NANOFILTRATION AS A TERTIARY TREATMENT FOR PHOSPHATE REMOVAL FROM WASTEWATER

by

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ABSTRACT

In an effort to determine the potential application of nanofiltration in environmental field, experimental investigations were conducted to evaluate the performance of nanofiltration for tertiary level phosphate removal in comparison with chemical precipitation and coupled chemical precipitation and microfiltration. The influence of pressure, initial feed concentration, pH, competing compound, membrane type, operation period on nanofiltration performance was also determined.

The experimental study ranges of pressure, concentration, pH were 400-1000 kPa, 2-10 mg/L P, 4-10 accordingly. DL and DK were the two different membranes (from Desalination Systems Asia), used in the experiments and ammonium sulphate was used as the competing compound.

Results showed that phosphorus removal efficiency for nanofiltration (>95%) is higher than that for conventional methods (<90%). Higher pressure, higher concentration and higher pH showed positive response, while presence of competing compound showed negative response on phosphorus rejection. DK is better than DL in terms of rejection, while DL is better in terms of flux.

Finally, an economic analysis was conducted to compare nanofiltration with conventional processes.
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ABBREVIATIONS

AOC Assimilable organic material
BDOC Biodegradable dissolved organic carbon
BOD Biochemical oxygen demand
DBP Disinfection by product
DK Tight nanofiltration membrane
DL Loose nanofiltration membrane
DOC Dissolved organic carbon
GAC Granular activated carbon
MF Microfiltration
MTC Mass transfer co-efficient
MWCO Molecular weight cut-off
NF Nanofiltration
NOM Natural organic matter
PAC Powdered activated carbon
RO Reverse osmosis
THMFP Trihalomethane formation potential
TOC Total organic carbon
UF Ultrafiltration

SYMBOLS

A Area of membrane
C Concentration
D Diffusivity
Fs Solute flux
Ks Solute mass transfer coefficient
Kw Solvent mass transfer coefficient
m Membrane
n no of moles
P Pressure
Qf Amount of feed
Qp  Amount of permeate
R   Gas constant
T   Absolute temperature
V   Molar volume
Vp  Permeate flux
Xf  Feed concentration
Xp  Permeate concentration
y   co-ion
z   Charge
Δ   Difference
π   Osmotic pressure
CHAPTER I

INTRODUCTION

1.1 General

Phosphorus occurs in natural water and wastewater mainly as inorganic phosphates such as orthophosphates and polyphosphates. Organically bonded phosphate is a minor consideration. Both domestic and industrial activities are the major sources of phosphorus discharge into wastewater. About 30-50% of the phosphorus in domestic wastewater comes from human wastes such as feces, urine and waste food disposal. The remaining 50-70% comes from synthetic detergents, as these contain phosphate builders and are used for cloth-washing. The industrial sources of phosphorus generally originate from potato processing, fertilizer manufacturing, certain metal finishing, flour processing, dairy, commercial laundry and slaughterhouse industry wastes.

The presence of excess phosphorous in the effluent discharged to natural bodies has long been known to be responsible for algal bloom and eutrophication of lakes, ponds etc. Phosphorus can also interfere with coagulation and with lime soda softening. Because of these harmful effects, effluent discharge standards to natural bodies are continuously upgraded. The removal of phosphorus is therefore necessary not only to prevent eutrophication but also to maintain the required water quality.

There are two conventional methods for phosphate removal from wastewater. One is the physico-chemical or chemical precipitation method and the other is biological process. Both processes have certain disadvantages. In chemical precipitation, higher chemical, operation & maintenance cost and problems associated with their dealings, the disposal of the large amount of sludge produced are the main disadvantages. The biological process requires highly efficient secondary clarifier and maintenance of BOD : TP ratio (at least 20:1), large area requirements are the disadvantages. The common and important limitation of these two processes is that neither of them can produce an effluent containing less than 0.5 mg/L P.

Membrane processes, on the other hand, can provide higher removal efficiency with better
water quality and little or no sludge production. Nanofiltration is a newly developed membrane process which can remove macromolecules, di- and multivalent ions more effectively and economically. More than 95% rejection of divalent ions like SO$_4^{2-}$, Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$ by nanofiltration has been reported (ERIKSSON, 1988a; TAN et al. 1991; HOFMAN et al. 1993). However, no extensive research has been done particularly on phosphate removal by nanofiltration. Since phosphate is a trivalent ion, its effective and economic removal by nanofiltration can be expected.

1.2 Objectives of Study

This research work was carried out with the following objectives:

1) to investigate the capability of nanofiltration membrane for phosphate removal from wastewater and compare it with that of chemical precipitation and combined chemical precipitation with microfiltration.

2) to investigate the influence of different operating parameters such as membrane type, initial feed concentration, applied pressure, competing compounds, feed pH, operating period on nanofilter membrane performance.

1.3 Scope of Study

This research was mainly an experimental work. The boundary of this research was as follows:

1) A lab-scale experimental set-up was installed with nanofiltration plate and frame module in batch mode.

2) Synthetically-prepared wastewater containing phosphate (Na$_3$PO$_4$.12H$_2$O) was used in all experimental runs.

3) Membrane process performance was evaluated by measuring filtration flux and percentage rejection of phosphorus.

4) For chemical precipitation experiments, alum was used as the coagulant and the microfiltration experimental runs were conducted using 0.05 and 0.2 µm membrane.

5) Ammonium sulphate was used as the competing compound.
CHAPTER II

LITERATURE REVIEW

2.1 Membrane Filtration Processes

2.1.1 Introduction

At present all industries are focusing their attention on wastes from different angles and looking for different options in order to meet the environmental regulations. The four available options are end of pipe solution, water management, waste management and zero discharge (Fig.2.1.1).

Fig.2.1.1 Different options of industrial processes

(CHILEKAR, 1993)

The most costly option is the end of pipe solution, which needs crude separation of impurities from water. To improve the economics, water management or waste management option has to be considered. Waste management requires selective separation of solids and provides some economic benefit by recovering reusable solids while water management is possible by nonselective separation, and it provides recovery of good quality water for reuse. Zero discharge can be termed as the golden option. It considers both product recovery and water recycling, which can be achieved by complete separation of solids from water. So the recovery and reuse of valuable by-products and process water has become the new trend for all industrial processes for reducing the production cost as well as the pollution load.

The advent of membrane processes has created a new dimension in separation and purification techniques for both solid-liquid and gas-gas system. They play a significant role in water and wastewater treatment. The main difference between conventional processes (chemical precipitation and biological oxidation) and membrane separation is that membrane separates impurities from water without destruction of either of the components. In addition, there are other major advantages: low energy consumption, small land area requirement, easy up-grading of existing facilities, continuous separation, better effluent quality, avoidance of any chemical addition. So membrane technique is the preferred choice to achieve the golden option.
Due to the increasing need for waste minimization through recycling, reuse and recovery and for highly pure effluent, a number of membrane processes has been developed. Separation and purification is accomplished by using different driving forces, namely pressure, concentration, electric potential, temperature and partial pressure (Table 2.1.1).

### Table 2.1.1 General Information about Different Membrane Processes

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### 2.2 Nanofiltration (NF)  
#### 2.2.1 Introduction

Nanofiltration (NF) is a recent development in membrane technology. It is a pressure-driven process falling in between Reverse Osmosis (RO) and Ultrafiltration (UF) (ERIKSSON, 1988a). RO has lower flux at higher operating pressure and is used for demineralization or total
dissolved solid removal, while UF can provide higher flux at lower operating pressure and can remove macromolecules (humic acid, fulvic acid etc.). However, it can not remove salts, acids, sugars etc. On the other hand, the NF process combines the attributes of RO and UF with the ability to reject macromolecules and multivalent ions effectively at moderate operating pressure (138-827 kPa) (AMY et al. 1990). Effective removal of salts, Trihalomethane formation potential (THMFP), heavy metals, colour, all viruses, bacteria and parasites from water and wastewater is possible by NF (CLUFF, 1992). Thus NF can play a significant role as an advanced treatment of water and wastewater.

2.2.2 History

In the 1970's, Israel Desalination Engineering coined the word "Hybrid Filtration" for a process which operates between RO and UF pressure ranges. This process showed sodium chloride rejection in the range of 50-70% and organics in the range of 90%. The main disadvantage with the name Hybrid Filtration is that it does not in itself describe clearly what type of filtration it is. It might as well be something between media filtration and cartridge filtration.

In the early 1980s, FilmTech developed a new type of membrane. At permeate flux of about 34 L/m².h, this membrane showed a solute rejection of about 10% for high strength sodium chloride solution and about 99% for sucrose solution. It did not seem right to call it a RO membrane because of its low rejection of sodium chloride, or to call it an UF membrane because of its almost complete rejection of sucrose.

Again, there is no universally accepted definition of RO and UF membrane, which would force this new membrane into one of these categories. It is widely accepted that solvent and solute transport through a RO membrane is by diffusion and through an UF membrane is by convection flow through pores. Then the new membrane should probably be a RO membrane. But to distinguish it from RO membrane with high rejection of sodium chloride, FilmTech coined the term nanofiltration (NF) membrane. In fact the name NF is derived in way analogous to microfiltration (MF). When more than 95% of solute of minimum size in the order of 1 nm can be removed by a membrane, it is MF; that in the order of 1 nm can be removed by a membrane it is NF (ERIKSSON, 1988b). NF membrane process is commercially available since 1986 (CLUFF, 1992).

2.2.3 Operating Range

Figure 2.2.1 recapitulates the NF separation range in comparison to other membrane processes.
Fig. 2.2.1 Separation Range of NF membrane  
(RAMAN et al. 1994)

The operating pressure of NF membrane is 138-827 kPa (TAN & AMY, 1991). However, some NF membrane can be operated up to 4000 kPa, depending on the nature of feed solution and the rejection requirements.

2.2.4 Membrane Properties

2.2.4.1 Membranes and Modules

The material used for NF membrane fabrication is organic in nature and most NF membranes are multiple layer thin-film composites of organic polymer. The active membrane layer usually consists of negatively charged chemical groups. The membranes are believed to be porous, with an average pore diameter of 2nm (RAMAN et al. 1994).

The modules used for NF are flat sheets (plate and frame type), hollow fibre and spiral wound. Hollow fibre and spiral wound type are suitable for pilot and industrial scale, while flat sheet type is used for laboratory scale operation. Flux in spiral wound is higher than that of hollow fibre, but the major advantage of hollow fibre module is that its removal efficiency is higher so less pretreatment of feed water is required (LAINE et al. 1987).

2.2.4.2 Membrane Characterization

Since pore size of NF membrane is very small, like RO, NF membranes are sometimes characterized by molecular weight cut-off (MWCO) (the lowest molecular size efficiently rejected by membrane). The MWCO for NF ranges from 100-200 (Fig. 2.2.2).

Fig. 2.2.2 Molecular weight Cut-off Range of Different
NF membranes (RAMAN et al. 1994)

The MWCO for UF is greater than 1000 and that for RO is less than 500 (ERIKSSON, 1988a). In fact, no membrane has a sharp cut-off range. There must be some grey area between RO, NF and UF. The cut-off range for NF may be closer to RO or UF or in between the two, depending on the rejection requirements.

2.2.4.3 Separation Mechanisms

Separation by NF membrane follows two mechanisms, namely:

1) Physical: Due to its very small pore size (in the order of few nm), neutral organic compound with molecular weight above 200 will be rejected by the sieving mechanism.

2) Electrostatic interaction: Since, in general NF membranes are negatively charged, salt rejection occurs by electrostatic repulsion of anions. The higher the charge on the anion, the greater the salt rejection.

2.2.4.4 Higher Flux and Improved Fouling Resistance

Most NF membranes contain negatively charged hydrophilic groups attached to a hydrophobic UF support membrane and they have higher water flux. This is due to the favourable orientation of water dipoles. Again due to the surface active groups, they also have improved fouling resistance against hydrophobic colloids, oils, proteins and other organics (RAMAN et al.1994).

2.2.5 Performance Parameters

Permeate Flux (Vp): This is the flow rate of permeate per unit area of membrane, L/m².h

Percent Rejection: This is the amount of solute or ions rejected by the membrane compared to the amount in the feed. It is given by

\[
\text{Rejection(%) = (1- Xp/Xf)* 100}
\]

where \( X_p \) = concentration in permeate
\( X_f \) = concentration in feed

Recovery (R): This is normally defined as the amount of water that could be recovered in the permeate. It is expressed as:

\[
R = \frac{Q_p}{Q_f}
\]

where \( Q_p \) = amount of permeate
\( Q_f \) = amount of feed

Water Mass Transfer Co-efficient (MTC): This is the amount of permeate per unit
area of membrane per unit transmembrane pressure. It is expressed as

\[ \text{MTC} = \frac{Q_p}{A \cdot P} \]

where \( A \) = area of membrane  
\( P \) = transmembrane pressure

Water flux describes only water production, while water MTC relates water production to energy (BLAU et al. 1992), thus this parameter is used to measure NF production efficiency.

### 2.2.6 Transport Models for NF membranes

Two models can be used to describe the solute fluxes through NF membranes.

I) Donnan Exclusion Model

NF membranes are often negatively charged. When a charged membrane is placed in a salt solution, a dynamic equilibrium occurs. The counter ion (opposite to that of membrane charge) concentration is higher while the co-ion (same sign charge as the fixed membrane charge) concentration is lower in the membrane phase than in the bulk solution, creating a "Donnan potential". This potential prevents the diffusion of the counter ion from the membrane phase to the bulk solution and the diffusion of the co-ion from the bulk solution to the membrane phase. A potential also occurs when an applied pressure gradient forces water flow through the membrane. The effect of "Donnan potential" is to repel the co-ion from the membrane, and because of electroneutrality requirements, the counter ion is also rejected.

For the salt \( \text{Mz}_y\text{Yz}_m \) which ionizes to \( \text{M}^{zn+} \) and \( \text{Y}^{zy-} \), at equilibrium, the salt distribution coefficient \( K^* \) is given by

\[
K^* = \frac{c_{y(m)}}{c_y} \frac{\Xi}{\Xi_m} \frac{c_m}{c_m^*}
\]

where \( z_i \) represents the charge of species \( i \), \( c_y \) and \( c_{y(m)} \) are the concentrations of co-ion \( y \) in the bulk solution and membrane phase, respectively, \( \Xi \) and \( \Xi_m \) are activity coefficients, and \( c_m^* \) is the charge capacity of the membrane.

The rejection is then approximated as \( R^* = 1 - K^* \)
This model predicts that the rejection is a function of the membrane charge capacity, the feed solute concentration, and the charge of the ions. It provides a qualitative description of solute rejection but does not take into account diffusive and convective fluxes which are also important in the charged membrane like NF (BHATTACHARYYA and WILLIAMS, 1992b).

II) Extended Nernst-Planck Model

According to this model, the flux of ions through a charged membrane is given by the equation,

\[
J_j = \frac{D_j(m) z_j \hat{a}_j(m) (c_j(m) - E m \beta)}{F} - \frac{c_j(m) - \frac{E m \beta}{F}}{m}
\]

where \( J_j \), \( c_j(m) \), \( D_j(m) \), \( z_j \), \( \hat{a}_j(m) \) are the flux, concentration, diffusivity, charge and the activity coefficient of ion \( j \) respectively. Here, \( m \) indicates the membrane phase. \( E \) is the Donnan potential and \( F \) is Faraday's constant. In the above equation, the first term represents solute flux due to convection, the second term accounts for flux due to Donnan potential, and the last two terms describe the salt flux due to diffusion. As with the Donnan equilibrium model, this model predicts the solute rejection is a function of feed concentration and charge of the ion. However, the Nernst-Planck equation includes the effects of convective and diffusional fluxes, which can be important for NF membrane (BHATTACHARYYA and WILLIAMS, 1992b).

Solvent flux in NF membrane is sometimes described by a homogeneous solution-diffusion model (BLAU et al., 1992). This model assumes that both the solute and solvent dissolve in the nonporous and homogeneous surface layers of the membrane and then each diffuses across it due to the chemical potential gradient which is the result of both concentration and pressure difference across the membrane. Solubility and diffusivity of solute and solvent in the membrane phase are important in this model.

According to this model solvent flux (\( V_p \)) through the membrane can be given by

\[
V_p = k_w(\bar{\Delta}p - \bar{\Delta}\tilde{o})
\]

where \( k_w = \) solvent mass transfer coefficient across the membrane

\( \bar{\Delta}p = \) pressure difference across the membrane

\( \bar{\Delta}\tilde{o} = \) osmotic pressure difference across the membrane
Again the osmotic pressure difference can be defined as

$$\Delta \pi = (nRT)/V = \Delta CRT$$

Here \(n\) = no of moles of solute

\(V\) = molar volume of water

\(R\) = gas constant = 8.32 J/mol.K

\(T\) = absolute temp., K

\(\Delta C\) = molar concentration of solute

This equation indicates that if \(\Delta C\) increases, \(\Delta \pi\) will increase and solvent flux will decrease.

Solute flux (\(F_s\)) is expressed as

$$F_s = K_s(C_m - C_p)$$

where \(K_s\) = solute mass transfer coefficient

\(C_m\) = solute concentration at the membrane surface

\(C_p\) = solute concentration in permeate

This equation shows that solute flux increases if the solute concentration at the membrane surface increases.

### 2.2.7 Some Commercially Available NF membranes

Due to attractive flux performance and selective separation, research on NF is rapidly increasing. Manufacturers are producing different NF membranes to meet the increasing interest of the researchers on this field. At present many new types of NF membranes are commercially available (Table 2.2.1), although the complete data for all of them is not yet investigated.
Table 2.2.1 Characteristics of some NF membranes
CHAPTER-III

EXPERIMENTAL SET-UP AND METHODOLOGY

3.1 Experimental Set-up

A schematic diagram of the experimental set-up is shown in Fig. 3.1. The main components of the set-up can be separated into the following:

1) Feed Tank
2) Pipe Network
3) Membrane Module
4) Cooling System
5) Pressurized Cylinder

3.1.1 Feed Tank

This was a cylindrical tank made of stainless steel (Fig.3.2). The tank was 80 mm in diameter and 600 mm in height with a capacity of 3L. It had an inlet at the top and outlet at the bottom. It was equipped with a stainless steel coil of 10 mm diameter for the purpose of cooling the feed solution.

3.1.2 Pipe Network

All parts of the piping network were of 6 mm diameter stainless steel. The unit was driven by two different pumps in order to meet the pressure requirements in the system. The IWAKI centrifugal pump with maximum capacity, 11-12 L/min and head 1.5-2.1 m, was used for operating the system up to 500 kPa and the high pressure speed control pump was operated up to 1000 kPa. At the suction end of the pump, the pipe diameter was 13 mm. There were two pressure gauges of 0-1500 kPa range. One was installed at the top of the feed tank for measuring the pressure of the tank as well as the inlet pressure of the membrane and the other was installed for measuring the outlet pressure of the membrane. 6 mm Tee joints, nipples and ball valves had been connected to the piping system for recirculation of the feed solution. Fig.3.3 shows detail of the pipe network.

3.1.3 Membrane Module

A plate and frame type membrane module (Fig.3.4 to 3.7) made of stainless steel was used for this study. The module contained three segments. The middle segment can be fixed tightly with the top and bottom segments using O-ring-type rubber gaskets. In the bottom segment there was a circular stainless steel porous support for flat sheet membrane. At the bottom of this support media
there were few channels through which the permeate can come out. In this module, the inlet was connected at the top, permeate outlet at the bottom and concentrate outlet at the middle segment.

3.1.4 Cooling System

Due to high recirculation maintained in the system, the feed solution temperature was expected to increase. In order to reduce the increased temperature, 10 mm diameter stainless steel cooling coil, equipped with the feed tank was used. The inlet of the coil was connected with tap water line and outlet to the drain. Using this cooling system temperature of the feed solution was maintained in the range of 27-30 °C.

3.1.5 Pressurized Cylinder

Commercially available N₂ cylinder equipped with a pressure regulator was used to maintain high pressure in the system. The purity of nitrogen was 99.5%.

3.2 Experimental Methodology

3.2.1 Preparation of Wastewater

Wastewater was synthetically prepared by dissolving sodium phosphate (Na₃PO₄.12H₂O) in distilled water. This phosphate is a colourless crystalline solid with molecular weight 380. Since phosphate solution could not be stored for a long time, solution of 100 mg/L P was prepared and diluted to required concentrations for each experimental runs. To prepare 100 mg/L P solution, 1226 mg of sodium phosphate was diluted in 1000 mL distilled water.

3.2.2 Dilution of Wastewater

Maximum 3000-4000 mL of synthetic wastewater was required for each experimental run. Table 3.1 shows the detailed dilution procedure to prepare 3000 mL of wastewater of different concentrations.

Table 3.1 Detailed Dilution Procedure

<table>
<thead>
<tr>
<th>Required Conc. (mg/L P)</th>
<th>Amount taken from 100 mg/L P solution, mL</th>
<th>Amount of distilled water added, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>60</td>
<td>2940</td>
</tr>
</tbody>
</table>
3.2.3 Chemical Precipitation Experiments

At this stage, experiments were conducted using alum as the coagulant. Both optimum pH and alum doses were determined in terms of effluent phosphate concentration and phosphate removal efficiency was observed at optimum conditions. Ferric Chloride was also used to compare with alum. The measurement of phosphate concentration was carried out using the Stannous Chloride Method. Table 3.2, shows the detailed schedule.

Table 3.2, Detailed Schedule for Chemical Precipitation runs

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Feed Conc., mg/L P</th>
<th>pH</th>
<th>Coagulant</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>5.5-7.5</td>
<td>Alum</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>opt. pH</td>
<td>Alum</td>
<td>Diff. dose</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>5.5-7.5</td>
<td>Alum</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>Opt. pH</td>
<td>Alum</td>
<td>Diff. dose</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>5.5-7.5</td>
<td>Alum</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>Opt. pH</td>
<td>Alum</td>
<td>Diff. dose</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>5.5-7.5</td>
<td>Alum</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>Opt. pH</td>
<td>Alum</td>
<td>Diff. dose</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>5.5-7.5</td>
<td>Alum</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>Opt. pH</td>
<td>Alum</td>
<td>Diff. dose</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>4-6</td>
<td>FeCl₃</td>
<td>Fixed dose</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>Opt. pH</td>
<td>FeCl₃</td>
<td>Diff. dose</td>
</tr>
</tbody>
</table>
3.2.4 Chemical Precipitation and Microfiltration (MF) Experiments

At this stage of experiment, pretreatment of synthetically prepared wastewater was done by chemical precipitation using optimum doses of alum obtained in the earlier set of experiments, and this was then allowed to pass through a microfilter membrane using the same NF membrane module arrangement presented in Fig. 3.1. Table 3.3, shows the detailed schedule.

Table 3.3, Detailed schedule for coupled chemical precipitation and MF runs

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Conc., mg/L P</th>
<th>Pressure, kPa</th>
<th>Pore size, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>50</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>100</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>150</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>200</td>
<td>0.05</td>
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<td>10</td>
<td>50</td>
<td>0.2</td>
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<tr>
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<td>10</td>
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<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>150</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>200</td>
<td>0.2</td>
</tr>
</tbody>
</table>

3.2.5 Nanofiltration (NF) Experiments

In this set, a series of experiments was done with synthetically-prepared wastewater by changing the operating parameters such as NF membrane type, transmembrane pressure, feed concentration, competing compound and pH and their influence on flux and % phosphorus removal was observed. The details of the experimental schedule has been shown in table 3.4 to 3.6.

Table 3.4, Detailed schedule for NF runs with different pressure and conc.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Conc., mg/L P</th>
<th>Pressure, kPa</th>
<th>NF Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>200</td>
<td>DL</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>300</td>
<td>DL</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>400</td>
<td>DL</td>
</tr>
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<td></td>
<td></td>
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<tr>
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<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>500</td>
<td>DL</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>600</td>
<td>DL</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>700</td>
<td>DL</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>800</td>
<td>DL</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>900</td>
<td>DL</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>1000</td>
<td>DL</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>200</td>
<td>DL</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>300</td>
<td>DL</td>
</tr>
<tr>
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<td>400</td>
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</tr>
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<td>4</td>
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<td>DL</td>
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<td>14</td>
<td>4</td>
<td>600</td>
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</tr>
<tr>
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<td>700</td>
<td>DL</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>800</td>
<td>DL</td>
</tr>
<tr>
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<td>4</td>
<td>900</td>
<td>DL</td>
</tr>
<tr>
<td>18</td>
<td>4</td>
<td>1000</td>
<td>DL</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
<td>200</td>
<td>DL</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>300</td>
<td>DL</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>400</td>
<td>DL</td>
</tr>
<tr>
<td>22</td>
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<td>500</td>
<td>DL</td>
</tr>
<tr>
<td>23</td>
<td>6</td>
<td>600</td>
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</tr>
<tr>
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<td>6</td>
<td>700</td>
<td>DL</td>
</tr>
<tr>
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<td>6</td>
<td>800</td>
<td>DL</td>
</tr>
<tr>
<td>26</td>
<td>6</td>
<td>900</td>
<td>DL</td>
</tr>
<tr>
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<td>6</td>
<td>1000</td>
<td>DL</td>
</tr>
<tr>
<td>28</td>
<td>8</td>
<td>200</td>
<td>DL</td>
</tr>
</tbody>
</table>
The same schedule was followed while considering pressure and concentration as the operating variables using DK membrane.

Table 3.5 Detailed Schedule for NF runs changing pH

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Conc., mg/L P</th>
<th>Pressure, kPa</th>
<th>pH</th>
<th>NF membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>500</td>
<td>4</td>
<td>DL</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>500</td>
<td>5</td>
<td>DL</td>
</tr>
</tbody>
</table>
The same schedule was followed for DK membrane also.

Table 3.6 Detailed Schedule for NF runs with Competing Compound

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Conc., mg/L P</th>
<th>Pressure, kpa</th>
<th>((\text{NH}_4)_2\text{SO}_4) mg/L</th>
<th>NF membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>1000</td>
<td>2</td>
<td>DL</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>1000</td>
<td>6</td>
<td>DL</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1000</td>
<td>10</td>
<td>DL</td>
</tr>
</tbody>
</table>

Experiments with DK membrane were conducted according to similar schedule

### 3.2.6 Cleaning of Membrane

Membrane cleaning is usually essential in order to recover the flux reduced by fouling and reuse the same membrane for different experimental runs. Here membrane fouling was not a major problem mainly due to two reasons. One is that synthetic wastewater contained only distilled water and sodium phosphate and the other reason is that phosphate itself acts as a cleansing agent. Initially only distilled water was used to find the flux for each type of membrane. A very small decrease in distilled water flux was observed after each experimental run (Fig. 3.8).

This flux drop was recovered by cleaning the membrane with distilled water flash only. No chemical cleaning was performed. After every run feed, the feed tank was filled with distilled water and the membrane was cleaned by flushing at higher flow rate (5 L/min). This flushing was done two times after each run. After cleaning distilled water was allowed to pass through the membrane in order to compare with initial distilled water flux. This test indicated whether the membrane had been cleaned properly or not. Table C-28 and C-29 (appendix C) shows the representative result for cleaning the membranes. With two times cleaning after each run, one small piece of membrane sheet was used for five runs. After five runs a small distortion in membrane sheet was observed. This was noticed by the unusual increase in flux.
CHAPTER IV
RESULTS AND DISCUSSION

This chapter presents the results obtained from the laboratory scale experiments for removing phosphate from wastewater by Nanofiltration. The main objective was to study the effectiveness of NF for phosphate removal compared to other conventional methods and the effect of different parameters on NF performance. NF performance was basically measured in terms of permeate flux and % rejection of phosphorus.

4.1 Characteristics of the Wastewater

Synthetic wastewater was used for all experiments. This wastewater was prepared by dissolving Orthophosphate in distilled water. The chemical name of this phosphate is Sodium Phosphate (Na$_3$PO$_4$.12H$_2$O). The wastewater was alkaline in nature, having a pH range of 9-10. It was almost free of colour and turbidity.

Since phosphate solution is very difficult to preserve, fresh solution of 100 mg/L was prepared for all experimental runs and this solution was diluted to required concentrations.

4.2 Chemical Precipitation Experiment

Alum and Ferric Chloride are the most commonly used chemicals for removing phosphorus from wastewater. The literature reports that these chemicals are mainly used in primary and secondary level. Tertiary level chemical precipitation of phosphate is rare. However data reported for secondary level treatment shows that optimum pH for phosphorus removal using alum is in the range of 5.5-6.5 and that by using ferric chloride is in the range of 4.5-5. By stoichiometry the weight ratio of alum to phosphorus is 9.6:1 and ferric chloride to phosphorus is 5.2:1. However, the actual quantities of chemicals required is higher than the stoichiometry due to the competing reactions which vary with the wastewater (BOWKER et al., 1987).

In this experiment, alum was used as coagulant. Results are shown in figure 4.1a and 4.1b (Table A-1 and A-2 in Appendix A). Here the optimum pH was observed as 7. The feed concentrations were 2, 4, 6, 8 and 10 mg/L P and the corresponding alum doses were 10, 20, 50, 60 and 80 mg/L. Ferric chloride was used only with feed concentration of 10 mg/L P in order to compare with alum. The optimum pH and optimum dose for ferric chloride were 5 and 40 mg/L. The removal efficiency for alum was found in the range of 75-80 % and that for ferric chloride was 76 %. Results using ferric chloride are shown in table A-3 and A-4 in appendix A.
Here, the optimum pH was higher than the reported value. This was because of the high alkalinity of the synthetic wastewater (9-10), and as such, the pH depression was not so prominent. The required chemical doses were lower, due to the better quality of synthetic wastewater, which contained almost no suspended solids. The removal efficiency of phosphorus was also lower. The possible reason is that the chemical precipitation experiment with the synthetic wastewater that contained no suspended solids produce dispersed metal phosphate flocs. This dispersed characteristic of flocs significantly decreases the phosphate removal efficiency.

### 4.3 Chemical Precipitation and Microfiltration Experiments

At this stage, chemical precipitation was carried out by using optimum alum dose and optimum pH obtained in the earlier set of experiments (as reported in section 4.2) and then filtration was performed by microfilter membrane. Two different types of microfilter membrane with pore sizes 0.05 µm and 0.2 µm were used here. The operating parameters were pressure and pore size.

#### 4.3.1 Effect of Pressure

In general, pressure has a significant influence on flux and % rejection for microfilter membrane. At lower pressure, flux usually shows linear behaviour, but at higher pressure, it becomes steady state due to internal clogging of pores by higher penetration of particles.

Fig. 4.2a (Table B-1 and B-2 in Appendix B) presents the relationship between flux and pressure. Pressure was varied from 50 to 200 kPa. Crossflow velocity was kept constant at 0.53 m/s. The plot shows that flux variation was linear at pressure below 100 kPa, and thereafter, it becomes steady-state, conforming to the general trend. Phosphorus removal efficiency as a function of pressure has been shown in fig. 4.2b (Table B-3 in Appendix B) which shows that removal efficiency decreases with pressure. This is because at higher pressure, the dispersed alum-phosphate flocs may pass through the membrane pores.

#### 4.3.2 Effect of pore size

Usually, flux increases but removal efficiency decreases with increasing pore size. The reason for this is that more of the flocculated suspension can pass through the larger pore size. Fig. 4.2a and 4.2b also shows the higher flux and lower phosphorus removal for the membrane of the larger pore size. At 200 kPa pressure, the steady state flux for 0.2 µm membrane was 50 L/m².h and that for 0.05 µm membrane was 23.54 L/m².h, while the phosphorus removal was accordingly 81% and 84%.

### 4.4 Nanofiltration (NF) Experiments
In this step flat sheet NF membrane was installed in the membrane module (section 3.1.3 in chapter III) and a series of experimental runs were carried out. Synthetically prepared phosphate solution was used as feed in the feed tank. The operating variables were transmembrane pressure, feed concentration, pH, competing compound and membrane types. Flux and phosphate concentration of permeate were the measuring parameters. All experiments were conducted for four hours to obtain the steady state flux. Due to the very small membrane area, the permeate flow was very low, thus the permeate samples were collected every half an hour interval. Because of the preservation problem, the phosphate concentration of all permeate samples were measured immediately after each experimental run. The results obtained with changing the operating variables (as stated above) can be discussed as follows.

4.4.1 Effect of Transmembrane Pressure

Flux for NF membrane, in general, increases with pressure according to solution-diffusion model equation. The results reported by SCHIRG and WIDMER (1992) (section 2.3.2) also indicate the same behaviour. Rejection by NF membranes increases with pressure, because at high pressure, solvent permeability increases compared to solute (ERIKSSON, 1988a).

The present experiment was conducted by varying pressure from 200 to 1000 kPa. Negligible flux was observed at 200 and 300 kPa, because operating pressure of NF membranes is higher than this. So flux obtained for pressures from 400 to 1000 kPa was used as representative values while plotting the graphs. The observed flux range for DL membrane was 4.33-26.37 L/m².h and that for DK membrane 1.79-12.9 L/m².h. Phosphorus rejection for DL membrane was 94-97% and that for DK membrane 96-99%. Fig.4.3a and 4.3b (Table C-1 to C-10 in Appendix C) present the relationship of flux with pressure for different feed concentrations. The figures show that both the NF membranes provide linear flux increase with pressure which is similar to that reported in literature. It can be noticed from the figure that flux increase rate for DL membrane is higher than that for DK membrane. The possible reason for this is that DL is loose membrane compared to DK (as reported by the supplier). So water permeability through DL membrane will be higher. However, at higher pressure such as 1000 kPa, a minor deviation of flux from linearity was observed. This can be explained by the fact that DL is closer to UF and at higher pressure flux may tend to be decline due to gel layer formation.

Fig.4.3c and 4.3d (Table C-11 to C-20 in Appendix C) presents the effect of pressure on phosphorus rejection. The data obtained for different concentrations were much closer and random. So only the point diagrams have been shown here. It is clear from the figure that phosphorus rejection increases with pressure for both DL and DK. The increased solvent permeability with pressure may be the possible reason of this. Then questions may arise that although the solvent permeability for DL is higher than DK, why is the rejection by DK (95.5-99.2%) is higher than DL (94.3-97.5%). The possible explanation is that rejection by NF is not only determined by solvent
permeability. Charge capacity of membrane is another important factor that plays a significant role in rejection. And here the ultimate rejection may depend on the combination of solvent permeability and membrane charge capacity. DK may have higher charge capacity than DL.

4.4.2 **Effect of Feed Concentration**

Concentration effect on NF flux has not been reported extensively. Only the experimental result reported by SCHIRG and WIDMER (1992) (section 3.2 in chapter III) shows that flux increase with increasing concentration. This is because at higher concentrations, higher Donnan Potential may create and allow more solvent to pass through the membrane. The rejection by NF membranes are expected to decreases with increasing concentration because at higher concentration solute permeability increases (ERIKSSON,1988a).

The present experiment was carried out with the concentration range of 2-10 mg/L P. Fig.4.4a and 4.4b (Table C-1 and C-10 in Appendix C) are plotted to present the effect of feed concentration on flux. The maximum fluxes (26.37 L/m².h for DL and 12.9 for DK) were observed at the lower feed concentration (2 mg/L P) and the minimum fluxes (4.33 L/m².h for DL and 1.79 For DK) were observed at the higher feed concentration (10 mg/L P). These results were not similar to those found in the literature. Here flux decreases with the increase of feed concentration. The possible reason for this is that at higher concentrations, osmotic pressure increases and that may reduce the flux. It can be seen that at lower concentration flux decrease rate is higher than at higher concentrations. The possible reason is that at lower concentration osmotic pressure effect is more predominant while at higher concentration, the Donnan Effect (section 2.2.6) provides some more flux.

Another important feature which can be noticed from the figure is that at higher pressure such as 1000 kPa, flux in DL membrane does not decrease significantly with concentration as compared to DK, while at lower pressure such as 400 kPa, reduction in flux is higher for DL than for DK. Since DL is closer to UF, the higher pressure may force some monovalent ions to pass through the membrane and so osmotic pressure effect may be reduced, while ions can not easily pass through the tighter DK membrane and even at higher pressure osmotic pressure may affect the flux. On the
other hand, at lower pressure not much ions will pass through DL and osmotic pressure may affect the flux. But DK membrane have same osmotic pressure but may have some higher Donnan effect compared to DL. Thus at lower pressure DK may have some higher flux than DL.

Fig.4.4c and 4.4d (Table C-11 to C-20 in Appendix C) present the effect of feed concentration on phosphorus rejection. Phosphate rejection for DK membrane increases a little bit with feed concentration, because at higher concentrations, diffusion of phosphate ion from bulk solution to membrane phase will be strongly prevented by increased Donnan potential. However, for DL membrane no significant effect on phosphorus rejection was observed. The possible reason may be the lower charge capacity of DL membrane compared to DK membrane. Another interesting point which can be noticed is that at higher pressure and higher concentration, both DL and DK gives attractive phosphorus rejection efficiency. The possible explanation is that higher pressure provides higher solvent permeability and higher concentration provide higher rejection by Donnan potential. So the combined effect gives the best phosphorus removal. The Donnan Potential created by DL may be lower than for to DK. However, data obtained with feed concentration 10 mg/L P and operating pressure 1000 kPa were used for most of the plots.

4.4.3 Effect of Operating Time

Usually for NF membranes, flux decreases with time because of the increase in osmotic pressure by increasing concentration at the membrane surface but permeate quality remains the same (TAYLOR et al., 1987).

Here, each experimental run was conducted for four hours, because during this period steady state flux was observed. Fig.4.5a and 4.5b (Table C-9 and C-10 in Appendix C) show the flux variation with time. A very small decrease in initial flux was observed for both the two membranes. Initial decrease in flux may be due to osmotic pressure, but when concentration increases further, Donnan Potential may reduce ion concentration at the membrane surface and thus offset the osmotic pressure effect.

Fig.4.5c and 4.5d (Table C-19 and C-20 in Appendix C) shows the phosphorus rejection for different pressure as a function of time. Initial range of phosphorus rejection was 95.6-97.5 %for DL and 97-99.5 %for DK. After four hours of operation the final ranges were 94.2-97.3% and 96-99.2% accordingly. This minor loss in rejection may be due to the minor decrease in solvent permeability.

4.4.4 Effect of Feed pH

The pH has a significant influence on flux and % rejection for NF membranes. Both flux and percentage rejection increases with pH for ionizable compounds (BHATTACHARYYA and WILLIAMS, 1992).
Experiments with pH variation were accomplished when the NF unit was equipped with the IWAKI pump (section 3.1 in chapter III) for operating up to 600 kPa pressure. Feed concentration was taken as 6 mg/L P and operating pressure was 500 kPa. The pH was varied from 4-10. Fig.4.6a (Table C-21 and C-22 in appendix C) shows the relationship of flux with pH. For DL membrane, a minor increase in flux occurs at pH 7, while for DK membrane no significant change was noticed. The possible explanation is that with the increase of pH, ionization of phosphate salt increases (as shown in the ionization reaction below) and produces more monovalent sodium ions which may easily pass through DL membrane.

\[
\begin{align*}
\text{Na}_3\text{PO}_4 & \rightarrow \text{Na}^+ + \text{Na}_2\text{PO}_4^-, \text{pH}=2 \\
\text{Na}_2\text{PO}_4^- & \rightarrow \text{Na}^+ + \text{NaPO}_4^{2-}, \text{pH}=7 \\
\text{NaPO}_4^{2-} & \rightarrow \text{Na}^+ + \text{PO}_4^{3-}, \text{pH}>7
\end{align*}
\]

So an improvement of flux in DL membrane occurs by lowering the osmotic pressure. But a further increase in pH produces more ions, which may adsorb the membrane surface and reduce path available for solvent transport and as such flux again decreases. On the other hand, ions can not easily pass through the tighter DK membrane and a balance between osmotic pressure and Donnan effect keeps the flux unchanged.

Fig.4.6b (Table C-25 in Appendix C) presents the effect of phosphorus rejection with pH. Rejection was observed to increase with pH. The possible reason is that at higher pH more trivalent phosphate ions will form and they will be easily repelled by the charged membrane.

4.4.5 Effect of Competing Compounds

The effect of competing compound on flux for NF membrane has not been reported in any literature. But percentage rejection significantly decreases with the increase of competing compound concentration because more ions will pass through the membrane in order to maintain electroneutrality on both sides of the membrane (Donnan effect) (RAUTENBACH and GROSCHL, 1992).

In this experiment, Ammonium Sulphate ((NH₄)₂SO₄) was used as a competing compound, because at tertiary levels of treatment ammonium compound may be present in wastewater. Concentration of competing compound was varied from 2-10 mg/L as SO₄. Phosphate concentration was kept constant at 10 mg/L P. Operating pressure was 1000 kPa. Here flux was observed to decrease with the increase of ammonium sulphate concentration. The possible reason is that osmotic pressure increases with the increase of ammonium sulphate concentration and so flux decreases. Phosphorus rejection also decreases with the increase of competing compound concentration. The possible explanation is that more positive ions are available to shield the charge of the membrane (as
shown below) and so repulsion of phosphate ion by membrane will decrease.

Another reason may be the electroneutrality requirements on both sides of the membrane. Because positive monovalent sodium and ammonium ion can easily pass through the membrane and so negative phosphate ions are then forced to pass through the membrane to maintain electroneutrality. The third reason may be the decrease in solvent permeability with the increase in osmotic pressure affect the % phosphorus rejection. Fig.4.7a and 4.7b (Table C-23, C-24 and C-26 in Appendix C) present the effect of competing compound on flux and % phosphorus rejection.

4.4.6 Effect of Membrane Types

Membrane type has a significant effect on flux and rejection. Two different NF membranes (DL and DK) were used here. Fig.4.8a compares the two membranes in terms of flux and percentage rejection with pressure. Feed concentration was taken as 10 mg/L P. The figure shows that DL gives higher flux and lower rejection compared to DK. The possible explanation is that DL is loose membrane and closer to UF, while DK is a tight membrane. DK may have higher charge capacity than DL. So solvent transport through DL was easier compared to DK, while repulsion of trivalent phosphate ion by DK was higher than DL.

Fig.4.8b compares DL and DK in terms of flux and percentage rejection with concentration. Here the operating pressure was 1000 kPa. It can be noticed that flux decreases with feed concentration for both the two membranes due to higher osmotic pressure. But DK gives higher rejection at higher concentration while for DL membrane no effect was found. The possible reason is the higher charge capacity and higher Donnan Potential for DK compared to DL.

Fig.4.8c compares two membranes with flux vs time and rejection vs time plot. Both the parameters decrease minutely with time for the two membranes. This was basically due to decrease in salt permeability and increase in osmotic pressure.

Fig.4.6a and 4.6b compares the two membranes in terms of flux and rejection vs feed pH. For DL flux was maximum (14.60 L/m².h) at feed pH 7. For DK membrane no significant change in flux was observed. Phosphorus rejection was found to increase with pH for both the two membranes. The possible explanation has been given in section 4.4.4.

Fig.4.7a and 4.7b shows the effect of competing compound on the performance of two membranes. Flux and phosphorus rejection decreases with the increase in competing compound concentration for both the two membranes. The possible explanation has been given in section 4.4.5.
4.5 **Comparison Among Three Different Processes**

Fig. 4.9 (Table C-27 in Appendix C) shows the comparison among three different processes in terms of phosphate removal. Phosphorus removal using chemical precipitation was in the range of 75-78%. Using chemical precipitation as pretreatment and filtering with a 0.2 µm microfilter membrane gives the removal efficiency in the range of 78-80% while for 0.05 µm membrane phosphorus removal was in the range of 83-85%. The lower removal of chemical precipitation is due the dispersion characteristics of flocs. Smaller pore sized (0.05 µm) microfilter membrane could significantly separates these dispersed flocks. On the other hand NF membranes provide phosphorus rejection above 95%. The rejection by DK membrane was up to 99%.

Table 4.3.1 (detail calculations are in appendix D) presents the cost comparison among three different processes.

<table>
<thead>
<tr>
<th>COST ITEMS</th>
<th>Chemical Precipitation</th>
<th>Chemical Precipitation &amp; Microfiltration</th>
<th>Nanofiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost (includes equipment, land, utilities, auxiliary facilities etc)</td>
<td>52.5 mB</td>
<td>34.9 mB</td>
<td>31 mB</td>
</tr>
<tr>
<td>Annual operating Cost (includes O &amp; M cost, labour, energy, chemical etc)</td>
<td>3.2 mB</td>
<td>21.2 mB</td>
<td>19.7 mB</td>
</tr>
<tr>
<td>Capital Recovery Cost</td>
<td>5.3 mB</td>
<td>3.53 mB</td>
<td>5.25 mB</td>
</tr>
<tr>
<td>Total Cost</td>
<td>61 mB</td>
<td>59.7 mB</td>
<td>55.95 mB</td>
</tr>
<tr>
<td>Advantages</td>
<td>low operating cost</td>
<td>low capital cost</td>
<td>lower capital cost, no chemical addition, no sludge production, better permeate quality</td>
</tr>
</tbody>
</table>
Disadvantages | higher capital cost, low permeate quality, chemical addition, higher amount of sludge production | higher operating cost, low permeate quality, chemical addition, higher amount of sludge production | new technique, enough information is not available for its real world application

mB=million baht

This comparison shows that the choice of nanofiltration is better from economic point of view also. Although the operating cost for nanofiltration is higher than chemical precipitation technique, the capital cost is quite low mainly because of small land area and less auxiliary facilities requirement. It does not require any chemical addition and here no sludge is produced. Only the liquid containing high phosphate, will be produced as concentrate which can directly be used as fertilizer for agricultural purpose.

4.6 Results of a Typical Long-Run Experiment

This particular experiment was carried out to investigate the maximum concentration of phosphorus that can be achieved in the concentrate, amount of permeate that can be recovered and the flux behaviour of NF membrane while operating for a long period.

Here DL membrane was used. 3 L of feed containing 10 mg/L P was taken in the feed tank and the experiment was continued for 49 hours with the transmembrane pressure of 1000 kPa. The total amount of permeate recovered in this long run was 2552.5 mL and the concentrate remaining was 447.5 mL. The concentration of the concentrate was observed as 65 mg/L P. The following table presents the mass balance of feed, concentrate and permeate.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Permeate</th>
<th>Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount(mL)</td>
<td>3000</td>
<td>2552.5</td>
</tr>
<tr>
<td>Conc.(mg/L P)</td>
<td>10</td>
<td>0.12-0.5</td>
</tr>
</tbody>
</table>

Fig.4.10 (Table C-30 in Appendix C) shows the effect of time on flux and % rejection. No significant flux decrease was observed even after long period of operation. Initial flux was 25.4 L/m²·h and the final flux was 24.5 L/m²·h. The percentage rejection of phosphorus was in the range of 95-98. This result again confirms the small osmotic effect at the beginning and predomination of Donnan effect over osmotic effect finally. A small decrease in phosphorus rejection may be due to the shielding effect of positive ions on negative membrane surface that allows the negative phosphate ions to pass through the membrane.
4.7 **Numerical Equation Relating Flux and Osmotic pressure**

The osmotic pressure effect on flux is usually expressed as

\[ V_p = k_w (\Delta P - \Delta \pi) \]

Here \( \Delta \pi \) is the osmotic pressure difference which can be defined as

\[ \Delta \pi = \Delta CRT \]

where \( R = \text{gas const.} = 8.32 \text{ J/mol.K} \)

\( T = \text{absolute temperature} \)

\( \Delta C = \text{molar concentration of feed} \)

\( k_w = \text{mass transfer coefficient} \)

\( k_w \) depends on feed water quality parameters like temperature, pH, ionic strength etc. and it may also change with membrane structure.

The plot of \( V_p \) vs \( (\Delta P - \Delta \pi) \) gives a straight line, the slop of which is \( k_w \). Based on this concept regression analysis of the experimental results leads to the following numerical equations (Table 4.6.1) which relate the osmotic pressure and permeate flux for both DL and DK membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL</td>
<td>( V_p = 0.033(\Delta P - \Delta \pi) - 8.17 )</td>
</tr>
<tr>
<td>DK</td>
<td>( V_p = 0.0164(\Delta P - \Delta \pi) - 5.097 )</td>
</tr>
</tbody>
</table>

*Note: \( V_p = \text{L/m}^2\text{h}, \Delta P, \Delta \pi = \text{kPa} \)*

If the feed concentration and pressure are known, above equations can directly be used to estimate the permeate flux. Detail of the regression analysis has been shown in Appendix D.

The above equations clearly show that flux in NF cannot completely satisfy osmotic effect equation. The remaining constants in each equations indicate that there must be some other parameters like membrane charge, Donnan potential which are also related to NF flux.

The validity of above equations can be checked by comparing some experimental results with that obtained using the equations (Table 5.6.2).

*Table 5.6.2 Comparison of experimental flux and that obtained from numerical equation*
<table>
<thead>
<tr>
<th>Membrane</th>
<th>Press., kPa</th>
<th>Conc., mg/L P</th>
<th>Flux, L/m²h</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL</td>
<td>900</td>
<td>10</td>
<td>21.66</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>4</td>
<td>18.17</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>6</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>8</td>
<td>5.24</td>
</tr>
<tr>
<td>DK</td>
<td>900</td>
<td>10</td>
<td>9.65</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>8</td>
<td>8.01</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>8</td>
<td>4.73</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>10</td>
<td>1.79</td>
</tr>
</tbody>
</table>

In addition, the plot of predicted and experimental flux for both DL and DK membrane can be presented in fig.4.11.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The experimental investigations conducted to remove phosphate from synthetic wastewater using both conventional and advanced techniques provide the following conclusions

1) Alum and ferric chloride have almost similar performance in removing phosphate by chemical precipitation. Removal efficiency is less than 80% because of the dispersed characteristic of flocs.

2) Coupled chemical precipitation and microfiltration has better removal performance compared to chemical precipitation. With increasing membrane pore size, the flux increases and phosphate removal decreases.

3) NF has excellent phosphate removal efficiency compared to chemical precipitation and coupled chemical precipitation and microfiltration.

4) Flux for NF membrane linearly increases with pressure according to solution-diffusion model. Rejection of phosphorus also increases with pressure due to increasing solvent permeability compared to solute.

5) Minor flux reduction with time is due to the small increase in osmotic pressure, and operation period has also a small effect on phosphorus rejection.

6) Flux decreases with feed concentration due to osmotic pressure effect. But NF with higher charge capacity can reduce osmotic pressure effect by creating Donnan Potential. At higher concentration Donnan Effect contributes in increasing rejection.

7) Flux with less charged NF membrane is affected by feed pH, while membrane with higher charge capacity is not much affected.

8) Presence of competing compound reduces both flux and rejection.

Finally it can be concluded that the application of nanofiltration in tertiary phosphorus removal may be a better alternative to conventional processes.
5.2 Recommendation for future work

1) Testing of new membranes

In the present study only two types of NF membranes were tested to see the effectiveness of phosphate removal.

More different types of membrane are required to check the potentiality of phosphate removal.

2) Testing of different modules

In the laboratory scale study only a small sized flat-sheet module was used. Other modules such as spiral wound and tubular should be tested in order to operate such a unit in pilot scale or industrial scale.

3) Testing NF with actual wastewater

Presence of suspended solids, different salts and other impurities is very common in secondary treated wastewater. These impurities may affect NF performance. Examining NF with the actual secondary treated wastewater will give more reliable data that can be used for real world application.

4) NF as a hybrid process

The increasing nitrate concentration in wellwater is one of the major problem that is faced by some municipal water supply department. RO can concentrate nitrate together with other solutes and discharge of this concentrate is another problem. Ion-exchange can take up di- and multivalent ions but frequent regeneration of resin is a major problem. A combination of NF and ion-exchange may be the best alternative. Because NF can easily reject di-and multivalent ions, then ion-exchange can take up monovalent nitrate ions from NF permeate and finally ion-exchange permeate can be combined with NF concentrate to maintain the mineral content of potable water. So the hybridge process of NF and ion-exchange for nitrate removal can be the further step study in the field of nanofiltration.

5) NF as a colour removal technique

Ozonation is the conventional colour removal technique which transforms colour causing matter that may still function as a disinfection by-product precursor. The formation of ozonation by-
product is another problem in this method.

On the other hand NF removes colour by physical removal of colour bodies. The use of NF as a competitive colour removal technique can be an interesting research focus.

6) **NF as pesticides removal technique**

Powered activated carbon (PAC) or granular activated carbon (GAC) filtration is the conventional technique for non-polar pesticides removal. Oxidation with ozone or ozone in combination with hydrogen per oxide can be used for both polar and non-polar pesticides removal. But in oxidation method natural organic matter is also oxidised that causes large increase in assimilative organic matter. Besides, bromate or brominated organic compound is produced as by-products for bromide containing water.

On the other hand NF can reject high molecular weight pesticides and avoids the by-product formation. So future NF research may be carried out to observe its potentiality for effective and economic pesticides removal.
REFERENCES


FANE, A.G. and HLAVACEK, M. (1993), Membrane application for environmental problems, UNESCO centre for Membrane Science and Technology, School of Chemical Engineering and Industrial chemistry, University of New South Wales, PO Box 1, Kensington 2033, Australia.


Calculation of Osmotic Pressure:

Osmotic Pressure, $\Delta \pi = \Delta CRT$

Here $R=8.32 \text{ J/mol.K}$
$T=303 \text{ kPa}$

Let us take $\Delta C=2 \text{ mg/L P}$

So, $\Delta \pi = (2 \text{ mg/L})(8.32 \text{ J/mol.K})(303 \text{ K})(\text{N-m/J})(\text{mol/31 g P})(10^3 \text{ L/1 m}^3)(1 \text{ g/10}^3 \text{ mg})$
$=162.64 \text{ N/m}^2$
$=0.1626 \text{ kPa}$

Similarly the osmotic pressure for other feed concentrations can be calculated and tabulated as follows

<table>
<thead>
<tr>
<th>Feed Conc., mg/L P</th>
<th>Osmotic Pressure, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1626</td>
</tr>
<tr>
<td>4</td>
<td>0.3253</td>
</tr>
<tr>
<td>6</td>
<td>0.4879</td>
</tr>
<tr>
<td>8</td>
<td>0.6506</td>
</tr>
<tr>
<td>10</td>
<td>0.8132</td>
</tr>
</tbody>
</table>
Table C-30 Effect of Time on Flux and % Rejection during Long Run
Feed Conc.=10 mg/L P, Press.=1000 kPa, Membrane DL

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Flux, L/m²h</th>
<th>% Rejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>25.4</td>
<td>98.7</td>
</tr>
<tr>
<td>1.0</td>
<td>24.01</td>
<td>98.6</td>
</tr>
<tr>
<td>1.5</td>
<td>24.3</td>
<td>98.6</td>
</tr>
<tr>
<td>2.0</td>
<td>24.3</td>
<td>98.2</td>
</tr>
<tr>
<td>2.5</td>
<td>24.5</td>
<td>98.5</td>
</tr>
<tr>
<td>3.0</td>
<td>24.5</td>
<td>98.2</td>
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<td>3.5</td>
<td>24.5</td>
<td>97.9</td>
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<td>97.4</td>
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<td>24.8</td>
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<td>25.0</td>
<td>24.5</td>
<td>96.8</td>
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<td>28.0</td>
<td>25.1</td>
<td>96.5</td>
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<td>30.5</td>
<td>24.8</td>
<td>96.7</td>
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<tr>
<td>33.0</td>
<td>25.2</td>
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<td>95.7</td>
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