

**NITRATE AND PHOSPHORUS REMOVAL FROM SYNTHETIC WATER
AND THEIR COUPLING EFFECT USING NANOFILTRATION MEMBRANE**

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by

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LIST OF SYMBOLS

A	Effective area of membrane	m^2
C_f	Concentration of feed	mg/L
C_p	Concentration of permeate	mg/L
C_w	Concentration of wall	mg/L
D	Diffusion coefficient	m^2/s
J	Permeate flux	$(L/hr/m^2)$
k	Mass transfer coefficient	m/s
μ	Viscosity	Pa.s
ΔP	Pressure	bar
Q_p	Filtrate flowrate	L/hr
R	Rejection of nutrients	%
R_t	Total membrane resistance	m^{-1}
ω	Stirring speed	rpm

LIST OF ABBREVIATIONS

Ch-Z	Chitosan Coated Zeolite
DCMD	Direct Contact Membrane Distillation
DOC	Dissolved Organic Carbon
EBPR	Enhanced Biological Phosphorus Removal
HAD	Heterotrophic-Autotrophic Denitrification
HRT	Hydraulic Retention Time
LDH	Layered Double Hydroxides
MBR	Membrane Bioreactor
MCL	Maximum Contaminant Levels
MD	Membrane Distillation
MF	Microfiltration
MWCO	Molecular Weight Cut-off
NF	Nanofiltration
OMBR	Osmotic Membrane Bioreactor
PBS	Poly Butanediol Succinate
PNA	Anammox
RO	Reverse Osmosis
rpm	Rotation per minute
SEM	Scanning Electrode Microscopy

TMP	Transmembrane Pressure
UF	Ultrafiltration
US EPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X-ray Diffraction
ZVI	Zero-Valent Iron

PENYINGKIRAN NITRAT DAN FOSFORUS DARI AIR SINTETIK DAN KESAN GANDINGAN MEREKA MENGGUNAKAN MEMBRAN NF

ABSTRAK

Pencemaran nitrat dan fosfat air bawah tanah adalah masalah yang semakin meningkat di negara tidak kira membangun atau tidak maju. Punca pencemaran seperti ini adalah terutamanya dari penggunaan baja intensif dalam pertanian, pelepasan bahan buangan perindustrian dan cecair dari ladang intensif. Nanofiltrasi (NF) telah dipilih sebagai rawatan untuk penyingkiran nitrat dan fosforus daripada perairan yang tercemar. Penyingkiran nitrat dan fosfat dari air sintetik menggunakan membran NF270 dan NF90 komersial telah dikaji. Kecekapan kedua-dua membran dinilai pada pengaruh tekanan transmемbran, kelajuan kcau dan kepekatan awal setiap larutan pada penyingkiran dan fluks. NF90 menunjukkan penyingkiran yang lebih tinggi terhadap nitrat (97.8%) manakala NF270 menunjukkan penyingkiran fosfat yang lebih tinggi (99.1%) yang menunjukkan penyingkiran NO_3^- adalah disebabkan kawalan diffusional manakala penyingkiran PO_4^{3-} adalah disebabkan kawalan penolakan caj. Kesan gandingan nitrat dan fosfat juga disiasat dan terbukti bahawa penolakan nitrat sangat dipengaruhi oleh kehadiran ion fosfat akibat prinsip elektro-neutraliti. Akhir sekali, kesan kelajuan kcau pada fluks dan pekali pemindahan jisim juga dikaji untuk setiap membran. NF270 menunjukkan peningkatan linier dalam pekali pemindahan jisim terhadap kelajuan kcau untuk penyingkiran nitrat dan fosfat individu. Fenomena membran NF270 ini boleh dijelaskan dengan ukuran liang yang lebih besar daripada membran NF270 yang membolehkan lebih banyak larutan untuk melewatinya sehingga polarisasi yang kurang konsentrasi yang menggambarkan pengumpulan spesies yang disimpan dekat dengan permukaan membran.

NITRATE AND PHOSPHORUS REMOVAL FROM SYNTHETIC WATER AND THEIR COUPLING EFFECT USING NF MEMBRANE

ABSTRACT

Nitrate and phosphate contamination of groundwater is a growing problem both in developed and developing countries. Such contamination comes mainly from the intensive use of fertilizers in agriculture, improper discharges of industrial effluents and effluents from intensive farming. Nanofiltration (NF) is chosen as the treatment for nitrate and phosphorus removal from contaminated waters. In this work, the removal of nitrates and phosphate from synthetic water using a commercial NF270 and NF90 membrane is studied. The efficiency of both membranes is evaluated based on the influence of transmembrane pressure, stirring speed and initial concentration of each solute on rejection and flux. NF90 shows higher rejection on nitrate (97.8%) while NF270 shows higher removal of phosphate (99.1%) which shows that NO_3^- removal is via diffusional control while PO_4^{3-} removal is via charge repulsion control. The coupling effect of nitrate and phosphate was also investigated. It was proven that rejection of nitrate is greatly influenced by the presence of phosphate ions due to the electro-neutrality principle. Lastly, effect of stirring speed on flux and the mass transfer coefficient were also established for each membrane. NF270 shows linear increase in mass transfer coefficient against stirring speed for both individual nitrate and phosphate removal. This behavior of the NF270 membrane can be explained by relatively larger pore size of the NF270 membrane allowing more solution to pass through thus less concentration polarisation which describes the accumulation of the species being retained close to the surface of the membrane.

CHAPTER ONE

INTRODUCTION

1.1. Research Background

Phosphorus and nitrogen, mainly as phosphate and nitrate respectively, are two key elements responsible for the eutrophication phenomenon in water ecosystems, such as in fish farm water. This phenomenon produces aquatic environment degradation, either by changing their species composition, harmful algal blooms or caused bottom anoxia problem. Eutrophication of water bodies caused by the increased amount of nutrients has become an issue throughout the world and poses a serious problem for different usage of water uses (Boeykens et al. 2017).

Nitrate pollution of water due to intensive agricultural activities has become a major environmental problem since 1970s. Nitrate is highly soluble in water and does not readily bind to the soil causing it to be highly susceptible to leaching. There are several potential sources of nitrate, including animal wastes, septic tanks, and municipal wastewater treatment systems and decaying plant debris. However, nitrogen enriched fertilizers for farming is considered as the main source of nitrate pollution in the environment. To reduce the health hazard, a nitrate standard of 50 mg/L nitrate- NO_3^- or 10 mg/L nitrate-N in drinking water has been set by World Health Organization (WHO) and United States Environmental Protection Agency (US EPA). However, it has been reported that nitrate concentration in drinking water has exceeded from the maximum acceptable concentration in many parts of the globe. Therefore, controlling nitrate level in potable water below the standard level has become a major concern (Mohsenipour et al. 2014).

Phosphorus is an essential nutrient element that is used by all living organisms for energy transport and growth. It is habitually the limiting nutrient for primary production in terrestrial and aquatic ecosystems (Worsfold et al. 2016). Due to both industrial uses and ever-increasing food demands and with the expeditious economic development and continued growth in human population, phosphorus resources are being consumed with an unprecedented speed. Eventually, excessive phosphorus is released into natural water bodies and causes a significant environmental problem (Boeykens et al. 2017). In order to comply with the effluent quality standards which are in the range 0.5 to 1 mg/L phosphate-P, the removal of phosphate from wastewater prior to discharge into natural water is required (Ballet et al. 2007).

Treatment methods for wastewater contaminated with nitrates and phosphorus include membrane filtration, ion exchange, adsorption process and biofiltration (Fan and Zhang 2018). As of recently, Nanofiltration process (NF) has been widely being used in water treatment, food, pharmaceuticals and chemical industry and wastewater treatment. NF is a process in which membranes with nano-size pores are used to separate solutes or salts based on size or charge. NF has shown its effectiveness in the removal of great variety of undesirable components from water (Mahvi et al. 2011).

The surface charge is responsible for the rejection of ions of similar charge and the surface roughness has been shown to improve solute flux while also increasing the rate of membrane fouling. Its separation mechanisms are sieving effect, differences in diffusivity and solubility of solutes and electrostatic interactions between the membrane surface groups and ions. The advantages of NF processes are operational simplicity, reliability, no additive requirements and modular construction (Mahvi et al. 2011).

1.2. Problem Statement

In spite of all promising perspectives for NF, not only in drinking water production but also in wastewater treatment, the food industry, the chemical and pharmaceutical industry, and many other industries, there are still some unresolved problems that slow down its large-scale applications.

Nitrate and phosphate ions from water consists in that these ions are stable and easily soluble in water and having low settling capacity or adsorption. The challenges for NF include insufficient separation capability of nitrate and phosphate from water due to charge effect which is electrostatic interactions between ions and membrane charged sites. With the presence of other charges, Donnan effect between ions and membrane is weak and because of electroneutrality condition, its rejection is lower than other charges (Santafé-Moros et al. 2005).

In NF membrane, the rejection rates of monovalent ions were greatly reduced in the presence of the divalent ions or trivalent ions such as phosphate. Phosphate ions will be highly affected than nitrate ions by the surface charge of the membrane. In addition, monovalent ions are hydrated in aqueous solution more than phosphate ions which is a multivalent ion, resulting in less rejection of monovalent ions. Thus, the coupling effect between nitrate ions and phosphate ions will be investigated in this experiment.

The tightness of the NF membranes plays a major role in the removal efficiency. The concentration polarisation which describes the accumulation of the species close to the surface leads to dispersion and poor observed retention.

In view of this, synthetic water is used to test the separation capability of nitrate ions, phosphate ions and phosphate ions with the influence of nitrate ions using two

commercial NF membranes which are NF270 and NF90. By evaluating the operating conditions, this can improve the separation capability of nitrate and phosphorus from the synthetic water and at the same time study the coupling effect for both ions.

1.3. Research Objectives

The aim of this experiment is:

- 1) To test the separation capability of nitrate and phosphorus using both loose and dense NF membranes.
- 2) To evaluate the coupling effect of nitrate and phosphorus on the separation efficiency.
- 3) To estimate the mass transfer coefficient of nitrate and phosphorus under different stirring speed.

CHAPTER TWO

LITERATURE REVIEW

2.1 Availability of Fresh Water and its Degradation

Safe drinking water is essential to humans and other life. The earth is abundant with water where more than 70% of the area of earth is covered by water. However, availability of fresh water is a crucial complication across the world. Only 3% of total water on the earth is useable and out of this 3%, nearly 70% of fresh water is frozen, 29% is present as soil moisture or lies in deep underground aquifers as groundwater and less than 1% of the world's fresh water is in the lakes and rivers (Mohsenipour et al. 2014).

Water supply demands balance is critical in many regions of the world, especially in the arid and semiarid regions are facing with water scarcity (Hassan et al. 1989). “Water crisis decades” is the unforeseeable impact of global warming on the overall water scarcity and identification of a potential water shortage in the first and second decades of the twenty-first century (Mehdizadeh 2006).

The increasing demand for clean water is due to the rapid population growth and dwindling supply of fresh water. The obstructive activities that cause the degradation of fresh water can be categorized into five types, such as groundwater over exploitation, diffuse contamination sources, point contamination sources, artificial recharge and seawater intrusion. Among them, diffuse contamination due to human activities is a vital cause of water pollution (Mohsenipour et al. 2014).

2.2 Nitrate and Phosphorus Content in Water Resources

The presence of toxic contamination in drinking water resources has adverse effects on human and animal health as well as the aquatic life. Among these contaminants, the excess of fluoride ion causes major effects such as dental and skeletal fluorosis. The

excess concentration of fluoride which is more than 1.5 mg/L causes serious health effects. In addition, many adverse effects were found in different countries, such as China, India, Mexico, Africa and Iran (Yousefia et al. 2015).

Nitrogen and phosphorus are two key elements responsible for the excessive increase of nutrients inducing aquatic plants growth. Although algae production is needed as a first link in the food chain of aquatic ecosystem, excessive growth under eutrophic conditions could eventually lead to a significant deterioration of the water body. Therefore, the first step for eutrophication acceleration is the entry of these nutrients in the aquatic system (Yang et al., 2008).

According to von Sperling (2007), the natural origin of phosphorus compounds is due by the dissolution of soils compounds, the decomposition of organic matter and the cellular decomposition of microorganisms where its anthropogenic source is related to domestic and industrial wastes, detergents, fertilizers and animal excrement. Phosphorus is an element that occurs naturally in water, however, certain human activities contribute significantly to its accumulation in water bodies (Boeykens et al. 2017). Therefore, the phosphorous rate in discharging wastewater should be according to environmental and human health guidelines which are in the range 0.5 to 1 mg/L phosphate-P (Yousefia et al. 2015).

In the environment, the high concentration of nitrogen, as nitrates, not only favours the eutrophication of water bodies, but also produces very important implications for public health (Burkart and Stoner, 2002). Excessive nitrate levels in drinking water can lead to taste and odour problems and even contribute to a potential risk to human health such as methemoglobinemia, cancer, and tumours. As serious health effects are associated with excess nitrate, thus it is necessary to restraint the nitrate level in water resources to avoid the hazards of the nitrate contamination.

The control and treatment of excess aqueous phosphate and nitrate is a crucial task in environmental management due to the adverse effects of aqueous phosphate and nitrate on human health and natural ecosystems over both the short and long term (Vikrant et al. 2018). Due to the increasingly serious phosphorus and nitrate pollution, extensive efforts have been made to limit and recover phosphorus and nitrate from wastewater with different techniques (Ge et al. 2017).

2.3 Nanofiltration (NF) Membrane

Various physical, chemical and biological methods have been proposed for phosphate and nitrate removal from water or wastewater such as anion exchange, sorption, chemical precipitation, membrane technologies, reverse osmosis, electrodialysis and biological removal through constructed wetland, activated sludge and microalgal systems. In practice, the most widely used methods are biological removal and chemical precipitation for phosphorus removal. Nevertheless, they also present limitations such as undesired waste sludge production or dependence on water temperature and organic load regarding the biological removal, whereas chemical precipitation requires high input of chemical reagents (Mitrogiannis et al. 2017).

Along with these methods recently NF has been used for water purification. NF process has been widely used in water treatment, food, pharmaceuticals and chemical industry and wastewater treatment (Mahvi et al. 2011). NF falls between Ultrafiltration (UF) and Reverse Osmosis (RO) where its separation characteristics are based on sieve and charge repulsion effect. Most of commercial NF membranes are charged thus the rejection of ions by NF membranes is the consequence of the combination of electrostatic and steric interactions associated with charge shielding, Donnan exclusion and ion hydration. These interactions depend on the characteristics of the solution to be treated and the membrane itself (Santafé-Moros et al. 2005).

NF membranes are usually designed to remove multivalent ions but, in some cases, they show also rejection of monovalent ions such as nitrate, which is dependent on the conditions, employed and largely varies from one membrane to another. Due to its low-pressure requirement and hence lower energy consumption, research in nitrate removal by NF has recently attracted more attention (Hoinkis et al. 2011).

NF is a process in which membranes with nano-size pores are used to separate solutes or salts based on size or charge (Schafer et al. 2005). NF is a new membrane process comparing with RO, which require lower transmembrane pressure (TMP) necessary for the mass transport (Hurtado et al. 2016). This mechanism underscores the importance of the zeta potential, which is directly proportional to the surface charge density (Elimelech et al. 1997). The surface charge is responsible for the rejection of ions of similar charge. The advantages of NF processes are operational simplicity, reliability, no additive requirements and modular construction (Mahvi et al. 2011).

2.4 Nitrate

2.4.1 Nitrate Removal Methods from Wastewater

2.4.1 (a) Solid-Phase Denitrification

Solid-phase denitrification that uses both the natural materials and the synthetic biodegradable polymers has been studied widely in nitrate reduction from drinking water and groundwater. The types of bioreactor commonly used include the packed bed, biofilter and fluidized bed. Most applications use packed bed bioreactor due to the operational simplicity and ease of control. The advantage of the fluidized bed reactor is that it could avoid the problems of clogging and channelling (Wang and Chu 2016).

Healy et al. (2012) studied the denitrification of groundwater using different substrates, including pine woodchips, cardboard, pine needles and barley straw. The nitrate removal ranged 67–89% at steady-state period if pollution swapping was considered. The pine needle bioreactor showed the highest dissolved organic carbon (DOC) release and carbon fluxes were highest for cardboard and straw bioreactors.

Mergaert et al. (2001) reported that poly-3-hydroxybutyrate-co-hydroxyvalerate (PHBV) packed bed reactor was used for nitrate removal from drinking water. Its maximal surface-related denitrification rate was $14 \text{ mg Nm}^{-2}\text{h}^{-1}$ at $25 \text{ }^\circ\text{C}$. The effluent nitrate concentrations from groundwater in a packed reactor filled with polycaprolactone (PCL) were lower than 3.7 mg NL^{-1} at temperatures of higher than $24 \text{ }^\circ\text{C}$ and hydraulic retention time (HRT) of 3 to 6 hours during a long-term operation of 561 days. Nitrite and ammonium remained at low levels which is less than 0.32 and 0.78 mg NL^{-1} , respectively (Chu and Wang 2013). The studies by Yang et al. (2013) showed that a nitrate removal of 95% was obtained using poly butanediol succinate (PBS) as carbon source for denitrification of drinking water at a HRT of 0.5 hours and temperature of $25 \text{ }^\circ\text{C}$.

The studies by Rocca et al. (2006) showed that nitrate removal rate by the heterotrophic-autotrophic denitrification (HAD) reactor filled with cotton/zero-valent iron (ZVI) was higher than that of the denitrification reactor using cotton alone. Hydrogenotrophic denitrification contributed only 10%–20% of nitrate removal in HAD permeable reactive barrier to treat groundwater (Huang et al. 2015).

2.4.1 (b) Adsorption

Activated carbon is generally considered as a universal adsorbent for the removal of diverse types of aquatic pollutants especially organic pollutants. Afkhami et al. (2007) studied the effects of functional groups on the adsorption of NO_3^- and NO_2^- by carbon cloth. It was suggested that treatment of carbon cloth with acid produced positive sites on the carbon cloth. By protonation of surface hydroxy ($-\text{OH}$) groups caused an increase in electrostatic adsorption of anions. The dramatic increase in the adsorption of anions by treatment of carbon cloth with acid was attributed to the strong electrostatic interaction between the negative charge of anions and positive charge of the surface. The adsorption capacity of acid treated carbon cloth for NO_3^- and NO_2^- was 2.03 and 1.01 mmol/g, respectively. These values were much higher than those obtained for distilled water treated carbon cloth. The effect of competing ions was found to be negligible on the adsorption.

Hosni and Srasra (2008) investigated the adsorption of NO_3^- by various layered double hydroxides (LDHs), such as Mg-Al and Zn-Al. The samples were identified as Mg_3P_{10} , where M represents the divalent cation used to prepare the materials. The nature and content of divalent cations in LDHs showed a strong influence on the adsorption process. Calcined Mg-Al LDH with an Mg/Al molar ratio of 3.0 showed higher adsorption capacity compared to other calcined LDHs. The sorption capacity of $\text{Mg}_3\text{P}_{10-500}$ was found to be 35 mg/g, and that of $\text{Zn}_3\text{P}_{10-500}$ was 20 mg/g. This difference in

sorption capacity was explained by the fact that the nature of the divalent cation in LDH has a strong influence on the adsorption process.

Wang and Peng (2010) states that natural zeolites are hydrated aluminosilicate minerals of a porous structure with valuable physicochemical properties. Surface modified zeolites have also been tested for the removal of water pollutants by Arora et al. (2010). Surface modifications of natural zeolite were performed by coating it with a chitosan layer. The chitosan coated zeolite (Ch-Z) was protonated with either sulfuric or hydrochloric acid and tested for its suitability to capture NO_3^- from water at 20 and 4 °C. It was found that protonation with hydrochloric acid resulted a higher maximum NO_3^- exchange capacity when compared to sulfuric acid.

2.4.1 (c) Membrane Technology

Boubakria et al. (2014) studied the removal of nitrate from aqueous solution by direct contact membrane distillation (DCMD) using flat sheets polypropylene (PP) and polyvinylidene fluoride (PVDF) membranes. In all DCMD experimental runs, an almost complete nitrate rejection was achieved which is higher than 99.90% and the permeate nitrate concentration was largely below the maximum permissible level in potable water. Under the same operating conditions, PVDF hydrophobic membrane showed a higher permeate flux of 37.21 L/m²h than PP membrane with a permeate flux of 4.12 L/m²h. For both the membranes, feed temperature is the important operating parameter which enhanced exponentially the permeate flux. Likewise, a positive effect on permeate flux was found when feed flow rate was increased.

Younssi et al. (2018) studied the framework of understanding the transport mechanism that governs the filtration of NO_3^- solution through a $\gamma\text{-Al}_2\text{O}_3$ membrane with a nominal pore size of 5 nm at low UF with a series of various types of nitrate solutions and operating conditions. The experimental filtration results showed that high

NO_3^- rejection was observed when pH was close to the point of zero charge of the membrane for both binary and ternary solutions. NO_3^- rejection increased with an increase of applied pressure. The rejection gradually decreased when the initial NO_3^- concentration increased. It appeared that the valency and hydrated radius of associated cation had a dramatic effect on NO_3^- rejection, with the divalent cations being more rejected than monovalent cations. In addition, the best NO_3^- rejection is found for water presenting a low total mineralization and a low SO_4^{2-} ions concentration.

2.4.2 Nitrate Removal by NF Membrane

Choi et al. (2001) studied the influence of the co-existing ions such as Ca^{2+} , SO_4^{2-} and Cl^- on the nitrate rejection by two commercial “loose” NF membranes which had different surface potentials. In this study, nitrate rejection was between 72% and 86%. The experiment showed that when divalent cations cause a strong demand for anion permeation, the least repulsive anions in the feed solution could better pass through the membrane of higher surface potential than the membrane of lower surface potential.

Moreover, Paugam et al. (2004) studied the performance of several commercial NF membranes such as the “loose” Nanomax-50 as well as MPS44, NF 70 and DESAL with a variety of model salt solutions. They stated that the size effect mainly governed the ions transfer across the membrane. The more hydrated it is, the more difficult its passage will be. Due to the small radius of its hydrated anion, nitrate ions are less rejected over chloride, fluoride and sulphate ions. Wang et al. (2005) used the commercial “dense” ESNA 1 (Nitto Denko) membrane for their study. The experiments were carried out with model solutions of three nitrates such as NaNO_3 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ under various conditions by changing the applied pressure and salt concentration. The rejection of nitrate was as high as 96%.

The nitrate rejection of several NF membranes (NF 90, OPMN-P, OPMN-K) using nitrate salt at different concentration and different transmembrane pressures using a model solution similar to natural drinking water of the city of Caen, France was investigated by Garcia et al. (2006). For the anions, the retention sequence was sulphate > bicarbonate > chloride > nitrate. Thus, nitrate ions are the less retained by the membranes except for OPMN-K where the chloride and nitrate retentions are similar. The “denser” NF 90 performed best with a nitrate rejection of more than 85%, irrespective of the concentration. As far as the model solution similar to natural drinking water is concerned, the nitrate rejection is strongly reduced compared to the retention obtained with a NaNO₃ simple solution at the same nitrate concentration.

Santafé-Moros (2007) studied the influence of common co-ions such as SO₄²⁻, Cl⁻, Ca²⁺, Na⁺ and Mg²⁺ on the nitrate rejection in ternary ionic model solutions by the Dow NF 90 membrane. With this “dense” membrane a rejection generally higher than 90% was obtained not only for divalent but also for monovalent ions, which can be explained by its tight pore structure and the negative charge of the membrane hence its behaviour is approaching that of RO membranes. In ternary ionic mixtures, the increase in co-ion concentration always resulted in a decrease in nitrate rejection.

The NF 90 is a “dense” NF membrane, whereas the NF 270 can be regarded as a “loose” NF membrane. Loose connective tissue has relatively fewer cells and fibers per area than dense connective tissue, in which the cells and fibers are tightly packed. Dense connective tissue can be characterized as regular or irregular on the basis of fiber arrangement. The NF 90 is recommended for surface and groundwater treatment removing a high percentage of salts and organics whereas the NF 270 may be used in water treatment where only good organic removal is desired with partial softening. (Hoinkis et al. 2011)

2.4.3 Influence of Operating Conditions of NF Membrane on Nitrate Removal

According to Choi et al. (2001), the rejection rates of monovalent ions were greatly reduced in the presence of the divalent ions. The reductions in rejection rates were more significant for the membrane with low surface potential. Most of the negatively charged groups on the membrane are shielded by cations at high salt concentration, and therefore anions can readily pass through the membrane. However, despite the charge shielding effect, the rejection rates of divalent anions remained high and the membrane having a high negative surface potential rejected more ions.

Paugam et al. (2004) stated that the size effect mainly governed the ions transfer across the membrane. The more hydrated it is, the more difficult its passage will be. Due to the small radius of its hydrated anion, nitrate ions are less rejected over chloride, fluoride and sulphate ions. Furthermore, the higher the amount of divalent anions in the water to be treated, the lower the nitrate retention rate.

According to Garcia et al. (2006), the divalent ions are strongly repelled outside of the membrane due to a size effect and electrostatic repulsions more important than for monovalent ions. Consequently, the monovalent ions particularly nitrate ion are forced to pass through the membrane in order to assure the electroneutrality of the permeate. Moreover, the nitrate ions are the anions that less retained by the membrane compared to the other monovalent anions due to a less important hydrated size and hydration energy.

Koyuncu (2002) noticed that the retention of nitrate was strongly depend on operating parameters such as feed solution concentration, pressure and cross flow velocity. Experimental studies showed that the flux increased linearly with increasing pressure. The rejection rates of nitrate ions were affected by operating pressure. Nitrate ion rejections were increased with increasing pressure and the characteristics of rejection were similar for the NF (TFC-S) and RO (TFC-HR) membranes.

Permeate flux value increased linearly with increasing temperature. Rejection rate of nitrate ions also increased at the temperature range of about 15 and 25°C and after 25°C of temperature, rejection rates began to decrease for the RO (TFC-HR) membranes. The rejection rates of nitrate ions for the NF (TFC-S) membrane were slightly affected by the temperature and rejection rates changed at the low range with changing temperature (Koyuncu 2002).

From the results that have been reported by Causserand et al. (2005), at increasing flow rate, the nitrate removal efficiency is reduced. Indeed, this was due to the influence of amount of ion released over surface of membrane on solute transfer. This behaviour is characteristic of situations where concentration polarization still influences the solute transfer with, at the same time, a non-negligible contribution of diffusion in the pores and leads to dispersion and poor observed retention.

According to the result of study that have been confirmed by Paugam et al. (2003), with increased initial concentration of nitrate, the nitrate removal efficiency was reduced. These were due to the characteristics of the charged membranes and known as the screen phenomenon.

A continuous increase in retention with pH would be expected if charge exclusion was dominant because nitrate ion was of uniform charge and the charge of all membranes increased with pH. Minimum retention was observed at low pH near the membrane isoelectric point when charge repulsion is minimal. In general, the increase of pH from 7 to 9 resulted in a slightly higher nitrate rejection, irrespective of the concentration and the composition. The findings showed that it is possible to reduce nitrate concentration from polluted groundwater under the Maximum Contaminant Levels (MCL) of 50 mg/L (Richard 2010).

2.5 Phosphorus

2.5.1 Phosphorus Removal Methods from Wastewater

2.5.1 (a) Enhanced Biological Phosphorus Removal (EBPR)

According to Loosdrecht and Salem (2006), in municipal wastewater treatment plants, the centrate which is the digested sludge liquor is a small but concentrated stream, typically contributing 1% of the incoming flow, but 10–30% of the N- and P-load to the plant. The past two decades have seen the implementation of two major processes for nutrient removal and recovery in side-stream conditions which are anaerobic ammonium oxidation (anammox) for nitrogen removal and struvite precipitation for phosphorus recovery. Partial nitrification coupled with anammox (PNA) reduces the need for organic carbon by 100%, aeration requirements by 60% and sludge production by around 90% compared to conventional nitrification-denitrification.

Phosphorus recovery by precipitation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has been implemented in the full-scale treatment of centrate (Ueno and Fujii 2001). The precipitation is induced by an increase in pH, through CO_2 stripping or addition of base and addition of a magnesium source. Thus, input is required in terms of aeration energy and chemicals. However, precipitation can also be induced biologically by gradients in ion concentrations and pH created inside or between cells (Mann 2001).

In EBPR, part of the phosphorus removal is indeed considered to be due to precipitation of calcium phosphate initiated by the elevated phosphate concentrations during anaerobic phosphorus release (Maurer et al. 1999). Similarly, a part of the phosphate removal by aerobic granular sludge has been shown to be due to the formation of calcium phosphate inside the granules (De Kreuk et al. 2005). The presence of calcium phosphate has also been confirmed in anammox granular sludge and been found to be

important for granule mechanical strength (Lin et al. 2013), as well as functioning as a biomass carrier (Dapena-Mora et al. 2010).

Biologically induced precipitation of calcium phosphate was confirmed in partial nitrification coupled with PNA granular sludge. Granules with a high inorganic content settled due to gravity, which allowed for easy recovery. Harvested granules showed a high phosphate content (16 wt%), with a Ca/P ratio close to that of hydroxyapatite, the presence of which was confirmed by X-ray diffraction (XRD), although probably coexisting with amorphous calcium phosphates. The calcium phosphate formed without the addition of chemicals and is proposed as a novel phosphorus recovery product from wastewater (Johansson et al. 2017).

2.5.1 (b) Sorption Process

Loganathan and Vigneswaran (2014) states that the sorption process is generally considered to be an effective water treatment option because of convenience, ease of operation, simplicity of design, and economics, provided low-cost sorbents are used. As the phosphate removal mechanism is not always at the surface of the sorbent, the term sorption is used here to denote phosphate removal both at the surface and interior of the sorbent. With more emphasis on recovering the removed phosphorus and the need for very low P concentration in the effluent, sorption is an attractive process for wastewater plants in the future.

Sorbents are used as filter media in filter-based systems and as bed media in constructed wetlands. After a period of usage, they become saturated with phosphate and their efficiency of phosphate removal decreases. At this point the sorbent can either be used directly as a source of P if it has no contaminants or can be regenerated by removing the adsorbed phosphate. The phosphate can be recovered by precipitation with calcium

or magnesium salts and employed as phosphate fertilizers. Alternatively, they can be diluted with irrigation water for fertilizing irrigated crops.

The sorbents tested for phosphate removal can be classified as multivalent metal oxides and hydroxides, silicates, Ca and Mg carbonates, LDHs, natural and synthetic organic compounds, industrial by-products, and organic wastes. Most studies reported were conducted in laboratories where the batch method was prevalent while others mainly using the dynamic column. Of the sorbents, Fe, Al, and Zr metal oxides and hydroxides, LDHs, and highly porous metal oxide or polymer composites generally had the highest phosphate sorption capacities. Many anions coexist with phosphate in wastewater.

2.5.1 (c) Membrane Technology

According to Chang et al. (2017), membrane technology has been employed in water supply and is important for sustainable water production. Of all the membrane processes, membrane bioreactor (MBR) technology has become one of the most effective options for improving water sustainability because MBR promotes wastewater reuse, requires less space, and produces less sludge (Ramesh et al. 2006). However, MBR technology has some operational problems such as membrane fouling and high energy cost (Nguyen et al. 2016).

To overcome these limitations, a hybrid membrane bioreactor, known as the osmotic membrane bioreactor (OMBR), was developed by integrating the forward osmosis (FO) process into MBR technology. OMBR has the benefits of higher water quality, lower membrane fouling, and lower energy consumption (Yin Tang and Ng 2014). Notably, nutrients such as phosphorus, which is precious but overexploited by humans can also be recovered from water filtered through MF or UF. Qiu et al. (2015) demonstrated that with simple pH adjustment, the phosphorus can be directly recovered

from municipal wastewater using a hybrid OMBR–MF system, predominantly in the form of amorphous calcium phosphate.

From the research done by Chang et al. (2017), an OMBR–MD hybrid system combined with MF membrane extraction can effectively treat wastewater with low accumulation of salts and high recovery of phosphorus. The rejection of PO_4^{3-} and NH_4^+ -N was more than 99%. Moreover, the results of struvite recovery showed that phosphorus can be efficiently recovered from the MF permeate water at pH 10, and the amount of produced struvite was quantitatively determined to be 41 mg/L of the MF permeate. The MD process was used to recover the diluted MgCl_2 draw solution with an initial flux of 8.2 L/m^2 under a $30 \text{ }^\circ\text{C}$ temperature difference. However, the flux decreased slightly to $6.3 \text{ L/m}^2 \text{ h}$ after 6 hours of operation due to the drop of vapor pressure in the salt solution based on Raoult's law.

2.5.2 Phosphorus Removal by NF Membrane

Schütte et al. (2015) states that NF membrane which has a dense active layer contains charged functional groups on its surface. Therefore, NF membranes are not only size-selective, but also ion-selective and their performance depends heavily on the pH of operation. Under low pH conditions, NF membranes exhibit a strong positive surface charge and phosphorus is mainly present in the form of undissociated or only mono-dissociated phosphoric acid. This leads to a high efficiency of the separation process, in which multivalent metal cations are retained, while neutral and monovalent species pass the membrane to a high degree.

The highest fluxes were reached with Desal-DL membrane and NF270, probably because both membranes are highly hydrophilic (Plakas et al. 2006). As NF270 is more hydrophilic than DL, it is more permeable in the case of pure water filtration. However, if pre-treated feed from digested sludge was used, the flux measured with DL was higher

than with NF270, indicating that the permeability was influenced by feed characteristics such as osmotic pressure and viscosity to different degrees. Duracid and AS membrane are relatively dense membranes and therefore showed a significantly lower permeability for both water and pre-treated feed fluid. The lowest retention of phosphorus was measured with the AS membrane, while DL had the highest retention value. It has been shown that the zeta potential and thus, at low pH values, the positive charge density of NF270 is higher than that of DL (Mänttari et al. 2006).

Commercial membranes of DK5, MPF34, NF90, NF270, NF200 were characterized and tested in permeability and phosphorus removal experiments. NF90 membranes offer the highest rejection of phosphorus with a rejection of more than 70% phosphorus was achieved for a feed containing 2.5 g/L of phosphorus at a pH <2. Additionally, NF90, NF200 and NF270 membranes show higher permeability than DK5 and MPF34 membranes. The separation performance of NF90 is slightly affected by phosphorus concentration and pressure, which may be due to concentration polarization and fouling (Leo et al. 2011).

2.5.3 Influence of Operating Conditions of NF Membrane on Phosphorus

Removal

Qin et al. (2004) has been intensively investigated the effect of pH on the performance of NF on the removal of phosphorus. Using NF200 membrane, the phosphate retention increases when the pH of solution increases from 2.8 to 6. The large increase observed in the rejection of phosphate is due to the combination of the increase of phosphate anions percentage and the membrane charge becoming increasingly negative. As from pH 6 to 10 the phosphate rejection remained almost constant despite the both increasing of phosphate anions percentage and negative surface charge. Based on these experiments, it appears that an increasingly negative surface can only reject

negatively charged solutes to a certain level before the effect is offset by pore expansion or membrane swelling (Ballet et al. 2007).

The effect of ionic strength was investigated by adding different concentrations of NaCl ranging from 0.01 to 0.5 M. The phosphate anions retentions decrease when the concentration of NaCl increases. It is a characteristic of charged membranes and is generally interpreted by the shielding phenomenon. Increasing the concentration of sodium cations of the solution involves the formation of a screen which gradually neutralises the negative charge of the membrane. As the total charge of the membrane decreases, the retention of the phosphate anions decreases since the electrostatic effect of the membrane becomes weaker (Ballet et al. 2007).

According to Yousefia (2015), the phosphate removal efficiency decreases when flow rate and initial phosphorous concentration increases. The results are similar as experiment done by Ballet et al. (2007). This indicated that a NF could considerably reject the monovalent ions. These results can be mainly described by its tight pore structure and the characteristics of the charged membranes. It can be contributed to the transfer mechanism, including sieving and electrostatic interaction effects.

Furthermore, based on the research done by Schütte et al. (2015), it is assumed that the mono-dissociated components are attracted by the positively charged membrane, which leads to a high phosphorus yield in the permeate. All experiments showed significantly higher retention values when the TMP was increased. In all cases, the TMP dependence of the flux correlated well with Darcy's law. This indicates that the diffusive transmembrane transport becomes small in relation to the increasing water flux at high TMPs. Thus, for minimizing the phosphorus loss in the retentate, a low TMP is favourable. However, as a counter-effect, a low TMP did also lead to a lower retention of metals and thus a higher contamination of the permeate.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The experiments were carried out using a dead-end filtration cell unit from Sterlitech Corporation. Throughout the experiment, two commercial NF membranes namely DOW NF 90 (FILMTEC™ Flat Sheet) and DOW NF 270 (FILMTEC™ Flat Sheet) were used. The synthetic water was prepared using NaNO_3 , Na_3PO_4 and deionized water. The concentration of nitrate was measured using Vario NitraX reagent set (Lovibond) while concentration of phosphorus was measured using Phosphate HR tablet (Lovibond).

Table 3.1: List of materials, suppliers and its purposes

Material/Chemical	Supplier	Purpose
NaNO_3	EMSURE®	Synthetic water sample
Na_3PO_4	EMSURE®	Synthetic water sample
Deionized water	School of Chem Eng, USM	Synthetic water sample
DOW NF 90	FILMTEC™ Flat Sheet	Filtration process
DOW NF 270	FILMTEC™ Flat Sheet	Filtration process
Dead-end filtration cell unit	Sterlitech Corporation	Filtration process
Vario NitraX reagent set	Lovibond	Reacting agent to check nitrate content
Phosphate HR tablets	Lovibond	Reacting agent to check phosphate content

3.2 Research Plan

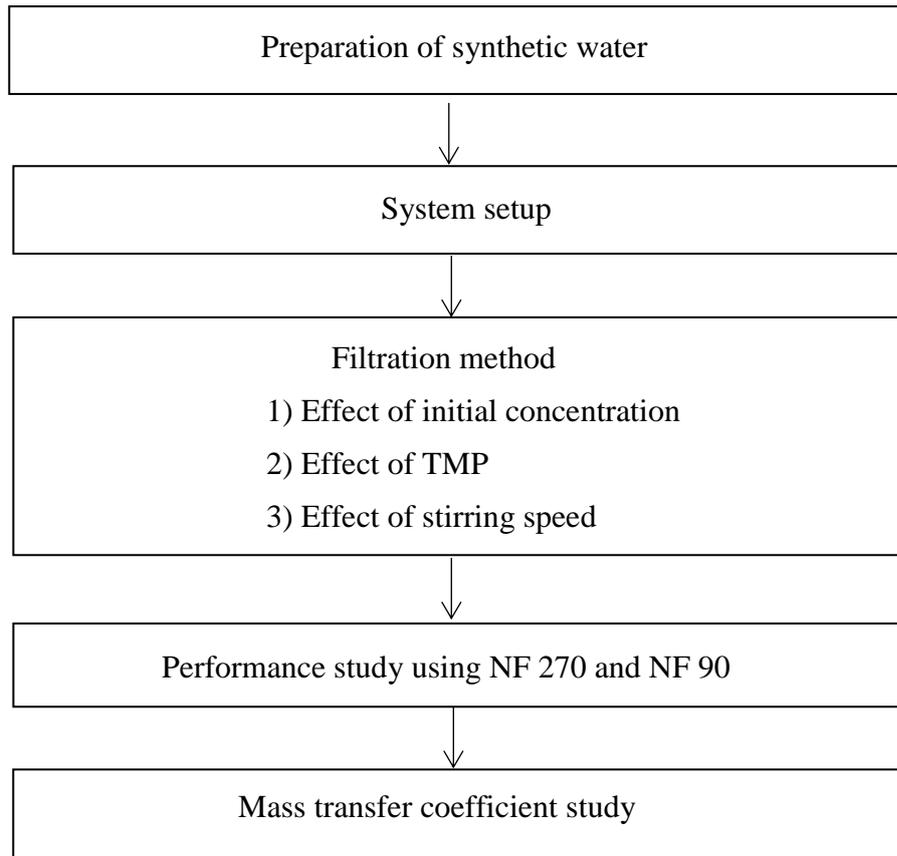


Figure 3.1: Research plan of the experiment

3.3 Preparation of synthetic water

The coupling effects of anions on nitrate and phosphate removal was determined by using NaNO_3 and Na_3PO_4 mixture. Standard nitrate solutions were prepared by dissolving the NaNO_3 with appropriate amounts of deionized water. In this stage, the synthetic sample were first prepared with nitrate initial concentration of $1000 \text{ mg NO}_3^-/\text{L}$ of NaNO_3 as stock solution and then diluted to different concentrations of 50, 100, 500 $\text{mg NO}_3^-/\text{L}$ of NaNO_3 . Similar steps were carried out for phosphate synthetic water.

For ion mixture, initial concentration of $100 \text{ mg NO}_3^-/\text{L}$ of NaNO_3 and then different concentrations of 100, 300 and 500 $\text{mg PO}_4^{3-}/\text{L}$ as Na_3PO_4 were added to the solution and finally the combined solution was filtered using NF membrane. The concentration of permeate is then determined using Lovibond equipment.

3.4 NF Membrane Filtration

A dead-end filtration cell test unit with an effective membrane area of 14.52 cm² was used for the filtration process. A schematic diagram of the experimental set-up is shown in Figure 3.2. The experimental processing about NF were conducted by two commercialized flat sheet membrane which are DOW NF 90 (FILMTEC™ Flat Sheet) and DOW NF 270 (FILMTEC™ Flat Sheet). The properties of the NF90 and NF270 are listed in Table 3.2.

Before the start-up of experiments, membrane was first soaked in deionized water for at least 2 hours. After soaking, the NF membrane compressed in the stirrer cell at pressure of 10 bar. After compressing the membrane, the feed water which is the synthetic sample is then charged onto the NF membrane for the dead-end filtration process.

Table 3.2: Properties of NF90 and NF270 (Hoinkis et al. 2011)

Material	NF 90	NF 270
	Aromatic polyamide	Piperazine-based polyamide
Molecular weight cut-off (MWCO) (Da)	200	300
Water permeability at 25 °C (L/m²h bar)	11.3	13.5
Zeta potential at neutral pH (mV)	-17.5	-21.6
Maximum temperature (°C)	35	45
Maximum pressure (bar)	41	35
Recommended pH range	4-11	3-10