FLUORIDE AND ORGANIC MATTER REMOVAL FROM GROUNDWATER USING NANOFILTRATION MEMBRANE

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ABSTRACT

High fluoride concentrations in groundwater, up to more than 30 mg/L, occur widely, in many parts of the world. Nanofiltration (NF) membrane performance on fluoride removal from high fluoride content water was investigated in this study. The aim of this work is, on the other hand, to observe the influence of some operational parameters on the defluoridation performance. Nanofiltration was selected in this research since it has the smallest porous size that exhibit good performance in separation process compare to ultrafiltration and microfiltration membrane. Nanofiltration was prepared by interfacial polymerization. Nanofiltration membrane were synthesized by reacting aqueous solution of triethanolamine and organic solution of trimesoyl chloride in hexane. Separation test was carried out by using single test by separating the fluoride and water using synthetic fluoride. Nanofiltration membranes successfully reducing fluoride with the acceptable levels.

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ABSTRAK

Fluoride yang berkepekatan tinggi didalam air bawah tanah sehingga mencecah 30mg/L berlaku ke hampir seluruh bahagian di dunia. Prestasi penyingkiran fluoride oleh nanofiltration (NF) membrane telah dikaji didalam kajian ini. Matlamat utama kajian ini adalah untuk mengkaji pengaruh beberapa parameter keatas proses penyingkiran fluoride. NF telah dipilih didalam kajian ini kerana ia mempunyai saiz poros yang paling kecil yang telah menunjukkan prestasi yang baik dalam proses pemisahan berbanding dengan penapisan ultra(UF) and penapisan mikro. NF telah disediakan oleh proses pempolimeran antaramuka. Membran NF telah disintesis melalui tindak balas larutan akueus triethanolamine (TEOA) and penyelesaian organik klorida trimesoyl dalam heksana. Ujian pemisahan telah dijalankan dengan menggunakan ujian tunggal dengan memisahkan kandungan florida yang menggunakan florida sintetik. Membran NF telah Berjaya mengurangkan kandungan florida dengan tahap yang boleh diterima.

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LIST OF SYMBOLS

Cp	Concentration of permeate
Cf	Concentration of feed
h	Hour
P	Permeability
b	bar
J	Permeate flux
L	Liter
M	Meter
ΔP	Filtration pressure
R	Rejection
Δt	Filtration time
V	Volume

LIST OF ABBREVIATIONS

TEOA	Triethanolamine
TMC	Trimesoylchloride
PES	Polyethersulfone
PVP	Polyvinylpyrrolidone
NMP	N-metyl-pyrrolidone
UF	Ultrafiltration
RO	Reverse Osmosis
NF	Nanofiltration
IF	Interfacial Polymerization

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Textile industries generally produced dye wastewater which generates from dyeing, printing, and other process of coloring in its daily operation. Facts shows, the dye wastewater contains many dangerous chemical such as dyes, detergents sulphide compound, solvents, heavy metals and other dangerous substances. Therefore, dye wastewater cannot directly discharged from the factory because it has striking effect on receiving water body which sooner or later can cause harm to the environment, aquatic life and especially human. Many textile industries out there use a huge amount of water to decrease the pollution load from discharged wastewater. That practice increase the textile industries operation cost just for water consumption. So, it is better if textile industries use one type of treatment system which profitable operation through recycling the dye wastewater and at the same time protecting the environment (Lau and Ismail, 2009). That treatment system is called Nanofiltration. This treatment system allow for recovery of water and valuable chemical compound from dye wastewater.

Nanofiltration membrane separation are widely use in various industrial fields. Wastewater treatment is one of the field that use this kind of technology to treat the water until the water reach the quality that it can be discharged to the environment or reusable for other process. Nanofiltration has been knew having the properties in between reverse osmosis and ultrafiltration (Mansourpanah *et. al.* 2010). Because of that, it has significant advantages including low operation pressure, higher permeation flux, high retention of multivalent salt, molecular weight compound more than 300, and low investments, operation and maintenance costs (Tang *et al.* 2008). Nanofiltration membrane are produced by using two preparation steps which is polymer phase inversion resulting a microporous support membrane and interfacial polymerization of a thin film composite (TFC) layer on top of a miroporous support membrane or other porous substrate (Mohammad *et al.* 2003).

The thin film composite layer can be prepared using interfacial polymerization. Thin-film composite membranes are usually studied in reverse osmosis and nano-filtration. The interfacial polymerization has significant advantages which involve rapid reaction rates under ambient conditions, no requirement for reactant stoichiometric balance and a low requirement for reactant purity (Li *et al.* 2008). The interfacial polymerization technique is an adequate method for the preparation of composite membranes with an ultra thin polyester active layer. In this study, thin-film polyester composite membranes were prepared using interfacial polymerization for dye removal.

1.2 PROBLEM STATEMENT

Dyes is one of the substance contain in textile wastewater. Dyes are considered as problematic because the families of chemical compounds that make good dyes are also toxic to humans. Each new synthetic dye developed is a brand new compound, and because it's new, no-one knows its risks to humans and the environment. Therefore, because of these reasons, dye from textile industrial wastewater need to be removed.

In this research, nanofiltration membrane process is used because of its advantages. The major advantages of nanofiltration are

- No chemical additive
- Removal for health-related contaminants
- Removal of suspended solids, some dissolve ions, and other non-health related contaminant.
- Cost effective and low maintenances costs.

Retrieved from (Nanofiltration article by Peter S. Cartwright)

`The chosen thin film composite membrane is polyester membrane which is considered new in the field of composite thin-film membrane development compared to polyamide for example. In addition, the future nanofiltration in textile industries is also provided in view of developing a more competitive nanofiltration membrane, especially for textile wastewater treatment.

1.3 RESEARCH OBJECTIVES

The objective of this experiment is to produce Nanofiltration Polyester membrane for dye removal.

1.4 SCOPES OF STUDY

In order to achieve the objective of this research, the scope of study has been determined based on two parameters to produce polyester. These are including effect of monomer concentration and reaction time on membrane performance.

1.5 SIGNIFICANCE OF STUDY

This research purpose is to prepare the NF membrane which suitable for dyes removing from textile industries. If the dyes completely can be removed by this filtration method, the wastewater discharged volume could be minimized and thus reducing impact on environment.

CHAPTER 2

LITERATURE REVIEW

This section will describe detail about the basic concepts of membrane separation technology, background of the membrane, type of membrane which will be use in the experiment which is nanofiltration membrane and also detail information about fluoride and organic matters. It will cover it characteristics and the mechanism filtration.

2.1 MEMBRANE REVIEW

Membrane separation is a technology which selectively materials via pores and/or minutes gaps in the molecular arrangement of a continuous structures. Membranes are widely used in various types of field such as wastewater treatment, dairy and pulp and also textile industries.

2.1.1 What is a membrane

The word membrane is originates from the Latin word *membrane* which means a skin. Membranes keep things separated in the living world. They pass materials selectively. The membrane can be defined essentially as a barrier which separates two phases and restricts transports of various chemicals in a selective manner. In other words, a membrane is defined as a structure having lateral dimensions much greater than its thickness, through which mass transfer may occur under a variety of driving forces. The membrane can be selective or a contacting barrier. (Ashok, 2008)

2.1.2 Membrane Separation Process

A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and sorption diffusion mechanism. Separation is achieved by selectively passing (permeating) one or more components of a stream through the membrane while retarding the passage of one or more other components. Membranes can selectively separate components over a wide range of particle sizes and molecular weights.

Membrane processes are characterized by the fact that a feed stream is divided into 2 streams: retentate and permeate. The most general process can be seen in the figure 2.1

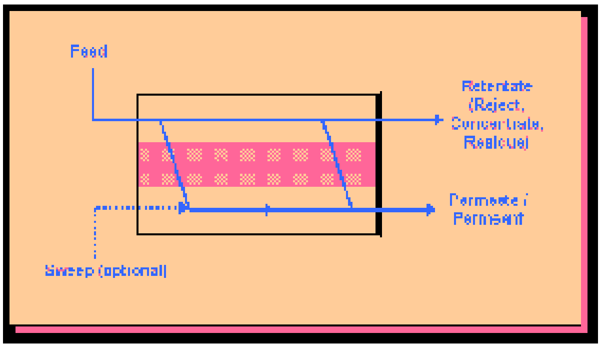

Figure 2.1 General process of membrane separation

The retentate is that part of the feed that does not pass through the membrane, while the permeate is that part of the feed that does pass through the membrane. The optional "sweep" is a gas or liquid that is used to help remove the permeate. The component of interest in membrane separation is known as the solute. The solute can be retained on the membrane and removed in the retentate or passed through the membrane in the permeate. (Wagner, 2001)

The flux through the membrane can be generally expressed as:

$$Flux = \frac{Membrane\ Permeability}{Membrane\ thickness}$$

This means that the flux depends linearly on both the permeability and the driving force. This driving force may be difference in pressure, concentration, temperature, chemical potential and so on. The flux also depends inversely upon the thickness of the membrane. The thinner the membrane, the higher will be the flux. (Louis-Francios, 2007).

2.2 PRESSURE DRIVEN MEMBRANE PROCESS

Based on the main driving force, which is applied to accomplish the separation, many membrane processes can be distinguished. An overview of the driving forces and the related membrane separation processes is given in Table 1.1

Table 2.1: Driving forces and their related membrane separation processes

Driving Force	**Membrane Process**
Pressure Differences	Microfiltration, ultrafiltration, nanofiltration, reverse osmosis or hyperfiltration
Chemical potential differences	Pervaporation, pertraction, dialysis, gas separation, vapor permeation, liquid membranes
Electrical potential differences	Electrodialysis, membrane electrophoresis, membrane electrolysis
Temperature differences	Membrane distillation

Source adapted from (Timmer, 2001)

Each membrane processes have their own mechanism and applications. For example, pressure driven membrane separation processes, electrodialysis and gas separation are industrially implemented and are generally considered as proven technology (Timmer, 2001)

2.2.1 Pressure Driven Membrane

Four pressures driven membranes are distinguished in practice (Timmer, 2001)

1. Microfiltration (MF), which is characterized by a membrane pore size between 0.05 and 2 µm and operating pressures below 2 bars. MF is primarily used to separate particles and bacteria from other smaller solutes.

2. Ultrafiltration (UF), this is characterized by a membrane pore size between 2 nm and 0.05 µm and operating pressures between 1 and 10 bars. UF is used to separate colloids like proteins from small molecules like sugars and salts.

3. Nanofiltration (NF),this is characterized by a membrane pore size between 0.5 and 2 nm and operating pressures between 5 and 40 bars. NF is used to achieve separation between sugars, other organic molecules and multivalent salt on one hand and monovalent salts, ions and water on the other.

4. Reverse osmosis (RO) or hyper filtration, which is characterized by a membrane pore size in the range of 0.0005 microns. Some researchers consider the RO membrane as without have pores. Transport of the solvent is accomplished through the free volume between the segments of the polymer of which the membrane is constituted. The operating pressures in RO are generally between 7 and 100 bar and this technique is mainly used to remove water.

2.2.2 Membrane Applications

Membrane processes are no longer bound in the domains of laboratory but have found their way into the industries as viable separation techniques. These processes have achieved impressive industrial importance for the resolution of aqueous liquid mixtures, purification of chemical and biological products, waste water treatment, and many more. Table 2.2 gives an overview of selected industrial application of membrane processes.

Table 2.2 Selected industrial application of membrane process

Industrial sector	*Membrane process*
Drinking water	RO, NF, UF
Waste water treatment	
Direct(physical)	MF, NF, RO, ED
Membrane bioreactor	MF, UF
Food Industry	
Dairy	UF, RO, ED
Meat	UF, RO
Fruit and Vegetables	RO
Beverages	
Fruit Juice	MF, UF, RO
Wine and brewery	MF, UF, RO, PV
Tea factories	MF, UF, NF
Biomedical	
Contro Release	Facilated transport\
Hemodialysis	Dialysis
Chemical Inductry	
Gas Separation	GS
H_2 recovery	GS
Hydrometallurgical processing	UF

RO : Reverse Osmosis ; NF : Nanofiltration ; UF : Ultrafiltration ; MF : Microfiltration ; ED : Electrodialysis ; GS : Gas Separation.

2.2.3 Advantages of Membrane Processes

Compared with the conventional methods, membrane systems offer more economical benefits over conventional systems. The followings are specific criteria of the membrane system (Mustaffar, 2004):

1. Flexibility and versatility; as this technology can be applied at wide spectrum of separation ranges comparable to conventional methods. The system can be operated in combination with the conventional methods and /or on its own.

2. Simplicity of operation; that is the system is relatively less complex and less sophisticated.

3. Low energy consumption; membrane systems consume less energy since separation does not involve phase change. Thus the system driving force is mainly pressure provided by using pump.

4. Low capital and maintenance cost; the overall membrane system is (30-40) % cheaper than the corresponding conventional systems.

5. Reliability; the membrane system is very reliable and requires minimum human intervention during operation.

6. Physical separation; separation is done physically thereby undesirable by products and no side reactions, no waste generation and is environmentally green.

2.3 NANOFILTRATION MEMBRANE

Nanofiltration is a liquid separation membrane technology positioned between reverse osmosis (RO) and ultrafiltration. Nanofiltration (NF) removes molecules in the 0.001 micron range. NF refers to a membrane process that rejects solutes approximately 1 nanometer (10 angstroms) in size with molecular weights above 200. Because they feature pore sizes larger than RO membranes, NF membranes remove organic compounds and selected salts at lower pressures than RO systems.NF essentially is a lower-pressure where the purity of product water is not as critical as with pharmaceutical grade water, or the level of dissolved solids to be removed is less than what typically is encountered in brackish water or seawater. This membrane is produced via phase inversion. While thin film composite membranes are both chemically and structurally heterogeneous. Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. This membrane can be made via several methods including interfacial polymerization, solution coating, plasma polymerization or surface treatment.

2.3.1 The Asymmetry

The Nanofitration membrane is asymmetry membrane. It will not allow the larger molecule to pass through the membrane and will stop at the surface. While the smaller molecule will pass through the membrane and known as permeate.

2.3.2 Pore Size

There are many types of membrane use in industry and one of them is nanofiltration. The nominal pore size for this type of membrane is between 0.5 and 2 nanometer.

2.3.4 Mass Transfer in Nanofiltration

A representation of the mass transfer process occurring in NF is given in Figure 2.2:

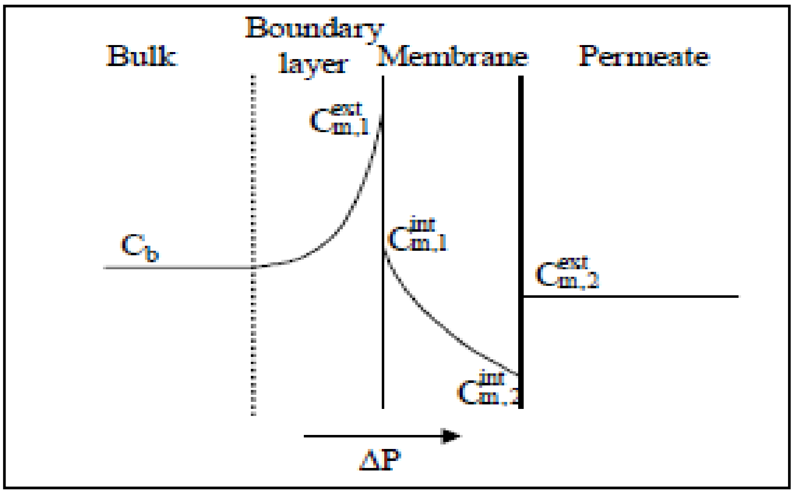

Figure 2.2 : Mass transfer in nanofiltration

When an external pressure *ΔP* is imposed on a liquid which is adjacent to a semi-permeable

membrane, solvent will flow through the membrane. The general terms that are used in the

description of membrane separation processes are the solvent flux (*J*) and the rejection (*R*). The solvent flux is given by:

$$J = \frac{W}{A\Delta t} \tag{2.1}$$

in which *W* is the mass of the obtained permeateat operation time Δt and *A* is the membrane area. By defining the solute rejection (R), we can use the equation 2.2 given ;

$$R = \left(1 - \frac{Cp}{Cf}\right) x\ 100 \tag{2.2}$$

Where *Cf* is the final concentration level and *Cp* is the concentration of the permeate before the filtration process.

The membrane permeance, *Pm* can be determined from the slope obtained by plotting the permeate flux J against ΔP :

$$Pm = \frac{J}{\Delta P} \tag{2.3}$$

2.4 THIN FILM COMPOSITE FILM

The semipermeable membrane used in the desalination process ordinarily will be thin in order to maximize the water flux. Thus the membrane often is formed on a porous support to provide strength, the combination being referred to as a thin film composite (TFC) membrane. The support should have pores which are sufficiently large so that the water (permeate) can pass through the support without reducing the flux of the entire composite. Conversely, the pores should not be so large that the thin semipermeable membrane will be unable to bridge the pores or will fill up or penetrate too far into the pores. *Scala et al* (1992) suggested that with pores above about 8 microns (8000nm) the rejection of impurities is reduced.

2.4.1 Interfacial Polymerization

The thin film composite was produced via polymerization which takes place at the interface of the two liquids which are insoluble to each other (Lau *et.al* 2011). It is carried out between two highly reactive monomers dissolved in two immiscible solvents (Dalwani, 2011). Even though the interfacial polymerization (IP) involves many complex parameters compared to spin coating, it is the major technique to produce commercial TFC membranes because composite membranes with surprisingly high flux could be made by interfacial crosslinking. The IP process consists of a sequence of steps, as shown in Figure 2.4. In the first step an ultraporous support is pretreated to make it suitable for the IP process. In the second step, the substrate is immersed in aqueous solution containing one of the monomer.

Then, continue immersed in second solution containing the second monomer. Since the two solutions in immiscible to each other, the interface is created between them. One of the monomer travels through the interface and react with the other polymer to produce polymerized product. IP layer usually dense and very thin due to high reactivity of two monomers and limited barrier created at interface.