CONENTRATING OF PHOSPHATE WITH SIMULTANEOUS REMOVAL OF SODIUM CHLORIDE VIA NANOFILTRATION

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by

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LIST OF SYMBOLS

Cl^-	Chloride ion
$NO3-$	Nitrate ion
$NO2$	Nitrite
$NaCl$	Sodium Hydroxide
PO_4^{3-}	Phosphate ion
$H_2PO_4^{--}$	Dihydrogen phosphate ion
HPO_4^{2}	Hydrogen phosphate ion
Cl^-	Chloride ion
Na^+	Sodium ion
H^+	Hydrogen ion
H_2SO_4	Sulfuric acid
Na^+	Sodium ion
Ca^{2+}	Calcium ion
K^+	Potassium ion
Al^{3+}	Aluminium ion
Fe^{3+}	Iron ion
MJ	Mega Joule
kg	Kilogram
%	Percentage
°C	Degree Celsius

LIST OF ABBREVIATIONS

NF	Nanofiltration
MF	Microfiltration
UF	Ultrafiltration
RO	Reverse osmosis
MT	Million tonnes
MWCO	Molecular weight cut-off
IEP	Isoelectric point
CP	Concentration polarization
TMP	Transmembrane pressure

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ABSTRACT

Recovery of phosphorus has been gaining importance due to its natural scarcity and high economical value. Aquaculture and poultry effluent with significant phosphate content required further treatment before discharging to the environment. However, its trace quantity makes the whole process not feasible. Moreover, the presence of salt (NaCl) makes the effort to recover the phosphate as fertilizer less attractive due to its unwanted salinity. In this study. nanofiltration had been tested to recover/concentrate the phosphate ions and at the same time removing the sodium chloride. The study was conducted using Desal DK5 membrane in dead-end mode using Dead End Stirred Cell at different pressures and concentration to investigate the effect of transmembrane pressure (TMP) and feed concentration on the rejection of phosphate ions, average permeate flux and concentrating factor. The highest phosphate ion rejection, 99.86%, was achieved at the lowest pressure, 2 bar, and lowest concentration of potassium dihydrogen phosphate solution (20 ppm). However, in the same parameter, the permeate flux and the concentrating factor (CF) obtained were the lowest compared to other sets of experiment which are 20.15 $L/m^2.h$ and 1.55 respectively. The maximum CF of could be achieved at 6 bar. The removal of NaCl increases with pressure, however the presence of NaCl further reduce the phosphate ion rejection, lowering the average permeate flux and concentrating factor. The results obtained is very promising in terms of harvesting the nutrient from aquaculture effluent and at the same time removing the unwanted salinity.

PEMEKATAN FOSFAT DAN PENYINGKIRAN NATRIUM KLORIDA

SECARA SERENTAK MALALUI NANOFILTRASI

ABSTRAK

Pengambilan semula fosforus telah menjadi penting kerana kekurangan semula jadi dan nilai ekonomi yang tinggi. Limbah dari industri akuakultur dan industri ayam dengan kandungan fosfat yang signifikan memerlukan rawatan lebih lanjut sebelum dibuang ke alam persekitaran. Walau bagaimanapun, kuantiti kecilnya menjadikan keseluruhan proses tidak dapat dilaksanakan. Lebih-lebih lagi, kehadiran garam (NaCl) menjadikan usaha pemekatan nutrien sebagai baja kurang menarik kerana kehadiran garam yang tidak diingini. Dalam kajian ini. nanofiltrasi telah diuji untuk pengambilan semula/memekatkan ion fosfat dan pada masa yang sama menyingkirkan natrium klorida. Kajian dilakukan dengan menggunakan membran Desal DK5 dalam mod buntu menggunakan 'Dead End Stirred Cell' pada tekanan dan kepekatan yang berbeza untuk menyiasat pengaruh tekanan transmembran (TMP) dan kepekatan larutan terhadap penapisan ion fosfat, purata fluks meresap dan faktor pemekatan. Penapisan ion fosfat tertinggi, 99.86%, dicapai pada tekanan terendah 2 bar dan kepekatan larutan yang terendah, 20 ppm. Walau bagaimanapun, pada parameter yang sama, fluks meresap dan faktor pemekatan (CF) yang diperoleh adalah yang terendah berbanding dengan set eksperimen lain yang masing-masing 20,15 L/m^2.j dan 1.55. CF maksimum dapat dicapai pada 6 bar. Penyingkiran NaCl meningkat dengan tekanan, namun kehadiran NaCl seterusnya mengurangkan penapisan ion fosfat, menurunkan rata-rata fluks meresap dan faktor pekat. Hasil yang diperoleh sangat menjanjikan dari segi pengambilan nutrien dari efluen akuakultur dan pada masa yang sama menghilangkan kemasinan yang tidak diingini

CHAPTER 1
INTRODUCTION

In this work, phosphate recovery and simultaneously removing sodium chloride by nanofiltration (NF) has been studied. The efficiency of phosphate recovery using NF membrane was investigated based on the different operating pressure and different phosphate concentration in feed solution with the absences and presences of sodium chloride. The concentrating effect over the time and the possibility of nutrient loss will be studied. Basically, in this chapter, the overview of this research and the significances of nutrient recovery, which focusses on the problems associated with the recovery of phosphate ions is introduced. This chapter summarizes the research background of nutrient recovery by using various technologies with the focus on nanofiltration. The problems associated with the current technology was discussed.

1.1 Research Background

Rapid industrialization, urbanization, and expansion of population have increased the global demand for food. In addition, the decrease in the arable land has led to an increase in the use of fertilizers by farmers to increase their yield. Declining availability of arable land per capita in various countries such as India, China, United States and others, is one of the major reasons for augmenting the demand for phosphorus fertilizers as they aid in enhancing the yield. Phosphate fertilizers contain essential nutrients and are used to maximize yield per crop and productivity of the land. Phosphate fertilizers can also be used to overcome soil fertility issues, as an extensive range of macronutrients and micronutrients are used as soil supplements to increase the productivity and quality of crops. In the meantime, the population is expanding, hence, crop-yields must increase to meet food production needs. The crop

protection is a key strategy adopted by farmers, to meet the global food demand. Usage of phosphorus fertilizers on crops is also a proven technology to meet the growing demand for food products. There is little scope for expansion of agricultural land in future due to robust industrialization and urbanization. Growing demand for meat and other diverse food products along with increasing population can augment the demand for phosphorus fertilizers. Growth potential in the Asia-Pacific and Latin American markets is expected to provide ample opportunity for the phosphate fertilizer market's growth at a considerable rate in the coming years. All these factors are increasing the consumption and demand for phosphate fertilizers, which is driving the growth of the market. The production of fertilizer depends heavily on the non-renewable energy and finite mineral resources such as phosphate from phosphate rock and the generation of ammonia from the Haber-Bosch process (Mehta *et al.*, 2015). However, the phosphate rock is facing depletion currently. This issue makes the price of the phosphate to increase drastically. Due to these reasons, the rate of production of phosphorus fertilizer might fail to meet the global demand if there is no alternative way to recover the phosphate in the near future.

The worldwide fertilizer demand annually increases by 4% to sustain the food source for 2.3 billion people by 2050 (Xie *et al.*, 2015). However, the global phosphate production might decline to about 50 Mt by 2080 if individual nations maintain existing production levels, due to the depletion of reserves in the United States and China (Cooper *et al.,* 2011). Maintaining current global phosphate production rates throughout the next century will need significant increases in output in certain nations to compensate for losses in others. However, the demand of phosphate is likely to increase causing additional pressure on global phosphate rock production to increase. According to **Figure 1.1**, analysis had been made assuming

that the demand of phosphate rock will increase by 1% every year between 2010 and 2050, and 0% between 2050 to 2100 as shown. The analysis shows that decreasing phosphate reserves combined with rising demand will result in a large phosphate production deficit in the future.
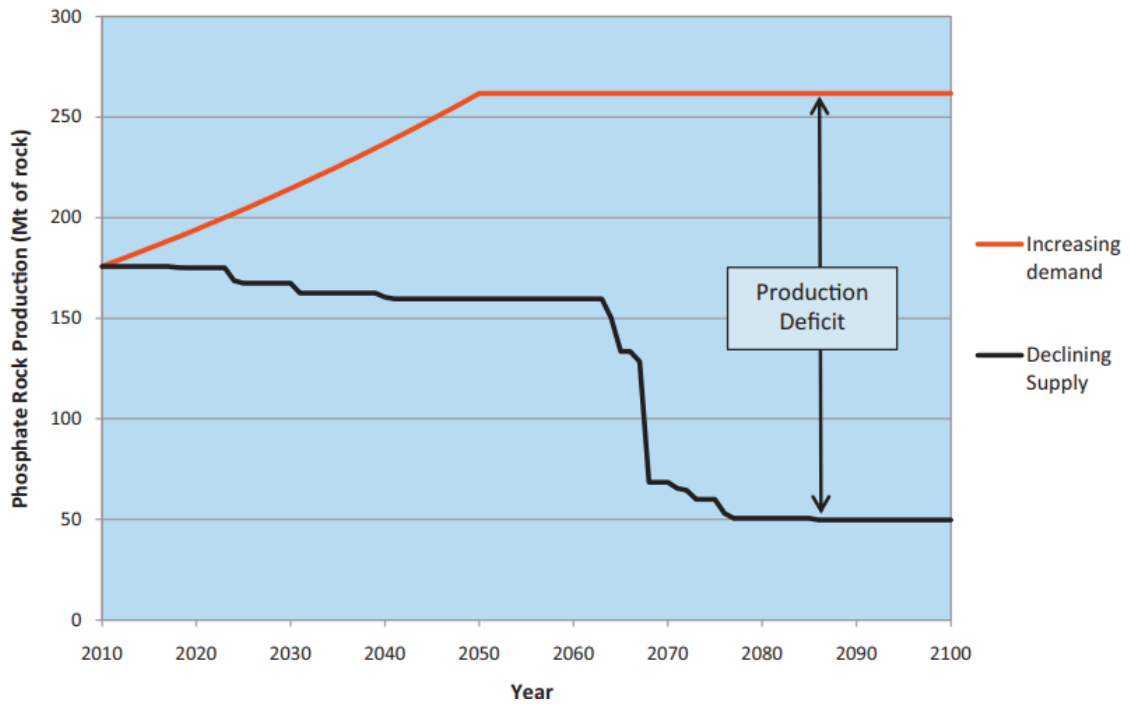
Figure 1.1 Future phosphate rock production deficit as a result of rising demand and reserve depletion based on constant individual country extraction rates (Cooper *et al.,* 2011)

Table 1.1 and **Table 1.2** show the world and Asia phosphorus demand and balance forecasted by fertilizer demand which depicts a significant resiliency in the past, as yearly application is required to sustain yields. Due to the extreme uncertainty created by the COVID-19 pandemic, forecasting growth for the 2020–2021 agricultural year and beyond may be more difficult than usual, as most of the world's economies were forced to follow government-imposed measures, causing disruptions in the food chain and supply networks that have impacted the fertilizer industry. Despite this, the International Fertilizer Association (IFA) expects demand to rise

somewhat. Even in the midst of the crisis, the fertilizer industry's fundamentals are robust. The rising usage of fertilizers in agricultural production to fulfil rising food demand is primarily driving demand (Ilinova *et al.,* 2021).

Table 1.1 World phosphorus supply, demand and balance 2016-2022
(thousand tonnes P2 O5) (FAO, 2019)

YEAR		2016	2017	2018	2019	2020	2021	2022
Phosphoric Acid	Capacity	57,295	60,224	61,464	62,357	52,612	63,552	63,702
	Supply Capability	46,308	47,564	48,620	49,510	50,520	51,520	52,066
	Other Uses	6,444	6,677	7,036	7,170	7,291	7,482	7,734
	Available for Fertiliser	39,864	40,887	41,584	42,340	43,229	44,038	44,332
	Fertilizer Demand	39,136	39,664	40,368	41,149	41,999	42,799	43,562
Phosphorus	Fertilizer Demand	44,481	45,152	45,902	46,587	47,402	48,264	49,096
Non-phosphoric Acid	Fertilizer Demand	5,345	5,488	5,534	5,438	5,403	5,465	5,534
Phosphoric Acid	Potential Balance	728	1,223	1,217	1,191	1,231	1,238	771

Table 1.3 Asia phosphorus supply, demand and balance 2016-2022
(thousand tonnes P2 O5) (FAO, 2019)

YEAR		2016	2017	2018	2019	2020	2021	2022
Phosphoric Acid	Capacity	29,474	31,344	31,394	31,794	31,894	32,094	32,244
	Supply Capability	23,639	24,149	25,459	24,911	26,213	26,521	26,673
	Other Uses	2,951	3,101	3,232	3,341	3,455	3,568	3,666
	Available for Fertiliser	20,688	21,048	22,227	22,570	22,758	22,953	23,007
	Fertilizer Demand	22,810	23,025	23,264	23,691	24,210	24,660	25,099
Phosphorus	Fertilizer Demand	25,445	25,719	26,100	26,357	26,774	27,217	27,662
Non-phosphoric Acid	Fertilizer Demand	2,363	2,693	2,837	2,666	2,564	2,558	2,563
Phosphoric Acid	Potential Balance	-2,122	-1,978	-1,037	-1,121	-1,452	-1,707	-2,092

Thus, the phosphorus fertilizer must be sustainable sources to secure the worldwide food source. In order to achieve a sustainable production of fertilizer, alternative source of phosphate need to be implemented significantly.

Recovering phosphate from wastewater generated from industries is one of the most promising approaches that could sustain the source of phosphate around the world. It is a sustainable approach because the wastewater is generated continuously from factories and the source of wastewater usually contain high amount of nutrient. Conventionally, the wastewater is treated in a biological way like aerobic nitrification and anaerobic denitrification before discharging to the environment. However, this treatment process consumes high energy that contributes to greenhouse gas emission of 0.9 kg CO^2 per cubic liter of treated wastewater (Xie *et al.,* 2015). In the urge to overcome these issues, wastewater nutrient recovery through membrane technology

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can be implemented as an alternative way to sustain the phosphate in sufficient amount to produce fertilizer.

The growing livestock population in Malaysia has resulted in increasing production of farm animal dung, making disposal of a significant volume of manure difficult. This might pose a serious pollution risk as well as a significant nutrient release into the ecosystem (Idaty *et al.,* 2014). As stated in Xiang *et al.* (2020), the composition of wastewater produced from poultry is quite complex. The total solid content in poultry effluent is considerably high because of the high concentration of organic suspended solids of manure and feed residues that are being discharged into the wastewater along with the flushing of water. Looking at the nutrient content, the poultry effluent also contains a significant high amount of phosphorus and nitrogen causing he eutrophication of the water bodies. Therefore, recovering phosphate from poultry effluent can perfectly fit to the demand of fertilizer in current days.

Besides, wastewater generated from the aquaculture industries is also one of a sustainable resource of phosphate and ammonium to be recovered for the production of fertilizers. This is because, aquaculture is one of the fastest growing industries for food production worldwide. The effluent contains a high amount of nitrogenous compound in the form of nitrate (NO_3^-) and nitrite (NO_2) as well as the phosphate content which lies in the range of 1-18 mg/L. It can be used to recover those nutrient for the production of fertilizers (Ahmad *et al.,* 2021).

Typically, sodium chloride (NaCl) also presents in a large amount in the aquaculture effluent. The removal of NaCl is important as it could hamper the benefit of the fertilizer. High levels of sodium can cause three effects on plant growth: (1) excess sodium accumulates in leaves, causing leaf burn and possibly defoliation; (2) development of poor soil physical conditions destroying natural particle aggregation

which limit plant growth due to osmotic pressure; and (3) calcium and magnesium deficiency through reduced availability and imbalance with respect to sodium (NSW Health *et al.,* 2000). Besides, the accumulation of salts on the soil surface will result in the surface evaporation of soil moisture (Evangelou *et al.,* 2017). This deteriorates the plant growth due to the difficulties for the plants to take up and retain water from the soil.

Nutrient recovery from wastewater can be achieved by several technologies such as membrane distillation, chemical precipitation, enhanced biological phosphorus removal (EBPR), ion exchange, and membrane filtration technologies. Unfortunately, each of these technologies has its own drawbacks that hinder its real application. For example, in membrane distillation technology, membrane pore wetting will occur due to the presence of certain component such as surfactants. It lowers the surface tension of liquid in the feed solution. This results in direct liquid flow through the wetted pore from the feed and deteriorates the distillate quality (Xie *et al.,* 2015). Moreover, membrane distillation contributes to concentrating of unwanted NaCl. Another technology that could reduce phosphorus recovery is chemical precipitation of phosphorus by aluminum (Al) and iron (Fe). However, the high chemical consumption and increased the volume of sludge makes this technology unperformable. Besides, this technology requires elevating operation and maintenance cost which is one of the major drawbacks (Visvanathan *et al.,* 1997). Looking at the enhanced biological phosphorus removal. when properly designed, the EBPR operational approach could achieve the phosphorus <1 mg/l target with minimal increase in sludge volume. Even phosphorus <0.1 mg/l is attainable under certain condition and with the addition of carbon source. However, like any biological process, EBPR suffers from large (relatively to physico-chemical processes)

fluctuations in effluent quality (Nir *et al.*, 2018). In ion exchange technology, the selectivity against specific ions is not sufficient to recover phosphate ion from wastewater. In current days, many other methods have been studied and utilized to recover phosphate from wastewater as the phosphate demand is increasing drastically. However, each of the method have its con and pros as shown in **Table 1.3**. Therefore, further polishing step is usually required for meeting low phosphorus discharge requirements.

Membrane technology for the recovery of nutrients from digestate is preferential over the other technologies to recover nutrients. It has emerged as the foundation for high-tech and long-term solutions to the world's present energy, resource, and pollution issues in recent decades. This technology is favorable to recover nutrients because of it benefits that includes the ease of scaling up, low operating and maintenance cost, chemical-free separations, compact and modular design and high selective separations (Gerardo *et al.*, 2015). Membrane technology includes forward osmosis (FO), electrodialysis (ED) and pressure-driven membrane process. However, electrodialysis technology consumes high energy and requires chemical additives for the membrane regeneration. This results in cost increment of the process which makes this technology less preferable (Mehta *et al.,* 2015).

Table 1.3 Different physical-, biological-, and chemical-based phosphorus removal technologies used in water and wastewater treatment processes

Category	Technology	Advantages	Disadvantages
Physical	Membrane purification	Easy and efficient	High initial investment, expensive membrane replacement, shorter membrane life, high energy consumption
	Adsorption	Most widely used mechanism for P removal (employed in coagulation)	Other P adsorption methods are not well established
	Sand filtration (particulate P removal)	Can remove all P compounds	To be used in the primary stage and with highly contaminated water with huge particles
	Ion exchange	Capable of handling hazardous wastes, can separate components from dilute wastes, high P removal	Lack of selectivity against specific ions, generation of wastes as a result of ion exchanger
	Artificial aeration	Effective for prevention of eutrophication in lakes	Not appropriate for shallow lakes
Biological	Enhanced biological phosphorus removal (EBPR)	No need for chemicals, eco-friendly	Low reliability and stability, microbial competition

	Photosynthetic microbes immobilized on cellulose, ceramic, or gel carriers	Can immobilize more than one microbe and remove pollutants efficiently, both live and dead microalgae can be used	Separation of the microbial cells from the treated water, most phototrophs are not easily removed from water
	Separation of the microbial cells from the treated water, most phototrophs are not easily removed from water	Many high-affinity phosphate-binding proteins are expressed in various microorganisms that can work in low P environments	Only a few microbes express the PstS protein; thus, the use of this protein is limited
Chemical	Precipitation via metal salts and lime	Very flexible, high P removal, cost effective	Requires a large amount of chemicals, P recycling is variable
	Crystallization	Different crystal formations, reusable, less hazardous for the environment, easily applied for industrial waste or WWTPs	Chemicals required, favorable conditions needed for reactions, sometimes lower stability or transformation occurs
	Coagulation and flocculation	Different crystal formations, reusable, less hazardous for the environment, easily applied for industrial waste or WWTPs	Effective on bigger molecules, efficiency depends on the charge of salt ions

Looking at FO, studies have been reported that phosphate recovery can be achieved by FO. For instance, Ansari *et al.* (2017) stated that FO membrane demonstrated almost complete rejection due to the electrostatic repulsion occurs between the negative charge phosphate ions and the negatively charged FO membrane which restricts the phosphate transport across membrane. Another mechanism of phosphate rejection by FO that explains the phosphate rejection is the size exclusion mechanism in which phosphate ions are rejected by sieving effect. Another study conducted by the same researcher also stated that the rejection of phosphate ion obtained from the investigation is high to preconcentrate phosphate ions and other ions in digested sludge centrate (Ansari *et al.,* 2016). However, as the main driving force of FO is only the osmotic pressure difference between two solutions, in other words, there is no need to apply an external energy, this results in low fouling propensity of membrane and minimization of irreversible cake forming which are the main drawbacks of phosphorus recovery applications (Eyvaz *et al.*, 2018). Therefore, FO is not suitable to recover phosphate ions from wastewater. Besides, pressure driven processes are also available to recover nutrients. However, the study for simultaneous rejection of phosphate ion and removal of NaCl is limited. Due to the rising attention on recovering phosphate eliminating NaCl content for high quality fertilizer production, membrane technology for nutrient recovery and simultaneous NaCl removal will be studied in this research work. For conventional membrane filtration technologies such as MF, UF, RO and NF, each of the membrane technology have their own drawbacks. However, due to the unique feature of NF technology which reject based on the charge could selectively concentrate nutrient like phosphate and simultaneously allow the permeation of salt.

1.2 Problem Statement

In order to meet the demand of phosphate fertilizer and as well as to eliminate the environmental pollution affected by phosphorus ions, many technologies have been introduced in recent years to recover the nutrient. However, most of the studies reported most of the technologies to recover nutrient have its own drawbacks to simultaneously recover nutrients and removing sodium chloride from wastewater. At the same time, the removal of sodium chloride is very crucial in producing a high and good quality of fertilizer. To overcome all these issues, alternative approach such as membrane technology need to be considered. A perfect technology with correct operational condition is vital to enhance the simultaneous phosphate recovery and sodium chloride removal. Pressure driven membrane filtration technology is one of the most promising techniques to recovery nutrients. However, to increase the rate of nutrient recovery and removal of NaCl via this technology is challenging because it is difficult to determine the correct operating parameters such pressure. This is because, the varying concentrations of the phosphate in the wastewater also affect the operating conditions. In order to solve this problem, the simultaneous recovery phosphate ions and removal of NaCl using NF membrane can be achieved by studying the effect of pressure and concentration of phosphate on the rejection of phosphate ions and the removal of NaCl. The concentrating effect of NF towards the dilute nature of the aquaculture effluent therefore is very challenging. This challenge can be alleviated by allowing the concentration polarization on the membrane surface, but the concentration polarization might induce higher ion diffusion through the membrane and resulted in nutrient loss. Balancing of the concentration as well as nutrient is time and process controlling which requires detail study.

1.3 Objectives

i. To study the efficiency of phosphate concentrating using NF membrane

ii. To investigate the concentrating efficiency of the phosphate at different feed concentrations and pressure

iii. To evaluate the performance of NF membrane in simultaneous phosphate concentrating and NaCl removal.

CHAPTER 2

LITERATURE REVIEW

In previous chapter, the importance of phosphate recovery simultaneously removing salt and the technologies employed to recover phosphate have been discussed. Chapter 2 summarizes previous research and studies based on authentic scientific records and sources that are relevant to the topic of this final year project. This chapter covers the overview of phosphate ions recovery and simultaneous removal of sodium chloride via pressure driven membrane filtration technologies. Besides, this chapter also highlights important information required for optimal performance of NF technology.

2.1 Concentrating phosphate ion via pressure-driven membrane separation

Membrane separation have become one of most promising technologies in optimum performance of phosphate recovery simultaneously removing sodium chloride from the concentrate as they are selective for pollutants and able to separate specific substance from phosphorus (Gerardo *et al.,* 2015). The pressure-driven membrane separation technique is the most well-known and commonly utilized membrane separation method. The general principle of membrane separation is shown in **Figure 2.1**. The pore diameters of the membranes used, and the requisite transmembrane pressures may be classified into four primary pressure-driven membrane processes which are the reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). Typically, these pressure-driven membrane technologies are distinguished by retentate stream and permeate stream (Li *et al.,* 2021). Different pressure-driven membrane separation process shows different separation mechanisms according to its requirement as shown in **Table 2.1**
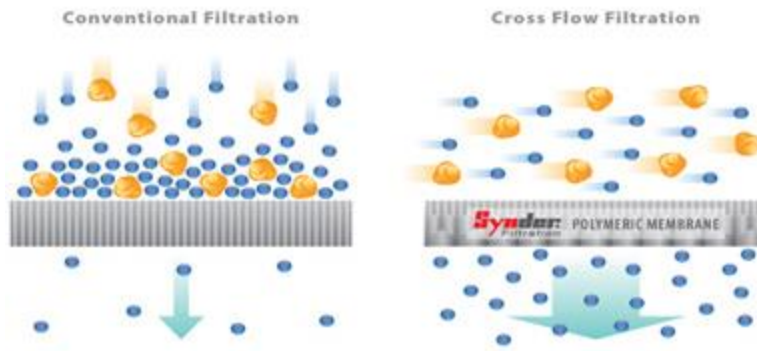
Figure 2.1 Membrane sepration in conventional filtration and cross filtration (*Pressure-Driven Membrane Filtration Processes*, 2021)

Table 2.1 Different pressure-driven membrane with properties

Pressure driven membrane separation process	Retentate	Permeate	Driving force	Separation mechanism	Membrane type
MF	Bacteria, suspended solids $MW > 5 \times 105$ Da	Water, dissolved solids	Pressure difference (0.01–0.2 MPa)	Sieve	Porous membrane
UF	Colloid, viruses, macromolecules $MW > 2 \times 105$ Da	Water, salts, low molecular weight compounds	Pressure difference (0.1–0.5 MPa)	Sieve	Asymmetric membrane
NF	Molecules, multivalent ions $5 \times 102 < MW < 2 \times 103$ Da	Water, monovalent salts	Pressure difference (0.5–1.5 MPa)	Sieve + solution/diffusion + exclusion	Asymmetric and composite membranes
RO	Salts, low molecular weight compounds	Water, solvent	Pressure difference (1–10 MPa)	Sieve + solution/diffusion + exclusion	Asymmetric and composite membranes

2.1.1 Microfiltration

MF is one of the pressure-driven membrane separation technology which is widely used to separate microorganisms and suspended particles from wastewater. MF basically separate

particle with the diameter between 0.1 and 10 m, while the aperture range of an MF membrane is 0.05 to 20 m. This membrane separation technology normally operates at the pressure difference between 0.01 and 0.2 MPa (Li *et al.,* 2021) . MF is only applicable to recover nutrients when it is combined with other membrane separation technologies such as FO, RO and UF (Jørgensen *et al.*, 2018; Qiu *et al.*, 2015). Studies on the phosphorus recovery via MF combined with FO in bioreactor have been conducted. The researchers reported that this hybrid technology has the potential for enhanced phosphorus recovery, if the main part of water leaves through the FO membrane and phosphorus leaves the reactor with the MF permeate (Jørgensen *et al.*, 2018). However, recovering phosphate by this hybrid technology have higher investment cost and maintenance for the entire system (Ivanova *et al.*, 2016).

2.1.2 Ultrafiltration

UF is a pressure-driven barrier that removes suspended particles, bacteria, viruses, endotoxins, and other pathogens from water, resulting in water that is extremely pure and low in silt density. UF is a membrane filtration technique that uses hydrostatic pressure to push water through the semi-permeable membrane. The UF membrane's pore size is generally between 103 - 106 Daltons. This membrane normally separates particle with sieving mechanisms and operates at a pressure range of 1-5 bar. UF membrane separates molecules in larger size and colloids with relative molecular masses more than 500 g/mol. Therefore, rejection of phosphate ion that has a molecular weight of 95.9793 g/mol is difficult to achieve via UF but the NaCl removal can be achieved easily. Studies have been conducted to study the effect of phosphate recovery using UF technology. More than 90% rejection of phosphate ion was achieved as reported by Muthumareeswaran *et al.* (2014). However, the high rejection of phosphate was attained due to the surface medication of the UF membrane which is also cost consuming process.

2.1.3 Reverse Osmosis

RO is the process by which water is forced from one side of a higher concentration to the lower side through a semipermeable membrane, thereby "reversing" the natural flow trend of water. Therefore, RO requires a higher hydrostatic pressure to overcome the larger osmotic pressure. The operating pressure is generally 1–10 MPa. In case of RO membranes, the pore size becomes smaller, and diffusion dominates over convection. The solution-diffusion model describes the transport sufficiently well. Although studies have reported high rejection of phosphate ion, this technology is not favourable due to the requirement of high operating pressure which is also a cost consuming factor (Balannec *et al.,* 2005; Vourch *et al.*, 2005).

2.1.4 Nanofiltration

NF is a membrane separation that possess the characteristics that lies between UF and RO, and functions by both pore-size flow (convective) and solution-diffusion mechanism. One of the factors that this technology is applicable to be effectively used in phosphate recovery in wastewater is because it can be operated at a lower pressure than RO. Similar to RO, NF membrane is efficient to remove ions. NF membrane is different from RO due to the characteristic of NF membrane that could remove selective multivalent ions such as HPO_4^-, HPO_4^{2-} and PO_4^{3-} or uncharged ion H_3PO_4 and organic substances and the greater flux of NF compared to RO (Leo *et al.,* 2011). Therefore, NF membrane is the most suitable membrane over the other pressure-driven membrane as it has the ability to reject phosphate ions from wastewater because the membrane has charge on its surface that resulted from the dissociation of different ionic groups present on the membrane as well as from the porous conformation of the membrane.

2.2 Concentrating phosphate ion via NF

Phosphate recovery via NF has emerged as one of the most promising technology as compared to the other conventional pressure-driven membrane separation process. NF is a membrane separation that possess the characteristics that lies between UF and RO, and functions by both pore-size flow (convective) and solution-diffusion mechanism. One of the factors that this technology is applicable to be effectively used in phosphate recovery in wastewater is because it can be operated at a lower pressure than RO. Similar to RO, NF membrane is efficient to remove ions. NF membrane is different from RO due to the characteristic of NF membrane that could remove selective ions such as $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} or uncharged ion H_3PO_4 and organic substances and the greater flux of NF compared to RO (Leo *et al.,* 2011). Therefore, NF membrane is the most suitable membrane over the other pressure-driven membrane as it has the ability to reject phosphate ions from wastewater because the membrane has charge on its surface that resulted from the dissociation of different ionic groups present on the membrane as well as from the porous conformation of the membrane.

There are few types of NF membrane that have been used in recent studies to investigate the capacity of phosphate rejection. The most common membrane used are NF90, NF720 and Desal DK5. These membranes are differentiate based on the characteristics own by each type of the membrane. The common type of characteristics that differentiate the type of membrane includes the permeability of pure water, molecular weight cut-off (MWCO) and the material of membrane as shown in **Table 2.2**. Permeability of water is important characteristic of membrane that need to be considered in the nutrient concentrating process. This is because when the permeability of the water is higher, the membrane can concentrate higher amount of phosphate ions. MWCO defined as the minimum molecular weight of a solute that is 90% can be retained

by the membrane. Therefore, MWCO of the membranes also significantly need to be considered. The membrane material plays an important role too in selecting membrane for the rejection of phosphorus. This is because, the rejection of phosphorus is controlled by one of the important factors that is charge of the membrane. The charge of the membrane is determined by the type of the material used to manufacture membrane as is contains ionic groups on the surface of the membrane based on the material (Enrico *et al.*, 2016)

Table 2.2 Properties of NF membranes (dos Santos *et al.*, 2015) (Leo, 2011) (Ben Amar *et al.*, 2009)

Membrane	Pure water permeability (21°C) L/(h m^2 bar)	MWCO (Da)	Material of membrane
NF270	10.66	200	Polyamide on polysulfone
NF90	7.63	110	Phenylene diamine and benzenetricarbonyl trichloride
Desal DK5	8.95	250	Polyamide on polysulfone
MPF34	2.05 exp -6	300	Composite on polysulfone

In order to optimise the performance of the NF membranes in rejection phosphate ion, affecting parameters on the performance such as the phosphate concentration in feed solution, pH and transmembrane pressure (TMP), of the feed solution and need to be consider. As reported by Leo *et al.* (2011) the NF270 performed well on the rejection of phosphorus at low feed concentration and not at a high phosphate concentration due to the reduction of Donnan

effect. According to Bartels *et al.* (2005), when a typical feed solution containing both positively charged ions (cations) and negatively charge ions (anions) comes in contact with the negatively charged membrane, the concentration of the cations in the membrane is greater than their concentration in the bulk solution. At the same time, the concentration of the anions in the membrane becomes less than that of the bulk solution. This ion shift creates an electrical potential known as the Donnan potential at the boundary between the membrane and the solution. The Donnan potential attracts cations to the membrane while repelling anions away, thus increasing anion rejection. At equilibrium, the co-ions which refers to the ions that have the same charge as the charge of the membrane will be less concentrated to the counter ions which refers to the ions that have opposite charge with the membrane surface charge. Leo *et al.* (2011) stated that the Donnan effects was dominant whereby the electrostatic interactions between the phosphate ions and the charge on the surface of the membrane is prominent at high concentration. Donan effects refers to the equilibrium and interactions between the ions present in the solution and the charge existing on the membrane. However, the NF90 membrane showed an opposite result from NF270. It was reported that the rejection of phosphorus achieved was more than 70% at high feed concentration. Therefore, at the researcher suggested NF90 is preferable over NF270 to separate phosphate ion under higher concentration whereby in this case the high concentration was 2.5g/L. Desal DK5 and MPF34 depicted the rejection of phosphorus were poor when comparing to the NF270 and NF90 membrane which may be related to the larger MWCO of the membranes as listed in **Table 2.2.** Another reason for the poor performance of the membranes were because the experiment was conducted in a low range of pressure. On the other hand, Chai *et al.* (2019) reported that both NF270 and NF90 the rejection of phosphate ion increases with phosphorus concentration from 62.4% to 80.5% and 54% to 75.9%, respectively

under 10 bar. The highest concentration used in this research was 15 mg/L. It was reported that the phosphate rejection increases with increasing phosphorus concentration from 2.5 mg/L to 15 mg/L. This increase in rejection was justified by the formation of additional thin layer caused by the phosphate deposition and adsorption on the surface of the membrane at the highest phosphorus concentration. Generally, NF membrane is negatively charge on its surface that able to attract only positively charge ions and repel the negatively charged ions. Therefore, when the phosphate ions concentration in the feed solution increases, more anions present in the feed solution causing more phosphate ions to be rejected by the membrane. In this case, it was stated the Donnan potential increases at high phosphate ion concentration preventing the diffusion of the phosphate ion to the membrane phase. This finding is in a good agreement by dos Santos *et al.* (2015) where phosphorus rejection increases at higher concentration due increased ionic strength in the bulk feed water, it was reported that the rejection ranges between 69 to 75% for the synthetic water with KCl and between 60 to 97% for the synthetic water with $CaCl_2$. In research done by Visvanathan *et al.* (1997) reported the similar trend using Desal DK5 membrane where the phosphate rejection increase with feed concentration due to the increase in Donnan effect. The rejection achieved by this researcher was more than 95% of 2 -8 mg/L phosphorus using Desal DK5. The experiment of phosphate rejection conducted by Niewersch *et al.* (2008) stated that the rejection of phosphate by MPF34 performed well compared to Desal DK5 which is not influenced by the MWCO of the membrane but the surface charge characteristics on each membrane caused the difference the phosphate rejection.

Besides concentration of phosphate ion in the feed solution, the pH of the solution also affects the permeability of the phosphate ion. The ions present on the surface membrane might be acidic, basic or amphoteric nature depending on the materials used for the fabrication of each

type of membrane. The dissociation of the ionizable group present on the surface of the membrane is significantly controlled by the pH of the feed solution (Singh *et al.*, 2020). As reported by Niewersch *et al.* (2010), Desal DK5 and NF270 exhibits an improved rejection of phosphorus at higher pH value. At higher pH, the concentration of H^+ is reduced and a poor electrical double layer of positive charges on the membranes. This phenomenon induce the transmembrane transmissions of anions, and therefore the rejection of phosphate ions is reduced (Li *et al.,* 2021). Schütte *et al.* (2015) reported that the rejection of phosphorus by commercial NF membranes decreased from 0.56 at pH 1.5 to 0.42 at pH 0.5 at an operating pressure of 7 bar. This result was supported by the study conducted by Cathie Lee *et al.* (2014) who perform phosphate rejection using NF270 and NF90 at pH below isoelectric point (IEP). According to Rice *et al.* (2011), the phosphate rejection decreased with increasing concentrations when below the net isoelectric point (IEP) of the membrane, however at pH values above this point there was no significant effect by concentration. Besides, the study conducted by Niewersch et al. (2010) also reported the same concept whereby the rejection of phosphate ion increase with increasing pH. The highest rejection achieved at the highest Ph values Ph 4 was more than 90% by NF270. Furthermore, the similar trend was also obtained by (Nir *et al.,* 2018) in which the study was conducted with the phosphate feed concentration of 0.1M. the result obtained from this study was more than 97% of phosphate rejection was achieved at pH 7-8 even at low permeate flux, while the rejection declines to 92-95% when the pH value is reduced to pH 6. As reported by Rice *et al.* (2011) the rejection of phosphate was the highest at high pH values. The general observation shows that the membranes were positively charged at low pH that allows low phosphorus rejection while the rejection increases with pH as the surface of the membrane is

negatively charged which enables the repulsion force to take place between the surface of the membrane and the phosphate ion causing more phosphate ion to be rejected.

Transmembrane pressure (TMP) is another factor that affects the phosphate rejection via NF technology. TMP is referred as the pressure difference between the feed side and permeate and it is a driving force in pressure-driven membrane like NF membrane (Cui *et al.*, 2010). Some studies have reported that the rejection of phosphate increase with TMP. One of the studies done by Visvanathan *et al.* (1997) reported that the rejection of phosphate increases from 96% to 99% when the pressure is increased to 4 to 10 bar using a slat sheet type Desal DK5 thin film NF membrane. According to the reporter, the when the pressure increases, the solvent permeability increases that increases the solvent flux too that results in high rejection of solute. A similar trend was reported by Roy *et al.* (1995) In this study DL and DK NF membrane were used and obtained a result of 95.5-99.2% and 94.3-97.5% of phosphate rejection respectively. Although the permeability of DK is lower than DL, membrane the rejection of DK membrane is higher. This is because the rejection of phosphate not only depends on the transmembrane pressure but also depends on the charge capacity of the membrane. Therefore, it is stated that DK may have higher charge capacity than DL that increases the rejection of phosphate. The increase in solvent flux relates to the reduction of diffusion transmembrane transport of solute. (Schütte, 2015). Besides, the TMP is a common factor that influence concentration polarization (CP) in the NF separation process. According to Cathie Lee *et al. (*2014) as the pressure increased further, concentration polarization increased. Hence, the retention of phosphorus increase (Roy *et al.,* 1995). The CP is more significant when convective flow is increased. Convective flow is defined as the transport of the mass due to the bulk fluid motion the feed side. The increase in TMP results in higher convective solute transport towards the membrane surface, increasing the

concentration polarization at the surface of the membrane. As the time goes by, diffusivity flux takes place to permeate the solute across the membrane (Chakraborty *et al.*, 2004).

2.2 Removal of sodium chloride in the presence of multivalent ion via nanofiltration

In order to produce a high-quality phosphate fertiliser, the content of NaCl should not be exceeded in the fertiliser. Usually, NaCl amount in aquaculture and poultry wastewater contains in a considerable amount that could declines the quality of phosphate fertiliser if it is not removed from the phosphate concentrated produced from the NF technology. Therefore, removal of NaCl is equally important as rejecting phosphate ion in the production of fertiliser. RO and NF would be applicable in separating the NaCl that provides monovalent ions (Na^+ and Cl^-) from the phosphorus which provides multivalent ions. As shown in **Table 2.1**, only these two technologies are applicable is separating ions. However, as mentioned in **Section 2.1.4 Nanofiltration,** NF has high selective in retaining multivalent ions of phosphorus and could also selectively remove monovalent ions from sodium chloride (Na^+ and Cl^-) simultaneously as compared to RO. NF membranes enable higher salt passage than RO membranes, which decrease the osmotic pressure (Petersen *et al.,* 1993). In addition, the high permeability of NF membranes lowers the pressure needed for phosphate recovery. Hence, NF is the most suitable technology in recovering phosphate ion and simultaneously reject sodium chloride to produce high quality phosphate fertilisers.

One of the specific features of NF membranes are mainly the very high rejections of multivalent ions which is more than 90% with low to moderate rejections of monovalent ions which is approximately 70%. (Nagy *et al.,* 2019). The surface of NF membrane generally is negatively charged that allows it to reject effectively multivalent ions, negatively charge ions