



UNIVERSITI PUTRA MALAYSIA

**RECOVERY OF HEAVY METALS FROM CHROME - PLATING RINSE
WASTEWATER BY REVERSE OSMOSIS**

KEETHANCHALI D/O NAGARETNAM

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**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA**

1999



**RECOVERY OF HEAVY METALS FROM CHROME – PLATING
RINSE WASTEWATER BY REVERSE OSMOSIS**

By

KEETHANCHALI D/O NAGARETNAM

**Thesis Submitted in Partial Fulfilment of the Requirements for the
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My dedication to :

OM AGATHISAYA NAMAA!

OM RENGARAJA THESIGA SWAMIYE NAMAA!

OM IDAIKADAR THEVAYA NAMAA!

OM KORAKKAR THEVAYA NAMAA!

OM ROMARISHI THEVAYA NAMAA!

OM BUJANDAR THEVAYA NAMAA!

GURUVE SARANAM GURUVE THUNAI

SATHIYAMAE AGATHIYAM AGATHIYAMAE JAYAM



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LIST OF ABBREVIATIONS

B	Channel height
B_1	Water permeation coefficient
B_2	Solute flux coefficient
C	Solute concentration
c_1	Molar concentration of the solute
D	Diffusion coefficient of solute
d_t	Channel diameter
J	Permeate flux
J_s	Solute flux
k_s	Mass transfer coefficient
L	Channel length
$\sum m_i$	Summation of molalities of all ionic and nonionic constituents.
P	pressure
ΔP	Pressure drop (Crossflow pressure)
ΔP_T	Average inlet and outlet pressure
ΔP_{TM}	Transmembrane pressure
Q_f	Feed rate
Q_p	Permeate rate
R	Gas constant
R	Rejection coefficient
R_b	Boundary layer resistance
R_s	Solute deposited resistance
R_m	Membrane resistance
T	Absolute temperature
T'	Temperature
v_1	Number of ions formed if the solute dissociates
v_s	Bulk velocity

Y	Recovery
$\dot{\gamma}$	Shear rate
π	Osmotic pressure
$\Delta\pi$	Osmotic pressure drop
α	Osmotic pressure coefficient
μ	Viscosity
θ	Sieving coefficient
δ	Thickness of boundary layer
DOE	Department of Environment
SIRIM	Standards and Industrial Research Institute of Malaysia

Subscripts

b	Bulk or feed
i	Inlet
m	Membrane surface
o	Outlet
p	Permeate or filtrate



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in partial fulfilment of the requirements for the degree of Master of Science.

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October 1999

Chairman : Fakhru'l – Razi Ahmadun, Ph.D.

Faculty : Engineering

Wastewater produced by industries contains harmful and toxic metals which danger the receiving waters. Chrome – plating rinse water which contains chromium is very toxic to the environment. Reverse osmosis is used with the tubular module B1 membrane to reduce the chromium, manganese, lead and copper to a reasonable level which is less harmful. Chromium (Cr) is reduced by 87.9% while Lead (Pb) is reduced by 94.3 % followed by Manganese(Mn) by 85.7% and Copper(Cu) by 91.9%.

The fluxrate increases with the transmembrane pressure from 43 l/m^2 . Hr at 40 bar to 63 l/m^2 .hr at 70 bar with a TDS of 2689 mg/l. The



permeate flux was directly proportional to the transmembrane pressure which follows the Resistance Model.

This method is quite appropriate for lead(Pb) , copper(Cu) and chromium (Cr) reduction. Nowadays reverse osmosis is gaining interest in the industries which produce wastewater containing high concentration of heavy metals.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi sebahagian keperluan untuk ijazah Master Sains.

**MENEMUPULIH SEMULA LOGAM BERAT DARI AIR SISA
PENYADURAN 'CHROME' MELALUI PROSES OSMOSIS
BERBALIK**

Oleh

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Air sisa yang dikeluarkan oleh industri mengandungi logam yang membawa kesan buruk dan toksik yang boleh mencemarkan air. Air sisa dari 'chrome – plating' yang mengandungi 'chromium' adalah sangat toksik kepada alam sekitar. Proses osmosis berbalik dengan membran model 'tubular B1' untuk mengurangkan logam seperti Chromium (Cr), Manganese (Mn), Plumbum (Pb) dan Kuprum (Cu) kepada satu tahap yang tidak membahayakan. Chromium dikurangkan sebanyak 87.9% manakala plumbum pula kepada 94.3% diikuti oleh manganese kepada 85.7% dan kuprum kepada 91.9%.

'Fluxrate' bertambah dengan tekanan transmembrane dari 43 l/m².hr pada 40 bar kepada 63 l/m².hr pada 70 bar dengan TDS sebanyak 2680 mg/l. 'Permeate flux" didapati berkadar terus dengan tekanan transmembrane yang mengikuti model 'Resistance'.

Kaedah ini amat berkesan bagi pengurangan kandungan logam berat plumbum, kuprum dan kromium. Kini, proses osmosis berbalik mendapat perhatian di industri yang menghasilkan air sisa yang mengandungi konsentrasi logam berat yang tinggi.

CHAPTER I

INTRODUCTION

Membrane separation processes are emerging as highly relevant unit operation in various industries. Developments of well adapted membranes came out of the application of physical chemistry, surface and polymer science. The manufacturing of membranes is now based on a mixture of science and practical experience closely to results obtained in applications.

Membranes

Membranes can be made of any materials which forms a thin wall ranging from 0.05 mm to 2.0 mm. It is actually a phase that acts as a barrier between other phases while permitting a degree of communication between them in a form of transferring of different constituents of a fluid, thus allowing the separation making up this fluid. This fluid can be a solid, a solvent-swollen gel or even a liquid.

It also acts as a physical barrier that prevents or reduces mass transfer. Suitable membranes should have high permeability, proper pore size and good mechanical stability. Membranes normally characterize their products by a series of conventional measurements which is :

- (a) ion exchange capacity
- (b) water content
- (c) burst strength
- (d) selectivity of various ions and concentration
- (e) permeability
- (f) conductivity
- (g) kinetic behaviour when transporting ions.

But the primary characteristics of any membrane are :

- (a) its pore size distribution which defines selectivity.
- (b) Solvent flow which depicts performance

Structure of Membranes

The first published works on what we now call reverse osmosis date back to about 1930. The first high performance reverse osmosis membranes are made of acetate or cellulose by Loeb and Sourirajan in the late 1950's followed by organic and inorganic membranes. In recent years, reverse osmosis has become the key method for water desalination competing successfully with distillation and electrodialysis. They are characterized by their structure which are :

- (a) Homogenous membranes - these membranes have been pierced with holes which are quasi cylindrical in shape, through a bombardment process followed by a chemical attack. Usually used in microfiltration.
- (b) Asymmetrical membranes - Made in one stage using polymer material. The selectivity permeable layer has been reduced to a very fine skin to

limit the resistance to transfer in proportion to the thickness of the layer. This layer rests upon another thicker substrate that has much slaker pores which intends to provide the membrane with satisfactory mechanical properties. This can be artificially improved by anchoring the membrane onto a fabric support, reinforcing the slack substrate.

- (c) Composite membranes - These membranes enable a permselective skin to be placed on a pre - existing porous support which is itself, often asymmetrical. Since the two materials placed together are usually of different types. The properties of each, mechanical in one, selective in another are used to their fullest extent.

Mechanism of Transfer through the Membranes

It can be divided into three groups that is :

- (a) Filtration : Semi - permeable membranes are used. The solution is concentrated due to selective passage of water whereas other constituents of fluid are sometimes retained at the surface of the porous medium depending on their size. An ideal membrane would only allow the passage of water.
- (b) Permeation : allowing the selective passage of one of the constituents in gas phase through the membrane.
- (c) Dialysis : Membranes used which allow the passage, selective or not, of ions, do not permit the passage of water. These membranes may not be neutral. If they are charged, they become selective in allowing the transfer of ions carrying opposite charges. Membrane can be :
 - (i) Cationic - permit the passage of cations only.

- (ii) Anionic - allows the passage of anions only.

What is Wastewater

Wastewater discharges are the sources of most anthropogenic pollution found in natural waters like oceans, lakes and rivers. Consequently, the cleaning of wastewater effluents is an important aspect of present water pollution control efforts.

Sources Of Wastewater

Four main sources of wastewater are :

- (a) Domestic Sewage - wastewater from household uses such as cooking, washing, cleaning etc.
- (b) Industrial wastewater - wastewater which comes as by-products from industries.
- (c) Agricultural Runoff - carries fertilizers and pesticides which constitutes a major cause of eutrophication of lakes.
- (d) Storm and urban runoff - In highly urbanized areas, may cause significant pollution effects.

Wastewater which is to be used in this course work is the industrial wastewater, electroplating effluent.

Determination of Wastewater Composition

Wastewater consists of many compositions. Tests are done to determine them. Among them are :

(a) BOD - Biochemical Oxygen Demand

This test is used to determine the amount of biodegradable contents in a sample of wastewater. It depends on the control of such environmental and nutrition factors such as :

- (i) pH and osmotic conditions
- (ii) essential nutrients
- (iii) constant temperature
- (iv) population of organism

(b) COD - Chemical Oxygen Demand Test

Total amount of overall oxidizable material is determined by this test. In this test, a very strong oxidizing chemical, usually potassium dichromate, is added to samples of different dilution.

(c) TOC - Total Organic Carbon Test

It is used to measure the organic matter that is present in the wastewater. This test is performed by placing a sample into a high - temperature furnace or chemically oxidizing environment. The organic carbon is then oxidized to carbon dioxide.

(d) TS - Total Solids

Total solids present in the wastewater is divided into :

- (i) suspended solids - solids that are too large to pass through the filter openings and are retained when a solution is poured.
- (ii) Dissolved particles - It is classified according to size as either soluble or colloidal.
- (iii) Total suspended solids - solids which are retained in the filter is heated to remove the water.

Heavy Metals in Wastewater

Heavy metals are metals or metalloids that have higher atomic weights. They also have a chemically significant classification of metal ions based on their classification into Lewis acids and bases. Heavy metals ions that are toxic to humans are important chemical contaminants. They are often referred to as trace metals which implies the presence of an essential requirements by organisms for that metal. Trace metals are divided into :

- (a) essential metals - aluminium, arsenic , zink, copper, iron, nickel and chromium
- (b) non - essential metals - Cadmium, lead, mercury, silver.

This metals are essential to live and have essential physiological roles. They usually occur in industrial wastewater from plating plants, paint and pigment industries. Among them are Hg^{2+} , As^{3+} , Cu^{2+} , Zn^{2+} , Ni^{3+} , Cr^{3+} , Pb^{2+} and Cd^{2+} .

Problem Statement

This method is currently being used to compare between distillation and electro dialysis. It's main use were in water desalination. And it has progressed from this to industrial wastewater, where it reduces the pollutants or heavy metals in the wastewater.

In this study , membrane system is being used to reduce heavy metals concentration in the electroplating effluent (car cooler). Main heavy metals in this wastewater are Chromium(Cr), Mangganese(Mn), Lead(Pb) and Copper(Cu). Heavy

metals in large, concentration and volume, can contaminate the environment , a reduction to an allowable level is needed.

Objectives

Two main objectives for these project are :

- a) To investigate the efficiency of heavy metals recovery from the electroplating effluent by reverse osmosis membrane filtration.
- b) The possibility to recover water from the wastewater for reuse purposes.

This system consists of a membrane system module , a cooling system, pressure gauges and a feed tank. This arrangement is needed to enable the system to work in an appropriate way to reach the goals.

CHAPTER II

LITERATURE REVIEW

Introduction

Industrial wastewater, can cause undesired effects to the environment. This is due to the chemical pollutants contained in them which have an adverse effect on the biological process and to the soil. Reverse osmosis, can be used to reduce this chemical pollutants. This still doesn't produce a bottleneck as faster processors are marketed at cheaper prices. Due to this, membrane separation technique have been for this purpose.

This review will trace out the history of the membrane system and its achievement, which is biased towards the reverse osmosis. This review continues with the manufacturing of membranes, latest technology of its wastewater processing, modules used in wastewater treatment, technical and economical problems related to the use of the membrane.

Papers that are reviewed in this chapter are mainly on the membrane technique and its related work with reverse osmosis application, since their applications are the leading way to implementing as the latest technique in the wastewater treatment.

