

POTENTIAL OF NANOFILTRATION FOR PHOSPHATE REMOVAL FROM WASTEWATER

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ABSTRACT

Experimental investigations were conducted to evaluate the performance of nanofiltration for tertiary level phosphate removal from wastewater. A flat sheet type Desal-5 thin film nanofiltration membrane in a plate and frame module, was used. The influence of pressure, initial feed concentration, competing compounds, on nanofiltration performance were determined. The experimental study range of pressure and concentration were 400-1000 kPa and 2-10 mg l⁻¹ P respectively and ammonium sulphate was used as the competing compound. Results showed that phosphorus removal efficiency for nanofiltration is high (>95%) and it can produce an effluent containing less than 0.1 mg l⁻¹ P as a tertiary level treatment. Higher pressure and concentration showed positive response, while presence of competing compound showed negative response on phosphorus rejection. A numerical equation relating osmotic pressure and permeate flux has also been developed based on the experimental results.

Keywords: nanofiltration, permeate flux, Donnan effect, osmotic effect, phosphorus.

INTRODUCTION

Phosphorus occurs in natural water and wastewater mainly as inorganic phosphates such as orthophosphates and polyphosphates. 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 faeces, urine and waste food disposal. The remaining 50-70% comes from synthetic detergents, as these contain phosphate builders that 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 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. Although the presence of nitrogen is also important, phosphorus is considered to be the limiting nutrient. Because the average molar ratio of nitrogen, phosphorus and carbon in algal protoplasm is approximately 15:1:105, if any of this component is less than this ratio, it will limit the algal growth. So from the ratio it can be seen that very small amount of phosphorus can cause algal growth and its removal is more essential compared to nitrogen to prevent eutrophication. Further, some blue-green algae have the capability of fixing nitrogen from atmosphere so that phosphorus becomes the

limiting nutrient in their life cycle. Phosphorus can also interfere with coagulation and with lime soda softening. Because of these harmful effects, effluent discharge standards of phosphorus to natural bodies are continuously upgraded. The removal of phosphorus is therefore necessary not only to prevent eutrophication but also to maintain the required effluent quality.

There are two conventional methods for phosphate removal from wastewater. One is the chemical precipitation method and the other is biological process. Both processes have certain disadvantages. In chemical precipitation, higher chemical, operation and maintenance cost and problems associated with handling and disposal of the large amount of sludge produced are the main disadvantages. While biological process requires highly efficient secondary clarifier and maintenance of BOD : TP ratio (at least 20:1). 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⁻¹ P [1].

At present, membrane processes are becoming more popular than conventional processes because membrane separates impurities from water without destructing either of the components. Moreover, small land area requirement, easy up-grading of existing facilities, continuous separation, better effluent quality, little or no sludge production and avoidance of any chemical addition are the major advantages. Nanofiltration (NF) is a recent development in membrane

technology, which is a pressure driven process in between Reverse Osmosis (RO) and Ultrafiltration (UF) [2]. RO produces lower flux at higher operating pressure and reject both salts and sugars, while UF has higher flux at lower operating pressure but allows both salts and sugars to pass. NF can provide higher flux at lower pressure than RO, retains sugars and multivalent salts but allows to pass monovalent salts. Ions containing higher charge density are effectively rejected by NF. More than 95% rejection of divalent ions like SO_4^{2-} , Ba^{2+} , Ca^{2+} , Mg^{2+} by nanofiltration has been reported [2,3]. However, no extensive research has been done particularly on phosphate removal potential by nanofiltration. Since phosphate is a trivalent ion, its effective and economic removal by nanofiltration can be expected. Thus the objective of this paper is to investigate potential of NF system for phosphate removal.

Theory of NF

NF membranes are usually multiple layered thin-film composites of polymers, with pore size in the order of 1 nm and the molecular weight cutoff ranges from 100-200 Dalton. These membranes are usually negatively charged and electrostatic interaction between ions and membranes play significant role in salt rejection. For solution containing different ions, an unequal distribution of ions results across the membrane based on the charge density of the ions and transport rate changes as the ion concentration changes, which is known as "Donnan Effect". Rejection of neutral species by NF follows sieving mechanism.

Different mechanism/models have been proposed to describe the mass transport through NF membrane. Homogeneous solution-diffusion model is often used to explain the mass transport through NF membrane [4,5]. This model assumes that both the solute and solvent dissolve in the nonporous and homogeneous surface layer 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 [6]. The equations associated with this model are as follows.

$$F_w = k_w (\Delta p - \Delta \pi) \quad (i)$$

where

F_w = solvent flux

k_w = solvent mass transfer coefficient

Δp = pressure difference across the membrane

$\Delta \pi$ = osmotic pressure difference across the membrane

$$= \frac{nRT}{V} = \Delta CRT$$

Here n = no of moles of solute

V = molar volume of solvent

R = Universal gas constant = $8.32 \text{ J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$

T = absolute temperature $^\circ\text{K}$

C = molar concentration of solute

Again,

$$F_s = K_s (C_m - C_p) \quad (ii)$$

where

F_s = solute flux

K_s = solute mass transfer coefficient

C_m = solute concentration at the membrane surface

C_p = solute concentration in permeate

[7] have reported that both osmotic and hydrostatic forces contribute to the mass transport through the NF membrane and flux results from the combination of convection and diffusion flux. Thus, the following equations describe the NF fluxes :

$$F_w = K_w (\Delta p - \sigma (\Delta \pi)) \quad (iii)$$

and,

$$F_s = K_s + (1 - (\sigma \Delta \pi)) F_w C \quad (iv)$$

Here ' σ ' is the reflection coefficient which is related to the fraction of molecules reflected back and responsible for the development of osmotic force. The value of σ varies from 0 to 1. At high pressure, σ is close to 1, then the flux is diffusive and correspond to RO membrane, while at low pressure, σ is close to 0, then the flux is convective and correspond to UF membrane. For NF membrane, σ is in between 0 and 1, indicating that flux is neither only diffusive nor convective.

MATERIALS AND METHODS

Description of experimental set-up

The research was carried out with a laboratory scale NF unit. The schematic diagram of the unit is shown in Figure 1. The main components are: feed tank, pipe network, membrane module, pressurized cylinder and permeate collection unit. Here 3L cylindrical stainless steel tank was used as feed tank. It was equipped with a stainless steel coil of 10 mm diameter for the purpose of cooling the feed solution because the temperature of the solution was expected to increase due to high recirculation maintained in the system. 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 $^\circ\text{C}$. A plate and frame type membrane ($1.452 \times 10^{-3} \text{ m}^2$) module made of stainless steel was used for this study.

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

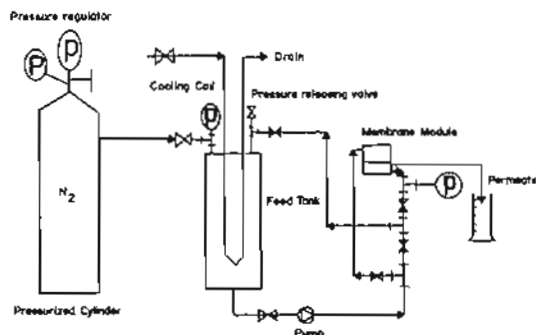


Figure 1. Schematic Diagram of Experimental Setup.

IWAKI centrifugal pump with maximum capacity, 11-12 Lmin⁻¹ was used for operating the system up to 500 kPa and a high pressure MOYNO pump with speed controller was used to operate up to 1000 kPa. A pressure gauge of 0-1500 kPa range 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 another was installed for measuring the outlet pressure of the membrane.

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

Flat sheet type Desal-5 (Desalination Systems, Asia) thin film nanofiltration membrane, named DK was used in the experiments. It is characterized by an approximate molecular weight cut-off of 150-300 Daltons. According to the manufacturer's specification, DK is a tight membrane, close to RO.

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 containing only distilled water and sodium phosphate was used and the other reason is that phosphate itself acts as a cleansing agent. Initial flux was measured using distilled water, and a very small decrease in water flux was observed after each experimental run.

This flux drop was recovered by cleaning the membrane only with distilled water. After every run the feed tank was filled with distilled water and the membrane was cleaned by flushing at higher flow rate (5 Lmin⁻¹). This flushing was done two times after each run. After cleaning, fresh distilled water was allowed to pass through the membrane in order to compare with initial distilled water flux. Table 1 shows the representative result for the membrane cleaning procedure.

Wastewater was synthetically prepared by dissolving sodium phosphate (Na₃PO₄·12H₂O) in distilled water. The phosphate is a colorless crystalline solid with molecular weight 380 Dalton. Since phosphate solution could not be stored for a long time, solution of 100 mg l⁻¹ P was prepared and diluted to required concentrations for each experimental run.

Membrane performance was basically measured in

Table 1 Filtration Flux at different Membrane Cleaning Stages (at 500 kPa).

Stage	Distilled Water Flux, Lm ⁻² h ⁻¹
Initial	6.00
After one run	5.37
After first cleaning	5.65
After second cleaning	5.90

terms of permeate flux and percentage rejection of phosphorus. These two parameters can be defined as

$$\text{Flux} = (\text{amount of permeate}) / (\text{time}) \times (\text{area of membrane})$$

$$\text{Rejection} = (\text{feed concentration} - \text{permeate concentration}) / (\text{feed concentration})$$

RESULTS AND DISCUSSION

All experiments were conducted for four hours to obtain the steady state flux. The results obtained with various operating variables like transmembrane pressure, feed concentration and competing compound are discussed as follows.

Effect of Transmembrane Pressure

[5] have observed that flux for NF70 membrane increases with pressure according to solution-diffusion model equation. But [7] have reported that nanofiltration can not be described by classical solution diffusion model. Rather it follows a mixed convection/diffusion mass transport mechanism. Rejection by NF membranes increases with pressure, because at high pressure, solvent permeability increases compared to solute [2].

The present experiment was conducted by varying pressure from 400 to 1000 kPa. The observed flux range was 1.79-12.9 Lm⁻²h⁻¹ and phosphorus rejection was 96-99%. The phosphorus concentration in the permeate was in the range of 0.04-0.4 mg l⁻¹. For the feed concentration of 2 and 8 mg l⁻¹ as the representative result, the relationship of flux with pressure is presented in Figure 2. It shows that the NF membrane provides linear flux increase with pressure. A correlation between solvent flux and pressure has been developed using the average mass transfer co-efficient calculated from the experimental results and can be represented as follows:

$$F_w = 8.85 \times 10^{-3} (\Delta p - \Delta \pi)$$

where,

$$F_w = \text{Lm}^{-2} \text{h}^{-1}, \Delta p, \Delta \pi = \text{kPa}$$

The flux calculated from the above equation and that observed experimentally for various experimental runs can be compared as shown in Figure 3.

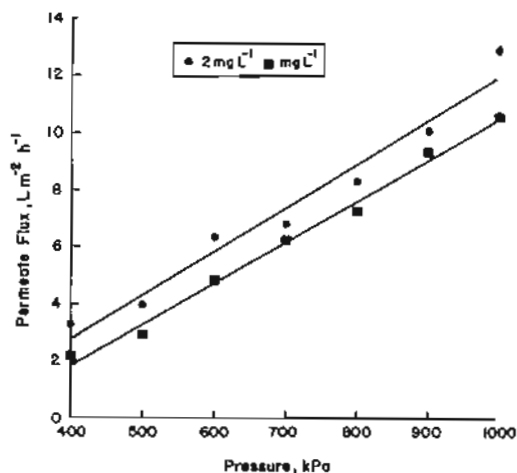


Figure 2. Effect of Pressure on Flux.

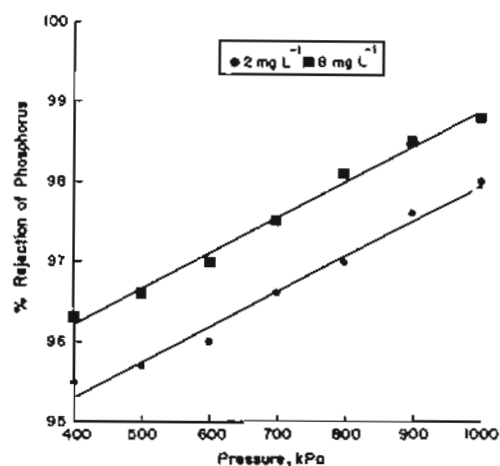


Figure 4. Effect of Pressure on Phosphorous Rejection.

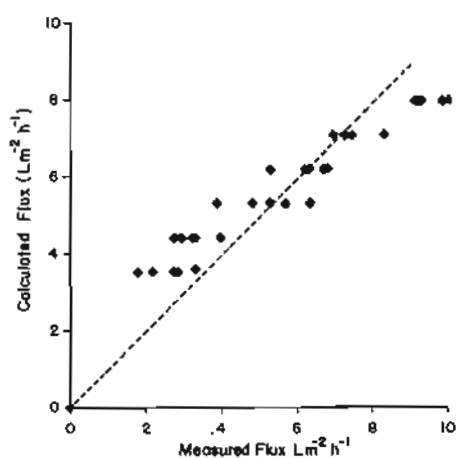


Figure 3. Measured versus Calculated Flux.

This figure shows a deviation from the theoretical line which indicates that NF flux can not be described only by solution-diffusion phenomena, indicating other parameters like membrane charge, Donnan potential may also affect NF flux.

Figure 4 presents the effect of pressure on phosphorus rejection. Here, it can be seen that the phosphorus rejection increases with pressure, which could be explained by the fact that the solvent permeability increased with pressure. These results clearly demonstrate that in NF, higher pressure provides higher flux as well as excellent phosphorus removal efficiency and the high quality effluent ($<0.1 \text{ mg l}^{-1} \text{ P}$).

Effect of Feed Concentration

As reported by [8], flux increases with increasing feed concentration. This is because at higher concentrations, higher "Donnan Potential" may create and allow more solvent to pass through the membrane. The present experiments were carried out with the concentration range of $2\text{--}10 \text{ mg l}^{-1}$

P. The maximum flux ($12.9 \text{ L m}^{-2} \text{ h}^{-1}$) was observed at the lower feed concentration ($2 \text{ mg l}^{-1} \text{ P}$) and the minimum flux ($1.79 \text{ L m}^{-2} \text{ h}^{-1}$) was observed at the higher feed concentration ($10 \text{ mg l}^{-1} \text{ P}$). The range of phosphorous rejection was 98–99% and effluent concentration was $0.04\text{--}0.09 \text{ mg l}^{-1} \text{ P}$. For applied pressures of 800 and 1000 kPa, the effect of feed concentration on flux has been presented in Figure 5.

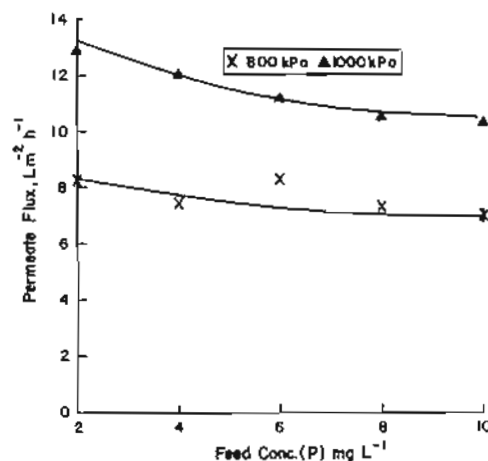


Figure 5. Effect of Feed Concentration on Flux.

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. Nevertheless, 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 provides some more flux (Figure 6.)

Figure 7 presents the effect of feed concentration on phosphorus rejection for the representative applied pressure of 800 and 1000 kPa.

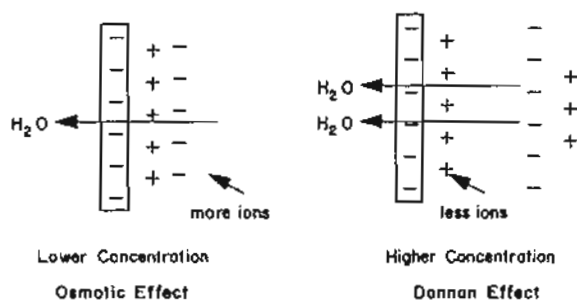


Figure 6. Illustration of Donnan and Osmotic Effects.

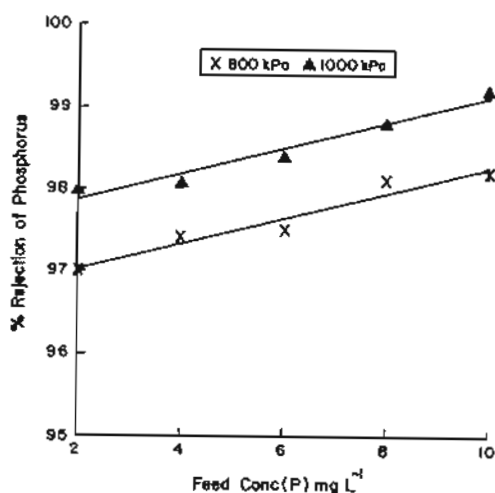


Figure 7. Effect of Feed Concentration on Phosphorous Rejection.

Here phosphate rejection was found to increase 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. Another interesting point which can be noticed is that at higher pressure and concentration, the membrane gives attractive phosphorus rejection efficiency. The possible explanation is that higher pressure provides higher solvent permeability and higher concentration provide better rejection by Donnan potential. So the combined effect gives the best phosphorus removal. These results clearly indicate that NF has a great potential for the treatment of wastewater containing higher phosphorus concentration.

Effect of Competing Compounds

The percentage rejection could significantly decrease 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).

In this study, ammonium sulphate ((NH₄)₂SO₄) was used as a competing compound, because at tertiary level of wastewater treatment, ammonium compounds are often

present. The concentration of competing compound was varied from 2-10 mg l⁻¹ as SO₄. Phosphate concentration was kept constant at 10 mg l⁻¹ P and the 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 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 percentage phosphorus rejection.

Figure 8 presents the effect of competing compound on flux and % phosphorus rejection. Here flux reduces from 12.9 to 8 L/m² h⁻¹ and rejection reduces from 99 to 95%. This result indicates that presence of competing compound is one of the limiting factor for NF application.

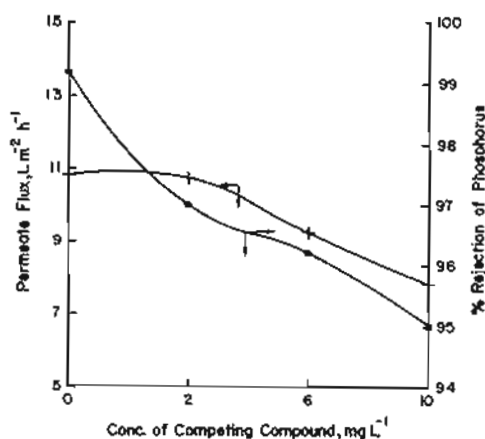


Figure 8. Effect of Competing Compound on Flux (Feed Conc. = 10 mg l⁻¹ P, Competing Compound = (NH₄)₂SO₄ Pressure = 1000 kPa).

CONCLUSIONS

The preliminary laboratory scale investigations were conducted to remove phosphate from synthetic wastewater using NF. Since a small plate and frame membrane module was used in this study, NF has been evaluated here only in terms of phosphorous removal potential, not in terms of water recovery. Once the phosphorous removal potential is established, other membrane module with higher effective area can be used to obtain higher flux and higher water recovery.

This investigation lead to the following conclusions,

namely : NF has excellent phosphate removal efficiency; it can produce a very high quality effluent, with only 0.04-0.09 mg l⁻¹ P that can limit eutrophication; flux for NF membrane linearly increases with pressure, but it does not depend only on solution diffusion mass transport mechanism; parameters like charge density, Donnan potential also influence NF flux; rejection of phosphorus also increases with pressure due to increasing solvent permeability compared to solute. Flux decreases slightly 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 phosphorus rejection; presence of competing compound reduces both flux and rejection. One of the limitation of this experimental study is that, while the synthetic wastewater used replicates levels of phosphate in natural secondary treated wastewater effluent, it neither

replicate the complex range of phosphate speciation, nor presence of the competing compounds and the colloidal composition of natural wastewater. Thus, this limitation should be taken into consideration while using NF in real scale application.

Finally it can be concluded that nanofiltration has great potential for tertiary phosphorus removal from wastewater. If the phosphorus content in the secondary treated wastewater exceeds the required limit, nanofiltration may be the possible solution to meet the effluent standards and thus it will help to prevent the eutrophication of lakes and river.

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