dan magnesium sulfat dan air mentah dari kawasan bekas perlombongan, Tasik Biru, Sarawak. Keputusan bagi larutan kuprum menunjukkan bahawa lebih tinggi tekanan yang digunakan dapat meningkatkan hasil fluks dan lebih tinggi kepekatan masukan larutan dan nilai pH, meningkatkan hasil penyingkiran. Walau bagaimanapun, interaksi parameter dua hala (tekanan lwn. pH, tekanan lwn. kepekatan larutan masukan dan pH lwn. kepekatan masukan larutan) tidak mempengaruhi dalam penentuan hasil fluks dan juga peratus penyingkiran kuprum. Untuk magnesium, semua parameter dan interaksi dua hala parameter mempengaruhi dalam menentukan peratus penyingkiran magnesium dan juga hasil fluks. Lebih tinggi tekanan yang digunakan, dapat meningkatkan hasil fluks dan juga peratus penyingkiran magnesium. Nilai pH yang tinggi menyebabkan hasil fluks berkurang. Walau bagaimanapun, ia akan meningkatkan peratus penyingkiran. Di samping itu, kepekatan masukan yang lebih tinggi juga akan menghasilkan peratus penyingkiran yang tinggi. Julat optimum untuk operasi tekanan bagi proses ini adalah antara 90 hingga 120 psi dan pada pH antara 5.5 dan 7.5. Model statistik yang optimum bagi proses ini menunjukkan bahawa tekanan adalah parameter penting dalam menentukan hasil fluks. Namun, analisis statistik untuk penyingkiran bahan cemar bersaiz mikro menunjukkan bahawa julat parameter dalam kajian ini tidak begitu mempengaruhi dalam membentuk model yang peka dan merangkumi proses. Ini berikutan daripada mekanisma pergerakan atau pemisahan antara bahan cemar bersaiz mikro dan permukaan membran, kesan daripada sifat kimia serta kesan daripada kompleksasi logam. Kesimpulannya, parameter operasi seperti tekanan dan pH adalah penting dalam merekabentuk sistem membran osmosis balikan bertekanan rendah bagi menghasilkan proses yang optimum dalam mencapai penyingkiran bahan cemar dan hasil fluks yang tinggi.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATION

ϕ	-	dimensionless potential fraction of force exerted on a solute molecule by pore wall
Δp	-	applied pressure difference
δ	-	membrane thickness
πX_s	-	osmotic pressure corresponding to a mole fraction of solute X_s
ρ	-	dimensionless radial position in pore
α	-	dimensionless solvent velocity in pore
$\Delta\Phi_D$	-	Donnan electrical potential (V)
τ	-	effective thickness of membrane
ε	-	fractional pore area of membrane
π	-	osmotic pressure
σ	-	reflection coefficient of solute
b	-	ratio of solute radius to the membrane pore radius
ΔC	-	concentration gradient
ΔP	-	pressure gradient
ΔT	-	temperature gradient
Δx	-	linear distance through the membrane
A	-	pure water permeability constant
ANOVA	-	Analysis of variance
APHA	-	American Public Health Association
As	-	Arsenic
AWWA	-	American Water Works Association
c	-	concentration

C	-	molar concentration of salt
C	-	molar density of solution
CCRD	-	Central Composite Rotatable Design
C_i	-	concentration of the *i*th solute in bulk solution (mol/l)
c_i	-	concentration of the *i*th solute inside membrane (mol/l)
$c_{j(m)}$	-	concentration of ion *j* in the membrane
Cr^{3+}	-	Chromate
Cu	-	copper
$CuCl_2$	-	Copper chloride
c_w	-	concentration of water in the membrane
D_{AB}	-	solute diffusivity in the free solution
$D_{j(m)}$	-	diffusivity of ion *j*
D_{sm}	-	diffusivity coefficient in the membrane
D_{sm}	-	diffusion coefficient of salt in the membrane
DSPM	-	Donnan Steric Pore Model
D_w	-	diffusivity of water
DWSS	-	Department of Water Supply and Sewerage
E	-	Donnan potential
EQA	-	Environmental Quality Act
EU	-	European Union
F	-	faraday constant (9.6487 x 10^4C/mol)
F	-	Faraday's constant
H_2O	-	Water
HCl	-	Hydrogen chloride
HNO_3	-	Nitrate acid
J_s	-	solute flux
J_w	-	water flux
J_v	-	refers to solvent volume flux.
K	-	solute distribution coefficient or partition coefficient
K	-	solute partition coefficient
K_i	-	refers to solute partition coefficient at location I

k_m	-	mass transfer coefficient on the upstream side of the membrane
k_s	-	distribution coefficient
l	-	membrane thickness
LPROM	-	Low pressure reverse osmosis membrane
m^2	-	meter square
m^3	-	meter cube
Mg	-	magnesium
Mg/L	-	milligram per liter
Mg_2SO_4	-	Magnesium sulfate
NaCl	-	Natrium chloride
NaOH	-	Natrium hydroxide
OFAT	-	One-factor-at-time
OH^-	-	Hydroxide
P	-	permeability coefficient of solute through membrane
P_s	-	solute permeability coefficient
PSCF	-	Preferential sorption-capillary flow
psi	-	pounds per square inch
R	-	gas constant
R	-	gas constant (8.31 J/mol K)
RO	-	reverse osmosis
RSD	-	Response surface design
RSM	-	response surface methodology
T	-	absolute temperature
TDS	-	Total dissolved solid
UP	-	Ultra-pure
USEPA	-	United States Environmental Protection Agency
V_w	-	partial molar volume of water
WHO	-	World Health Organization
WRF	-	World Research Foundation
X_{AB}	-	friction between the solute and the solvent
X_{AM}	-	friction between the solute and the membrane material

X_{s2}, X_{s3}	-	mole fractions of solute in the high and low pressure side
$\gamma_{j(m)}$	-	activity coefficient of ion *j* in the membrane
λ	-	frictional parameter

LIST OF APPENDICES

CHAPTER I

INTRODUCTION

This chapter presents an overview of the micropollutants contamination in ex-mining pools and previous studies conducted on membrane technology, especially using Low Pressure Reverse Osmosis Membrane (LPROM) to remove micropollutants for drinking water production. The objectives and background of the study are also stated in this chapter. The scope of work are defined and the importance of this study are presented. Lastly, this chapter also presents the structure of the thesis.

1.1 Background of the Study

Direct contamination of surface waters with micropollutants from mining, smelting and industrial manufacturing is a long-standing phenomenon. In Malaysia, water samples from ex-mining pools have been reported containing various micropollutants, especially heavy metals (Yusof *et al*., 1996; Morgensen *et al.*, 2001).

Heavy metals are conservative pollutants and some of them are harmful to health. Some of these compounds may suppress the immune system, leading to increased susceptibility to disease while some may be carcinogenic. For example, some heavy metals such as copper, mercury and arsenic, for which the proposed guideline values for drinking water quality are quite low (in the range of µg/L to a few mg/L) owing to their carcinogenic effects or other risk factors to public health (Crespo *et al.*, 2004).

Generally, these types of micropollutants contained in polluted raw water can cause problems in water treatment plants. They can inhibit the biological treatment processes and reduce the treatment efficiency of the treatment plants (Buckley *et al.*, 2001). Thus, various technologies have been applied to remove micropollutants in water and wastewater, such as coagulation, filtration, lime softening, activated carbon and membrane technology. Although many of them have proved to be technically feasible, other factors such as cost, operational requirements and aesthetic considerations have not been favourable in some cases.

Membrane technology is considered as one of the most effective processes for water and wastewater treatment. It is a compact system, economically feasible and has high rejection level of pollutants (Oh *et al.*, 2000). Membrane technology has been given special focus in water treatment processes because of its capability in removing physical and chemical matters at a higher-degree of purification. It is commonly divided into microfiltration, ultrafiltration and reverse osmosis (RO), which utilizes pressure differentials (Oh, 2001). Nowadays, RO is one of the effective technologies to remove almost all pollutants, especially those with low concentrations. RO technology is also used today in large water treatment plants. It produces good quality of potable water from brackish and seawater resources, reclaim contaminated water sources and reduce water salinity for industrial applications. In addition, the application spectrum of RO membrane elements covers household units to produce higher quality of drinking water (Wilf, 1998).

However, the use of RO system has been limited due to high operational cost to keep the pressure at high level and maintain its components. RO requires high pressure system and need extensive pre-treatment. Over the history of wastewater treatment and reclamation by RO, developments in membrane technology have resulted in a variety of advancements. These advancements included enhancements in salt rejection capabilities, chemical stability and perhaps most importantly, pressure requirements (Filteau and Moss, 1997). Hence, in the past few years, low pressure reverse osmosis membrane (LPROM) has been introduced to water and wastewater industries (Ujang and Anderson, 2000; Filteau and Moss, 1997; Hofman *et al*., 1997; Ozaki *et al*., 2001).

LPROM is not a new concept in membrane technology. Its inception could be traced back to the 1960s (Ujang and Anderson, 2000). At that time, LPROM system was not an attractive system because of low flux and non-reliable membrane materials. For the past 15 years, many improvements were made to the membrane and different models were introduced into the market. One of the goals of many studies carried out recently was to reduce the operating costs of RO, by lowering the required operating pressure of the system. In the mid-1990s, membrane manufacturers began marketing high-rejection-high-flux LPROM (Nemeth, 1998). Recently, LPROM with operating pressure less than 100 psi is available commercially to make the system more affordable and cost effective.

Most studies carried out so far on LPROM have been focused on bench-scale feasibility approach using various pollutants. The applications of LPROM for micropollutants removal, particularly the investigation of operating parameters effect (i.e. pressure, feed pH and feed concentration) on separation of metal chelates, study on transport phenomena based on electrostatic, steric hindrance and filtration effect of LPROM as well as the effect of metal complexation, have not been studied extensively up to date.

1.2 Objectives of the Study

The aim of this study was to produce high-quality drinking water, using LPROM system to remove micropollutants from feed water. This can be achieved by the following specific objectives:-

i. To evaluate the effectiveness of LPROM for rejection of micropollutants, using synthetic wastewater, i.e. magnesium and copper under different operating parameters, such as pressure, feed concentrations and pH.

ii. To analyze and optimize the pressure range and other associated operating parameters for rejection of micropollutants using response surface methodology.

iii. To investigate the feasibility of micropollutant removal from an actual ex-mining pool water, Tasik Biru, Sarawak and to study the effect of metal complexation.

iv. To develop a statistical model for the removal efficiency using LPROM.

1.3 Scope of the Study

This study focused on the performance of LPROM, which was evaluated by response parameters, i.e. permeate flux and the percentage of micropollutant removal. This study was conducted on an experimental rig and the analytical studies include physical and chemical procedures, particularly to evaluate the performance and effectiveness of 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. pressure, pH and feed concentration.

Two types of wastewater containing micropollutants were studied i.e. synthetic polluted water containing micropollutants i.e. copper (Cu) and magnesium (Mg) from copper chloride and magnesium sulphate solutions, and raw water from an ex-tin mining pool from Tasik Biru, Sarawak.

1.4 Importance of the Study

Various technologies have been applied to remove pollutants in raw water, such as ion exchange, activated carbon and membrane separation (Oh *et al*., 2000). Due to high costs of operation and maintenance of conventional high-pressure RO membrane system, LPROM has been introduced to the water and wastewater industries in the past few years (Ujang and Anderson, 1996; Filteau and Moss, 1997; Hofman *et al*., 1997; Ozaki *et al*., 2001). The importance of this study are as follows:-

i. Water and wastewater treatment using LPROM can remove more than 90% of micropollutants depending on the operating parameters of the system. In order to achieve the optimum value of removal and flux rate, this study will be useful to determine the best operating conditions for LPROM system.

ii. This study will provide insight on the transport phenomenon of solutes through the LPROM charged membrane, which can affect the overall performance of LPROM systems.

iii. This study will provide a statistical model which acts as the basic reference in identifying the effectiveness of LPROM system in treating water and wastewater.

1.5 The Organization of the Thesis

This thesis consists of five chapters. Chapter I gives an overview of micropollutants contamination in ex-mining pools and studies conducted on membrane technology, especially LPROM. An overview of the theoretical background of studies conducted on membrane technology, especially LPROM, and theory of membrane transport are presented in Chapter II. Chapter III presents the methodology used in this study including on the design of experiments. Factorial design analysis and response surface methods (RSM) were described in this chapter.

Chapter IV presents the results of the experimental studies that have been described in Chapter III. Findings are combined and discussed holistically in this chapter. The last chapter, Chapter V, stated the conclusions of this study. Recommendations for future studies are also outlined in this chapter.