NANOFILTRATION MEMBRANE FOR WATER PURIFICATION:

PRETREATMENT AND ITS FOULING PHENOMENA

by

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LIST OF SYMBOLS

$\dot{V}$	Volumetric flow rate (L/min)
ΔP	Applied pressure
A	Membrane surface area (m^2)
D	Diffusion coefficient (m^2/s)
D	Diameter of particle (m)
f(Ka)	Henry's function
J	Permeate flux ($L/hr.m^2$)
J_f	Feed solution flux before fouling
J_{if}	Feed solution flux after chemical cleaning
J_v	Permeate flux
k_B	Boltzmann's constant ($1.3807x10^{-23}$J/K)
M	Mass of water (g)
R	Rejection efficiency
R_c	Cake layer resistance
R_m	Membrane resistance
Rq	Force term ($kg/m^2.s^2$)
T	time (h)
T	Temperature (K)
U	Velocity in the open channel (m/s)
U_E	Electrophoretic mobility
V	Permeate volume (L)

Greek Letters

d_p	Particle diameter
δ_m	Thickness of membrane (m)
ρ_p	Particle solid density
B	Pore size morphology constant
ϵ	Dielectric constant
Ec	Cake layer porosity
Θ	Contact angle of liquid on membrane surface (∘)
P	Flow density (kg/m^3)
μ	Dynamic viscosity of the solution(kg/m.s)
η	Viscosity

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BOD	Biological oxygen demand
CECP	Cake enhanced concentration polarization
COD	Chemical oxygen demand
CP	Concentration polarization
DI	Deionized Water
DOC	Dissolved organic carbon
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-Ray
FR	Flux recovery
GAC	Granular activated carbon
HCl	Hydrochloride
HOCl	Hydrochlorous
KCl	Potassium chloride
MF	Microfiltration
$MgSO_4$	Magnesium sulfate
MMF	Multimedia filter
MWCO	Molecular weight cut off
$Na_2S_2O_4$	Sodium meta bisulfate
NaCl	Sodium chloride

NaOCl	Sodium hypochloride
NaOH	Sodium Hydroxide
NF	Nanofiltration
NOM	Natural organic matter
PA	Polyamide
PAC	Polyaluminium chloride
PES	Polyethersulfone
PhAC	Pharmaceutically active compound
POPs	Persistent organic pollutants
Ppm	Parts per million
PSF	Polysulfone
PTPs	Pesticide transformation products
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
Rpm	Rotation per minute
SDI	Salt density index
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SS	Suspended solid
SSF	Slow sand filtration
STP	Sodium tripolyphosphate
SW	Saline water
SWRO	Saline water reverse osmosis

TDS	Total dissolved solid
TFC	Thin film compound
TFM	Thin film membrane
TMP	Transmembrane pressure
TOC	Total organic carbon
TSP	Trisodium phosphate
TSS	Total suspended solid
UF	Ultrafiltration
UPW	Ultra pure water
UV	Ultraviolet

MEMBRAN PENURASAN NANO UNTUK PENULENAN AIR:

PRARAWATAN DAN FENOMENA PENGOTORAN

ABSTRAK

Pengotoran membran merupakan salah satu masalah utama teknologi membran dalam proses rawatan air. Pengotoran membran menyebabkan penurunan fluks dan menjejaskan kualiti air yang telah dirawat. Tujuan kajian ini adalah untuk menilai sifat pengotoran membran penurasan nano yang dikaitkan dengan proses prarawatan dan menentukan cara terbaik untuk pembersihan membran. Air suapan di kenali sebagai sebelum 3.00 µm, selepas 3.00 µm dan gabungan antara 0.45 dan 3.00 µm prapenapisan. Eksperimen skala bangku telah dijalankan ke atas penapisan aliran silang untuk menilai keberkesanan proses pra-rawatan. Rawatan air dijalankan dengan mengunakan membran penurasan nano yang diperolehi secara komersial (NF90 and NF270) dengan atau tanpa polialuminium klorida (PAC) sebagai dos pengumpal dalam larutan suapan. Didapati bahawa membran NF270 mempunyai rintangan lebih tinggi terhadap pengotoran berbanding dengan NF90 kerana ciri-ciri hidrofilik dengan sudut kenalan 7.18nm sebagai permukaan membrannya yang lebih licin dan kekasaran membranya 18.78nm. Disebaliknya, kadar pengotoran untuk NF90 mencapai 24%, kepada 18% apabila terdapat penurasan gabungan antara 3.00 µm and 0.45 µm prapenapisan. Walau bagaimanapun tanpa penambahan PAC mencapai kadar pengotoran yang rendah sebanyak 12%. Lagipun, NF270 membran proses dengan atau tanpa penambahan PAC memberikan pengurangan fluks yang tidak berkesan tinggi. Kesimpulanya, NF90 membran proses tanpa penambahan PAC dan penurasan yang gabung antara 3.00 dan 0.45 µm prapenapisan mendapati hasilan kualiti air yang tinggi

sebanyak 0.5 Mohm resistiviti kerana liang yang kecil. Seterusnya, sistem membran tersebut memerlukan pembersihan kaustik pada 0.5 Mol/L kepekatan untuk menyelesaikan masalah kerak sebanyak 76% di permukaan membran. Air yang dihasilkan melalui proses penapisan tersebut mematuhi kualiti air yang sesuai dijadikan sebagai larutan suapan membrane osmosis terbalik (RO).

NANOFILTRATION MEMBRANE FOR WATER PURIFICATION: PRETREATMENT AND ITS FOULING PHENOMENON

ABSTRACT

In water treatment processes, membrane fouling is one of the main drawbacks of membrane technology. Membrane fouling causes flux declination and reduces the treated water quality. This study aims to evaluate the fouling behavior of nanofiltration membranes with respect to the pretreatment process and to determine the best practice of membrane cleaning process. The feed water was introduced as solution before and after 3.00 µm pre-filtration and also after combination of 3.00 and 0.45 µm pre-filtration. The bench scale cross flow filtration were conducted to evaluate the efficiency of water pretreatment processes. Water treatment was carried out by using commercially available nanofiltration membrane (NF90 and NF270) with and without polyaluminium chloride as coagulant dosage in feed water. It was found that NF270 is more fouling resistance compared to NF90 due to its hydrophilicity characteristic with contact angle of 7.15 and smoother membrane surface with membrane roughness of 18.78 nm. The fouling rate of NF90 with PAC dosage was reduced from 24% to 18% after 3.00 µm and 0.45 µm pre-filtration. However, without PAC lower fouling rate of 12% can be achieved. NF270 membrane process with or without PAC gave insignificant flux reduction. In overall, NF 90 membrane without PAC with combination of 3.00 and 0.45 µm pre-filtration gave better permeate water quality of 0.5 MΩ due to NF90's tighter pore size. 0.5 Mol/L of NaOH was required to achieve cleaning efficiency of 76%. The water that is produced during filtration process

complies with the standard and is suitable to be used as feed to reverse osmosis (RO) membrane.

CHAPTER ONE

INTRODUCTION

1.1 Membrane fouling

Domestic water supply with high content of hard water is undesirable as it contributes to scaling and corrosions issues to machinery, metal pipelines, heat exchanger, and electrical appliances (Fang *et al.*, 2013). In addition, semiconductor and pharmaceutical industries require high quality feed water to produce ultra-pure water (UPW) for cleaning, sterilizing and mixing. The feed water must be free from colloidal particulates materials in order to avoid fouling problem to the subsequent water polishing step (Wang *et al.*, 2012).

Reverse osmosis (RO) or nanofiltration (NF) membranes are commonly used to purify water by removing the dissolved solids, hard water minerals and solutes that contain in city water (Fang *et al*., 2013). This diffusional based membrane process could remove the ions, dissolved solids, organic, pathogens, color, bacteria, colloids, and particulates from water solution.

Improper pretreatment for membrane process impeded the membrane performance due to the scaling and fouling problems (Chon and Cho, 2016). Fouling and scaling on reverse osmosis membrane lead to the unwanted phenomena such as pore blockage, cake formation or pore constriction in the membrane which cause the increased feed water pressure. As a conclusion, the higher energy is required to operate the reverse osmosis or nanofiltration system. Furthermore, fouling could impair the permeate water quality.

1.2 Importance of pretreatment for membrane process

Pre-treatment is an important step prior to RO/NF membranes by removing the suspended solids, particles, and bacteria. Several serious problems that faced in RO/NF membrane are particle fouling, oxidant fouling, biological fouling, and inorganics scaling. The inorganic multivalent salts such as calcium and magnesium and other foulants such as organics, biological substances and particulates must be removed during the pretreatment process. Therefore, pretreatments are particularly important here to eliminate the contaminants from city water.

Depending on the nature of the foulants, pretreatment can be done via physical and/or chemical methods. Physical methods such as prefiltration is able to remove most of the suspended solids based on the size screening effect. Removal of such particles could reduce the load to the polishing step such as ion exchange and RO/NF membrane process. By doing so, the membrane lifespan can be prolonged and the required operating costs could be greatly reduced due to the lower operating pressure (Tang *et al*., 2009, Costa and Pinho, 2006, Fang *et al*., 2013).

On the other hand, for suspended solids that have particle size smaller than the prefilter (normally 0.45 µm and above), the removal efficiency will be much reduced. Such particles can neither be removed using filtration nor sedimentation. Instead, a more energy intensive process such as centrifugation is required. However, such process requires longer operating time and is relatively difficult to scale up, therefore it is always not a good option. In view of this, chemicals are always dosed into the solution to coagulate or flocculate the fine suspended solids so that the growing particulate materials could be easily settled out or prefiltered during filtration process (Kohler *et al*., 2016, Gondar *et al*., 2008, Tang *et al*., 2013).

Chemical addition to the process stream is always an unwanted step as it may cause subsequent disposal problem as well as bring adverse environmental impact. Poly Aluminium Chloride (PAC) for example is an effective coagulant to remove suspended solids, however, overdose of PAC has been proven to cause effluent problem and also could foul the negatively charged membrane easily (Lin *et al*., 2013). The fouled membrane incurred additional operating cost, pumping energy increment and the water quality were out of recommended specification. Besides that, another important issue that is overlooked by most of the water industry is the impact of chemical dosage towards membrane processing difficulties. It is understandable that the membrane separation is a complicated process dealing with the physicochemical properties of both membrane and solution. The changes of the chemical components in the feed solution will alter the water chemical potential and change the interaction at the solution membrane interface. Such disturbed system could contribute to the irreversible fouling phenomenon because of the unwanted adsorption process.

1.3 Problem statement

Severe membrane fouling and scaling problem always occur in the process to produce reverse osmosis deionization (RODI) water from city water makeup system. It is either due to poor selection of membrane or due to improper pre-treatment process. In the current practice by most of the electronic industries, typical pretreatment was carried out by treating the city water with PAC as a coagulant for multimedia filter. Such system is able to produce ultrapure water with the expense of deteriorating membrane lifespan due to unavoidable fouling problem. Questions have been aroused on the suitability of the pretreatment method depending on the city water source and the feed water characteristics. PAC is widely used in water treatment industry to remove the contaminants. The usage of PAC as a coagulant could impose a serious problem of membrane fouling as reflected via the rapid flux declination or increasing flow resistance. An overdosage of PAC will cause organic fouling on RO membrane. On the other hand without the PAC dosage, suspended solids will not be properly filtered through multimedia filter. It is always a question whether chemical pretreatment is able to solve the membrane fouling problem or exerts more serious problems to the membrane operation.

To make things complicated, Sodium Meta Bisulfate (SMBS) which is dosed in pretreatment to control the chlorine level could cause oxidant fouling to RO membrane. Higher chlorine content might cause the severe damage to the membrane due to its oxidizing effect. However, without the chlorine to control the microorganism, bio-fouling will shorten the lifespan of membrane and subsequently requires frequent membrane cleaning. As of consequence, higher pumping energy will lead to higher operating costs.

The control of membrane fouling is a pressing challenge. Considerable efforts are underway both industrially and academically for finding the best way to minimize the fouling phenomena. Options include proper membrane material selection, control of operating conditions as well as pretreatment process. There are no fixed rules on the best scheme across the board as each industry deals with different sources of water supply. Without a proper pretreatment, any advanced membrane system will be broken down, therefore, it is imperative that the pretreatment step to be studied in greater detail with the following objectives.

1.4 Research objectives

i. To study the effect of pretreatment (prefiltration and coagulation) on the efficiency of nanofiltration membrane to treat the makeup water for electronic industry

ii. To investigate the performance and fouling tendency of the nanofiltration membranes

iii. To recommend the best membrane cleaning method to prolong the nanofiltration membrane lifespan

1.5 Scope of study

In this work, makeup water from electronic industry were pretreated using physical and chemical methods and its impact on the performance of nanofiltration was evaluated. The feed solutions were also subjected to two different physical pretreatments using prefilter of different screening size (3.00 µm and combination of 3.00 and 0.45 µm). Followed by, concentration of PAC at 18% was tested on the membrane performance to evaluate the chemical cleaning pretreatment method. PAC 18% selected as per typical industrial practice. Comparison between NF90 and NF270 membrane with different pore size was done to evaluate their fouling tendency for feed solution. The feed solution characterization conducted with or without PAC dosage and with and without prefiltration method. At various characterization tools were introduced to relate the properties of the membrane and solution. The surface properties were determined with the aid of Scanning Electron Microscopy (SEM),