Concentrating Fish Farm Effluent for its Nutrient Recovery via Nanofiltration

Loh Chian Yong, Nur Zahidah Zahid, Ooi Boon Seng*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang

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ABSTRACT

Excessive nutrients in aquaculture effluent have become an alarming environmental issue. However, current treatment methods for recovering nutrients are ineffective since the effluent contains trace amounts of nutrients. Pressure-driven nanofiltration (NF) is a potential solution to the problem of low concentration gradient. In this work, NF was applied to concentrate and recover the nutrients (ammonium (NH$_4^+$), phosphate, (PO$_4^{3-}$), and nitrate ions (NO$_3^-$)) from the synthetic and real fish farm effluents. The experiments were first carried out to study the effect of membrane type, feed concentrations, and operating pressures on membrane performance. It is found that NF 90 membrane was able to retain more nutrient ions but compromise with a lower flux compared to NF 270. This study also revealed that an increase in feed concentration enhanced the concentrating ability for both PO$_4^{3-}$ and NO$_3^-$ ions but reduced the concentrating factor of NH$_4^+$ ions. Moreover, both NF flux and concentrating factor increased with pressure. NF on actual fish farm effluents were investigated under optimal conditions (NF 90, 5 bar). Surprisingly, prefiltered effluent was found to have lower flux than raw effluent due to the presence of denser cake layer. NF could concentrate more nutrients from prefiltered fish farm effluent with concentrating factor up to 6.17 for PO$_4^{3-}$ ions and 1.55 for NH$_4^+$ions, claiming that NF was a promising approach for concentrating nutrients. These nutrients concentrate has an opportunity to be reapplied as fertilizer as a part of sustainable resource management.

Keywords: Nanofiltration, nutrient recovery, aquaculture effluent, flux, concentrating factor

1.0 INTRODUCTION

The expansion of the aquaculture industry has been accompanied by an increase in environmental impacts. Aquaculture effluents contain considerable quantities of organic matter and excess nutrients such as phosphorus and nitrogen compounds which can cause environmental deterioration of the receiving water bodies. These nutrients can be easily leached out from the feed pellets or feces to dissolve in the water and lead to a load of dissolved nutrients in the pond [1]. According to Enduta et al. [1], there is up to 85% of phosphorus and 52-95% of feed nitrogen in an aquaculture pond unutilized and remains as waste components of fish farming. Generally, these nutrients are dissolved in the form of NH$_4^+$, PO$_4^{3-}$ and NO$_3^-$. These excess nutrients can cause eutrophication that is associated with harmful algal blooms, low dissolved oxygen, and highly toxic compound concentration which results in deterioration of water quality and changes in aquatic communities [2-4]. For instance, higher than 100 μg/L of unionized ammonia-nitrogen is reported to be toxic to shrimp [5]. Because of various harmful effects on the environment, aquaculture
effluents cannot be discharged directly to the natural waters without being treated. Instead of removing, nutrient recovery is more desirable as the effluents produced from the aquaculture contain a lot of nutrients. These nutrients from the effluent can be harvested to become fertilizer [6-8]. Various conventional treatment techniques have been applied for nutrient recovery, which is chemical precipitation [9, 10], ion exchange and adsorption [11-13], air striping [14, 15], biological assimilation [3, 16], and membrane processing [17, 18].

However, there are trace amounts of nutrients concentration in the aquaculture effluent that may not be economical to be harvested as liquid fertilizer although the effluents give a huge impact on the environment. In this regard, it is indispensable to preconcentrate the nutrients by using a cost-effective approach, which is the main focus of this research. Among the treatment techniques, NF is a potential strategy to solve the problem associated with a low concentration gradient for concentrating such nutrients. Moreover, the NF membrane process can provide higher flux at lower pressure and require low investment, operation, and maintenance costs compared to reverse osmosis (RO) [18, 19]. NF can effectively remove multivalent salts, ions containing high charge density, small organic compounds, and natural organic matter (NOM). With that, NF membranes that can remove nutrients can also function to concentrate nutrients. However, insufficient attention has been paid to concentrating the ability of the NF membrane on nutrients.

The NF 90 and NF 270 membranes are two of the most commonly used tight NF membranes for wastewater treatment. Based on literature, NF 90 has a higher solute retention but a lower permeability than NF 270 [17, 20, 21]. Both of these membranes have their pros and cons. Thus, it is interesting to study their concentrating ability on nutrients. Furthermore, this pressure-driven process is susceptible to membrane fouling which can aggravate the membrane performance and increase operation cost [22]. The real fish farm effluents consist of not only nutrients but also suspended solids of various sizes. With that, the potential of the suspended solid present to form a cake layer will impede the flux of the membrane and slow down the concentrating process. Thus, the requirement for pre-treatment has been considered in this study to prolong the lifespan of the membrane.

In this work, NF membranes were employed to preconcentrate and recover the \( \text{NH}_4^+ \), \( \text{PO}_4^{3-} \), and \( \text{NO}_3^- \) ions from fish farm effluent. The effect of pressure, dosage of nutrients, and type of membrane used for concentrating process were studied by using synthetic fish farm effluents. The membrane performance for raw and prefiltered fish farm effluent was then studied by carrying out under optimum conditions.

2.0 METHODS

2.1 Chemicals and Membranes
Ammonium chloride, \( \text{NH}_4\text{Cl} \), potassium dihydrogen phosphate, \( \text{KH}_2\text{PO}_4 \), and potassium nitrate, \( \text{KNO}_3 \) (Merck Sdn. Bhd.) with the purity of 99.8 %, 99.5 %, and 99.0 %, respectively were utilized in this experimental work to mimic synthetic effluents. All of the reagents were made with deionized water (ELGA PURELAB Flex dispenser). The actual fish farm effluents were collected from the fish farm at Sungai Udang, Nibong Tebal. There were two different flat sheet type polyamide membranes used in this study, namely NF 90 and NF 270 that supplied by Dow Filmtec™. Each
membrane characteristic is depicted in Table 1 below based on information provided by the manufacturer.

**Table 1 Membrane characteristics**

| Type         | NF 90       | NF 270      |
|--------------|-------------|-------------|
| MWCO (Da)a   | 100 – 200   | 150 – 300   |
| Polymer      | Polyamide-TFC | Polyamide-TFC |
| pH           | 2-11        | 2-11        |
| Contact angle (°)b | 93.2     | 19.5        |
| Flux (GFD/psi) | 46-60/130 | 79-98/130  |
| Rejection    | 99.0%       | 99.2%       |

| Concentration (mg/L) | NH₄Cl (g) | KH₂PO₄ (g) | KNO₃ (g) |
|----------------------|-----------|------------|-----------|
| 10                   | 0.0148    | 0.0072     | 0.0082    |
| 15                   | 0.0222    | 0.0107     | 0.0122    |
| 20                   | 0.0297    | 0.0143     | 0.0163    |
| 25                   | 0.0371    | 0.0179     | 0.0204    |

2.2 Preparation of Synthetic and Real Fish Farm Effluents

There were two types of feed solutions used in this experiment such as synthetic and real fish farm effluents. The synthetic effluents were prepared according to the nutrient contents of the fish farm effluent. The synthetic solutions were prepared by dissolving the required nutrients which were NH₄Cl, KH₂PO₄ and KNO₃ reagent in deionized water to represent the ion presence (NH₄⁺, PO₄³⁻ and NO₃⁻) in the fish farm effluent. They were prepared by dissolving salts in deionized water. Synthetic feed solutions with four different concentrations (10 to 25 mg/L) were then prepared. The solution used for each run was fixed at 300.0 mL. The mass needed to prepare the feed solution for each concentration is shown in Table 2.

2.3 NF Experiment

2.3.1 Experimental Set-up

The experiments were performed using a commercial dead-end stirred cell (Sterlitech™ HP4750) with 300 mL holding capacity, as shown in Figure 1. The membranes were soaked in deionized water overnight prior to use before beginning membrane filtration. To eliminate any compression impact, each NF membrane was first compressed to 9 bar using deionized water for at least 30 minutes. The cell was then filled with prepared solution and operated at 25 ℃ with 350 rpm of stirring speed and desired pressure. An electronic weighing balance was applied to continuously measure the permeate mass at regular intervals of 5 minutes.
2.3.2 Experimental Parameters and Membrane Performance Evaluations

To elucidate the performance of the NF membrane, numerous parameters were investigated in this experiment, including operating pressure (4 to 7 bar), nutrients dosages (10 to 25 mg/L), and type of membrane (NF 90 and NF 270). The membrane filtration processes were first conducted by using synthetic nutrient solutions to study the effect of each parameter. After testing with synthetic effluent, the experiment was repeated with actual fish farm effluents and operated at the studied optimum condition. There were two types of actual fish farm effluents used for membrane performance analysis such as raw effluent and prefiltered effluent. One of the effluents was prefiltered by using filter paper for the removal of suspended solids.

The NF performance for each process was evaluated based on permeate flux and concentrating factors. The flux permeating through the membrane was determined by

\[ J_p = \frac{V_p}{A \Delta t} \]  

where \( J_p \) is permeate flux (L/m\(^2\).h), \( V_p \) is permeate volume (L), \( A \) is effective membrane area (m\(^2\)) and \( \Delta t \) is permeate collection time (h).

The efficiency of the separation process could also be analyzed by the ability of concentrating the nutrients during the NF process. The concentrating factor was determined by comparing the concentration of the nutrients in the solution before and after the separation process as shown in the equation below:

\[ CF = \frac{C_R}{C_F} \]  

where \( CF \) is the concentrating factor, \( C_R \) is retentate concentration (mg/L) and \( C_F \) is feed concentration (mg/L).
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Rejection efficiency can be computed by equation below:

\[ R = \left(1 - \frac{C_F}{C_P}\right) \times 100\% \quad (3) \]

where \( R \) is the rejection efficiency, \( C_F \) is permeate concentration (mg/L).

### 2.4 Nutrients Determination

The nutrient concentration in the feed, permeate and retentate samples were analyzed by using a Lovibond photometer (MD 600). The measurement of \( \text{NH}_4^+ \) concentration was tested based on the salicylate chemical method with a method number of 66. Phosphomolybdic blue was a chemical method that was used to analyze the concentration of \( \text{PO}_4^{3-} \) by pressing method number 324 in photometer system whereas for \( \text{NO}_3^- \), chromotropic acid method was applied with method number of 265. The measuring ranges for \( \text{NH}_4^+ \), \( \text{PO}_4^{3-} \) and \( \text{NO}_3^- \) concentration were 1-50 mg/L, 0.06-5 mg/L and 1-30 mg/L, respectively.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 The Effect of Membrane Type on Permeate Flux and Concentrating Factor

Figure 2 presents the permeate flux for the separation process using different types of the membrane (NF 90 and NF 270). As can be observed from Figure 2, permeate flux was relatively higher for NF 270 than for NF 90 with an average value of 80.30 L/m².h and 63.27 L/m².h, respectively. These results can be attributed to the characteristic of membranes that had stated in Table 1 which indicates that NF 270 has a more open polymeric matrix structure with larger MWCO, resulting in lower mass transport resistance compared to NF 90 [18, 23, 24]. In addition, NF 270 also has stronger surface hydrophilicity with a lower contact angle, resulting in higher water permeability. On contrary, due to greater pore restriction and lesser hydrophilicity, there is a higher possibility for fouling occurring on NF 90 rather than NF 270 in accordance with the declined flux [17].

Table 3 shows the \( \text{NH}_4^+ \) concentrating factor was obtained from the membrane separation process by applying different types of the membrane (NF90 and NF270). It is found that NF270 had a slightly higher retention ability with the concentrating factor of 1.68 than NF 90 with concentrating factor of 1.59. The possible reason that NF 270 had a better concentrating effect of \( \text{NH}_4^+ \) ions is NF 270 gives higher solvent permeability compared to \( \text{NH}_4^+ \) ion which could further concentrate the feed solution. Because of a very small difference (about 5 %) obtained from the effect of membrane types in terms of concentrating factor, the NF concentrating ability was further determined by rejection efficiency.

The results demonstrate that NF 90 could reject up to 65.03% of solutes which is much higher than NF 270 that reject only 17.59%. This can be explained by NF 90 having a tighter polymeric structure, leading to high steric hindrance and electrostatic effect [18, 24]. Therefore, NF 90 was a better option of membrane used in NF process of actual fish farm effluent as it performed almost similar concentrating ability as NF 270 and better rejection efficiency of nutrients.
Figure 2 Flux profile for NH₄⁺ solution with varying type of membrane (Concentration: 20 mg/L and pressure: 7 bar)

Table 3 Concentrating factor for the NH₄⁺ solution with varying types of the membrane (Concentration: 20 mg/L and Pressure: 7 bar)

| Membrane Type | Concentrating factor | Rejection (%) |
|---------------|----------------------|---------------|
| NF90          | 1.59                 | 65.03         |
| NF270         | 1.68                 | 17.59         |

3.2 The Effect of Initial Concentration on Permeate Flux and Concentrating Factor

The effect of nutrient concentration (10 mg/L to 25 mg/L) on the membrane performance concerning permeate flux at a fixed operating pressure of 7 bar is presented in Figure 3. As seen in Figure 3, the permeate flux increased with feed concentration and then decreased when reached a certain concentration where both NH₄⁺ and NO₃⁻ solution achieved the highest flux at 15 ppm with an average value of 60.63 L/m².h and 63.92 L/m².h, respectively and the flux started to reduce when increasing concentration over 15 ppm whereas PO₄³⁻ solution attained the highest flux at 20 ppm with an average value of 63.20 L/m².h. These findings were in line with the study done by Visvanathan and Roy [25]. The permeate flux was first increasing with solute concentration due to increasing of “Donnan Potential” which enables more solvent to pass through the membrane. On the other hand, the possible reason for the permeate flux declined with increasing feed concentration is that at higher solute concentration, the increase in osmotic pressure across the membrane would decrease the net driving force of mass transfer under constant pressure operation [26, 27]. As a result, permeate flux decreased.

In addition, the potential of NH₄⁺ ions that fouled the membrane was also justifiable with its lowest average flux value obtained in the range of 57.55 L/m².h to 60.63 L/m².h compared to PO₄³⁻ and NO₃⁻ solution. This is due to
the surface of the NF 90 membrane is negatively charged, it would tend to attract positive charged NH$_4^+$ ions via electrostatic attraction, leading to pore blocking. Hence, it would cause the membrane to foul and decrease the flux rate [17, 28].

**Figure 3** Flux profile for nutrients solution with varying concentration (Pressure: 7 bar and membrane type: NF 90)

Figure 4 shows the influence of nutrient concentration on the NF performance concerning concentrating factor obtained after separation. It can be observed that the nutrients were able to be concentrated using the NF membrane. The separation of the nutrients via NF membrane is contributed by one or a combination of mechanisms between physio-chemical interactions between membrane and solutes, Donnan exclusion as well as size exclusion [23].

Based on the results in Figure 4, NH$_4^+$ ions could be concentrated up to 2.13 factor for an initial concentration of 10 mg/L but the concentrating factor decreased by 40.85% when the initial concentration increased from 10 mg/L to 25 mg/L. A similar result was obtained by other researchers in which the retention ability decreased when the feed (NH$_4$Cl) concentration increased [29]. This phenomenon can be explained by increasing feed concentration enhances the concentration polarization taking place as more solutes accumulate on the membrane surface. As a result, it would enlarge the concentration gradient of nutrients between the feed and permeate sides and push more nutrients to pass through the membrane [29, 30]. Thus, the concentrating ability was diminished.

On the other hand, PO$_4^{3-}$ and NO$_3^-$ solutions gave a different trend compared to NH$_4^+$ solutions. Figure 4 shows that the concentrating ability of PO$_4^{3-}$ and NO$_3^-$ ions increased (1.35 to 1.82 and 1.35 to 1.59, respectively) with their initial concentration. An important reason for this effect is the rise in Donnan exclusion at higher
concentrations. Since the NF membrane was negatively charged, more anions were likely rejected by the membrane when the solution contained a high solute concentration. This would inhibit anions from permeating through the membrane; thus, more \( \text{PO}_4^{3-} \) and \( \text{NO}_3^- \) ions are retained on the feed side. These findings were also in agreement with works done by Chai et al. [17], dos Santos et al. [31], and He et al. [26]. However, it can be observed that the concentrating trend for \( \text{PO}_4^{3-} \) was fluctuating where the concentrating factor initially increased from 1.35 to 1.82 and then slightly decreased to 1.63 when \( \text{PO}_4^{3-} \) concentration increased over 15 mg/L. This could be ascribed to an increase in \( \text{KH}_2\text{PO}_4 \) concentration elevates the screen effect of dissolved counterions (\( \text{K}^+ \)) on the proper membrane charge. As a consequence, the membrane potential is reduced where the repulsive force between membrane and \( \text{PO}_4^{3-} \) is diminished; hence, lowering the concentrating ability. It can be deduced that Donnan exclusion plays a significant role in the separation of solute at lower \( \text{KH}_2\text{PO}_4 \) concentration whereas, at higher concentration, site-binding screen effect overwhelms and results in decreased concentrating ability. This statement was also further supported by Paugam et al. [32].

Overall, it is found that the concentrating ability of nutrients was in this sequence \( \text{NH}_4^+ < \text{NO}_3^- < \text{PO}_4^{3-} \) with increasing initial concentration. As expected, both concentrating ability of \( \text{PO}_4^{3-} \) and \( \text{NO}_3^- \) was higher than \( \text{NH}_4^+ \) due to electrostatic repulsion between negatively charge NF 90 and anions. The membrane tends to attract \( \text{NH}_4^+ \) ions, inducing them easier to diffuse through the membrane [28, 33, 34]. Moreover, concentrating ability of \( \text{PO}_4^{3-} \) was higher than \( \text{NO}_3^- \) because of the size exclusion mechanism [31, 35, 36]. NF 90 was more efficient in the rejection of multivalent ions (\( \text{PO}_4^{3-} \)) rather than a rejection of monovalent ions (\( \text{NO}_3^- \)) due to the bigger ion size of the former ions.

### 3.3 The Effect of Operating Pressure on Permeate Flux and Concentrating Factor

Figure 5 manifests the permeate flux profile and concentrating factor achieved following the filtration process at various operating pressure. When elevating the operating pressure from 4 to 7 bar at constant feed concentration, the permeate flux rose from 30.21 L/m².h to 66.13 L/m².h. The expected increment in permeate flux is attributed to the enhancement of driving force through the membrane at higher operating pressure [34, 37, 38]. Furthermore, it is revealed that the linearity increment of permeate flux with pressure, signifying that the effect of concentration polarization is insignificant [39]. This can be explained by using Darcy’s Law where membrane separation, in this case, is governed by a pressure-controlled region, indicating that the membrane is not further compressible in this operating pressure range.

Moreover, it can be seen from Figure 5 that the concentration efficiency of synthetic \( \text{NH}_4^+ \) solution also increased with pressure. The ion permeation through the NF membrane is based on a combination of convective and diffusive transport [40]. However, under pressure-controlled regions, convective transport becomes prevalent while diffusive transport is unaffected. This leads to enhancement of solvent permeability where the transport of water is greater than \( \text{NH}_4^+ \) ions through the membrane, which results in higher retention at higher pressure [31, 41]. In addition, the greater compressive effect of the membrane at higher pressure
increases the steric resistance; thus, more \( \text{NH}_4^+ \) ions are rejected on the retentate side. Therefore, the concentrating factor increased from 1.16 to 1.61 when operating at 4 bar to 7 bar.

![Figure 4](image1.png)

**Figure 4** Effect of nutrients concentration on concentrating factor (Pressure: 7 bar and membrane type: NF 90)

In short, these findings show that higher operating pressure facilitated higher permeate flux and achieved the better concentrating ability of nutrients. Nevertheless, lower operating pressure can reduce membrane fouling and prevent the development of a compacted fouling layer formed on the membrane surface. With that, the operating pressure of 5 bar (middle range) was chosen for concentrating actual fish farm effluent that contains other pollutants that might foul the membrane easier compared to synthetic effluent.

### 3.4 The Raw and Prefiltered Fish Farm Effluent

The fish farm effluents were tested under two conditions namely raw fish farm effluent and prefiltered effluent where the effluents had been filtered to remove the suspended solids that accumulated in the fish farm effluent. The collected fish farm effluent was greenish indicating algae blooming. Concentrating nutrients in both fish farm effluents were carried out under the optimized operating condition, 5 bar by using NF 90.

Figure 6 shows that permeate flux for the NF process of both fish farm effluents. It can be seen that both fish farm effluents gave a significant decreasing flux trend, indicating that fouling has occurred on both membrane surfaces via cake layer formation and even pore constriction [42]. The raw fish farm effluent exhibited higher flux than the prefiltered effluent with an average value of 20.94 L/m².h and
16.41 L/m².h, respectively. The permeate flux for the raw fish farm effluent is expected to be higher because of the coarser particle in the suspension that gives a loose cake layer while after prefiltration, the suspended particles left in the solution are relatively smaller, resulting in a dense cake layer. This result was supported by Zakmout et al. where the tight cake layer reduced the permeate flux [43].

![Figure 5](image-url) **Figure 5** Effect of operating pressure on permeate flux and concentrating factor for NH4⁺ solution (Concentration: 20 mg/L and membrane type: NF 90)

The collected raw fish farm effluents contain many particulate substances such as algae, suspended particles, and organic matters from uneaten fish feeds and also fish wastes which have larger particle sizes compared to the pore size of the membrane. Thereby, during membrane filtration, these miscellaneous particles with larger molecular weight fractions are mainly deposited on the membrane surface instead of pore blockage, and this phenomenon is commonly referred to as external fouling [42, 44]. In addition, the formed cake layer resistance is related to the particle size where the larger the particle size, the larger the porosity of the cake layer, and the smaller the cake resistance [45]. Hence, the permeate flux for raw fish farm effluent was higher than prefiltered effluent. However, under prolonged membrane filtration, the rate of flux declined for raw fish farm effluent was higher than prefiltered effluent. This can be explained by the high starting flux that boosts the transport of solutes towards the membrane, provoking severe fouling. Thus, prefiltration of raw fish farm effluent is still a need before the membrane filtration process to prolong the lifespan of the membrane.

Table 4 shows the nutrients concentration before and after the membrane concentrating process for both raw and prefiltered fish farm effluents. It can be observed that the three nutrient ions concentration in the feed of prefiltered effluent was lower than raw effluent. This could happen because some of the nutrients are adsorbed on colloid particles via hydrogen bonding, Van der Waals...
attraction, or extracellular molecule interactions which then together are eliminated by filter paper [43]. Overall, the results in Table 4 show that all the nutrients in the fish farm effluent were able to be concentrated with the NF process where all the measured retentates concentrations were relatively higher than feed concentration even though the NO$_3^-$ concentration in the raw feed solution could not be detected due to its trace amount.

The performance of NF membrane in terms of concentrating factor obtained after separation for both raw and prefiltered effluent is presented in Figure 7. It shows that more nutrients in prefiltered effluent (CF of NH$_4^+$: 1.55; CF of PO$_4^{3-}$: 6.17) could be concentrated by NF membrane rather than raw effluent (CF of NH$_4^+$: 1.49; CF of PO$_4^{3-}$: 3.57). The possible explanation is interferences with some particulates (foulants) other than nutrients ions in raw effluent could result in modification of membrane properties, deteriorating the performance of membrane and affecting the concentrating ability of nutrient ions [44, 46, 47]. Another reason might be for membrane filtration of prefiltered effluent, the formed dense cake layer induces stronger electrostatic interaction between ionic compounds and membrane surface charge especially repelling more co-ions, PO$_4^{3-}$ and NO$_3^-$ ions [48]. Moreover, to maintain electroneutrality, some counterions, NH$_4^+$ ions would adsorb to the membrane surface and some is distributed and retained near the surface membrane to balance excessive negative charges in solution although monovalent NH$_4^+$ ions could easily penetrate through NF membrane [36, 49].

Based on the results obtained, it can be summarized that the observed concentrating ability of nutrients by using NF membrane does not solely depend on the initial characteristic of the membrane, but also the nature of the foulants and even fouling state of membranes. All of these results show that the NF process is able to concentrate the nutrients in the fish farm effluent under proper operating conditions and the type of membrane used during the process.

![Figure 6](image-url)  
**Figure 6** Flux profile for membrane concentration process of raw and prefiltered fish farm effluents. (Pressure: 5 bar and membrane type: NF90)
Table 4 Nutrient concentration before and after for membrane concentration of raw and prefiltered fish farm effluent

| Type of Test | Ammonium | Phosphate | Nitrate |
|--------------|----------|-----------|---------|
|              | Feed Retentate | Feed Retentate | Feed Retentate |
| Raw          | 28.85 42.85 | 7.0 25.0 | UR 18.0 |
| Prefiltered  | 24.60 38.10 | 3.91 15.0 | UR UR |

UR: under range

Figure 7 Concentrating factor obtained for membrane concentration process of raw and prefiltered fish farm effluents. (Pressure: 5 bar and membrane type: NF90)

4.0 CONCLUSION

Focusing on the recovery of trace amounts of nutrients, this work has studied the preconcentration of nutrients from fish farm effluent by using NF. It is found that NF 90 membrane outperformed NF 270 with better retention ability in considering both concentrating factor and rejection efficiency. Due to effect of Donnan potential and size exclusion, the concentrating ability of nutrients was in the sequence of $\text{NH}_4^+ < \text{NO}_3^- < \text{PO}_4^{3-}$ with increasing feed concentration. The optimum pressure, in this case, was recommended to be 5 bar. NF process of actual fish farm effluent was then conducted with optimal process parameters using NF 90 at 5 bar. Owing to the denser cake layer and smaller suspended particles, the flux of prefiltered effluent was lower than raw effluent; but in terms of concentrating...
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ability, more nutrients could be concentrated from prefiltered effluent with the concentrating factor up to 6.17 for $\mathrm{PO}_4^{3-}$ ions and 1.55 for $\mathrm{NH}_4^+$ ions. It is thus concluded that the NF process could be an effective option for treating fish farm effluent and had great potential to preconcentrate the nutrients from the effluent for fertilizer usage. To further improve the retention ability of NF membranes, it is recommended adjusting the solution to alkaline condition to increase electrostatic repulsion between nutrients and membrane surface.

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REFERENCES

[1] A. Enduta, A. Jusoh, N. Ali, W.B. Wan Nik. 2011. Nutrient Removal from Aquaculture Wastewater by Vegetable Production in Aquaponics Recirculation System. Desalin. Water Treat. 32(1-3): 422-430. https://doi.org/10.5004/dwt.2011.2761.

[2] N. Kawasaki, M. R. M. Kushairi, N. Nagao, F. Yusoff, A. Imai, A. Kohzu. 2016. Release of Nitrogen and Phosphorus from Aquaculture Farms to Selangor River, Malaysia. Int. J. Environ. Sci. Dev. 7(2): 113-116. https://doi.org/10.7763/ijesd.2016.V7.751.

[3] H. Khatoon, S. Banerjee, M. Syakir Syahiran, N.B. Mat Noordin, A. Munafi Ambol Bolong, A. Endut. 2016. Re-use of Aquaculture Wastewater in Cultivating Microalgae as Live Feed for Aquaculture Organisms. Desalin. Water Treat. 57(60): 29295-29302. https://doi.org/10.1080/19443994.2016.1156030.

[4] H. Yin, M. Kong. 2014. Simultaneous Removal of Ammonium and Phosphate from Eutrophic Waters Using Natural Calcium-rich Attapulgite-based Versatile Adsorbent. Desalination 351: 128-137. https://doi.org/10.1016/j.desal.2014.07.029.

[5] T.-S. Chin, J.-C. Chen. 1987. Acute Toxicity of Ammonia to Larvae of the Tiger Prawn, Penaeus Monodon. Aquac. Environ. Interact. 66(3-4): 247-253. https://doi.org/https://doi.org/10.1016/0044-8486(87)90110-4.

[6] P. Xia, X. Wang, X. Song, H. Wang, J. Zhang, J. Zhao. 2016. Struvite Crystallization Combined Adsorption of Phosphate and Ammonium from Aqueous Solutions by Mesoporous MgO Loaded Diatomite. Colloids Surf. A: Physicochem. Eng. Asp. 506: 220-227. https://doi.org/10.1016/j.colsurfa.2016.05.101.

[7] L. Xie, S. Lu, M. Liu, C. Gao, X. Wang, L. Wu. 2013. Recovery of Ammonium onto Wheat Straw to be Reused as a Slow-release Fertilizer. J. Agric. Food Chem. 61(14): 3382-8. https://doi.org/10.1021/jf4004016.

[8] K. Xu, F. Lin, X. Dou, M. Zheng, W. Tan, C. Wang. 2018. Recovery of Ammonium and Phosphate from Urine as Value-added Fertilizer using Wood
Waste Biochar Loaded with Magnesium Oxides. *J. Clean. Prod.* 187: 205-214. https://doi.org/10.1016/j.jclepro.2018.03.206.

[9] B. Cichy, E. Kuzdzal, H. Krzton. 2019. Phosphorus Recovery from Acidic Wastewater by Hydroxyapatite Precipitation. *J. Environ. Manage.* 232: 421-427. https://doi.org/10.1016/j.jenvman.2018.11.072.

[10] W. K. Kim, Y. K. Sung, H. S. Yoo, J. T. Kim. 2015. Optimization of Coagulation/flocculation for Phosphorus Removal from Activated Sludge Effluent Discharge using an Online Charge Analyzing System Titrator (CAST). *J. Ind. Eng. Chem.* 21: 269-277. https://doi.org/10.1016/j.jiec.2014.02.034.

[11] H.-P. Jing, Y. Li, X. Wang, J. Zhao, S. Xia. 2019. Simultaneous Recovery of Phosphate, Ammonium and Humic Acid from Wastewater using a Biochar Supported Mg(OH)2/bentonite Composite. *Environ. Sci.: W. Res. Technol.* 5(5): 931-943. https://doi.org/10.1039/c8ew00952j.

[12] A. Khalil, N. Sergeevich, V. Borisova. 2018. Removal of Ammonium from Fish Farms by Biochar Obtained from Rice Straw: Isotherm and Kinetic Studies for Ammonium Adsorption. *Adsorpt. Sci. Technol.* 36(5-6): 1294-1309. https://doi.org/10.1177/0263617418768944.

[13] M. Zhang, B. Gao, Y. Yao, Y. Xue, M. Inyang. 2012. Synthesis of Porous MgO-biochar Nanocomposites for Removal of Phosphate and Nitrate from Aqueous Solutions. *Chem. Eng. J.* 210: 26-32. https://doi.org/10.1016/j.cej.2012.08.052.

[14] H. A. P. Dos Santos, A. B. de Castilhos Junior, W. C. Nadaleti, V. A. Lourenco. 2020. Ammonia Recovery from Air Stripping Process Applied to Landfill Leachate Treatment. *Environ. Sci. Pollut. Res. Int.* 27(36): 45108-45120. https://doi.org/10.1007/s11356-020-10397-9.

[15] A. Zangeneh, S. Sabzalipour, A. Takdatsan, R. J. Yengejeh, M. A. Khafaie. 2021. Ammonia Removal form Municipal Wastewater by Air Stripping Process: An Experimental Study. *S. Afr. J. Chem. Eng.* 36: 134-141. https://doi.org/10.1016/j.sajce.2021.03.001.

[16] R. H. Kadlec, D. L. Tilton, K. C. Ewel. 2009. The Use of Freshwater Wetlands as a Tertiary Wastewater Treatment Alternative. *CRC Crit. Rev. Environ. Control.* 9(2): 185-212. https://doi.org/10.1080/10643387909381671.

[17] Y. K. Chai, H. C. Lam, C. H. Koo, W. J. Lau, S. O. Lai, A. F. Ismail. 2019. Performance Evaluation of Polyamide Nanofiltration Membranes for Phosphorus Removal Process and Their Stability against Strong Acid/Alkali Solution. *Chin. J. Chem. Eng.* 27(8): 1789-1797. https://doi.org/10.1016/j.cjche.2018.09.029.

[18] A. Noubli, D. E. Akretche, J. G. Crespo, S. Velizarov. 2020. Complementary Membrane-based Processes for Recovery and Preconcentration of Phosphate from Industrial Wastewater. *Sep. Purif. Technol.* 234. https://doi.org/10.1016/j.seppur.2019.116123.
[19] M. S. Shalaby, H. Abdallah, A. Cenian, G. Sołowski, M. Sawczak, A. M. Shaban, R. Ramadan. 2020. Laser Synthesized Gold-nanoparticles, Blend NF Membrane for Phosphate Separation From Wastewater. Sep. Purif. Technol. 247. https://doi.org/10.1016/j.seppur.2020.116994.

[20] D. Dolar, K. Košutić, D. Ašperger. 2012. Influence of Adsorption of Pharmaceuticals onto RO/NF Membranes on Their Removal from Water. Water Air Soil Pollut. 224(1). https://doi.org/10.1007/s11270-012-1377-0.

[21] C. P. Leo, W. K. Chai, A. W. Mohammad, Y. Qi, A. F. Hoedley, S. P. Chai. 2011. Phosphorous Removal Using Nanofiltration Membranes. Water Sci. Technol. 64(1): 199-205. https://doi.org/10.2166/wst.2011.598.

[22] H. He, N. Zhang, N. Chen, Z. Lei, K. Shimizu, Z. Zhang. 2019. Efficient Phosphate Removal from Wastewater by MgAl-LDHs Modified Hydrochar Derived From Tobacco Stalk. Bioresour. Technol. Rep. 8. https://doi.org/10.1016/j.biteb.2019.100348.

[23] D. Dolar, A. Vuković, D. Ašperger, K. Košutić. 2011. Effect of Water Matrices on Removal of Veterinary Pharmaceuticals by Nanofiltration and Reverse Osmosis Membranes. J. Environ. Sci. 23(8): 1299-1307. https://doi.org/10.1016/s1001-0742(10)60545-1.

[24] C. S. Ong, W. J. Lau, A. F. Ismail. 2012. Treatment of Dyeing Solution by NF Membrane for Decolorization and Salt Reduction. Desalin. Water Treat. 50(1-3): 245-253. https://doi.org/10.1080/19443994.2012.719473.

[25] C. Visvanathan, P. K. Roy. 1997. Potential of Nanofiltration for Phosphate Removal from Wastewater. Environ. Technol. 18: 551-556.

[26] Y. He, G. Li, H. Wang, J. Zhao, H. Su, Q. Huang. 2008. Effect of Operating Conditions on Separation Performance of Reactive Dye Solution with Membrane Process. J. Membr. Sci. 321(2): 183-189. https://doi.org/10.1016/j.memsci.2008.04.056.

[27] M. Teixeira, M. Rosa, M. Nystrom. 2005. The Role of Membrane Charge on Nanofiltration Performance. J. Membr. Sci. 265(1-2): 160-166. https://doi.org/10.1016/j.memsci.2005.04.046.

[28] N. Li, X. Wang, H. Zhang, Z. Zhang, J. Ding, J. Lu. 2019. Comparing the Performance of Various Nanofiltration Membranes in Advanced Oxidation-nanofiltration Treatment of Reverse Osmosis Concentrates. Environ. Sci. Pollut. Res. Int. 26(17): 17472-17481. https://doi.org/10.1007/s11356-019-05120-2.

[29] S. Gui, Z. Mai, J. Fu, Y. Wei, J. Wan. 2020. Transport Models of Ammonium Nitrogen in Wastewater from Rare Earth Smeltery by Reverse Osmosis Membranes. Sustainability. 12(15). https://doi.org/10.3390/su12156230.

[30] A. Kargari, F. Khazaali. 2014. Effect of Operating Parameters on 2-chlorophenol Removal from
Wastewaters by a Low-pressure Reverse Osmosis System. *Desalin. Water Treat.* 55(1): 114-124. https://doi.org/10.1080/19443994.2014.913993.

[31] C. dos Santos, A. Ribeiro, M. Ribau Teixeira. 2014. Phosphorus Recovery from Waters using Nanofiltration. *Desalin. Water Treat.* 1-8. https://doi.org/10.1080/19443994.2014.925831.

[32] L. Paugam, S. Taha, G. Dorange, P. Jaouen, F. Quéméneur. 2004. Mechanism of Nitrate Ions Transfer in Nanofiltration Depending on Pressure, pH, Concentration and Medium Composition. *J. Membr. Sci.* 231(1-2): 37-46. https://doi.org/10.1016/j.memsci.2003.11.003.

[33] E. M. van Voorthuizen, A. Zwijnenburg, M. Wessling. 2005. Nutrient Removal by NF and RO Membranes in a Decentralized Sanitation System. *Water Res.* 39(15): 3657-67. https://doi.org/10.1016/j.watres.2005.06.005.

[34] I. Koyuncu. 2002. Effect of Operating Conditions on the Separation of Ammonium and Nitrate Ions with Nanofiltration and Reverse Osmosis Membranes. *J. Environ. Sci. Health - Toxic/Hazard. Subst. Environ. Eng.* 37(7): 1347-59. https://doi.org/10.1081/ese-120005991.

[35] N. Hilal, H. Al-Zoubi, N.A. Darwish, A. W. Mohammad. 2007. Performance of Nanofiltration Membranes in the Treatment of Synthetic and Real Seawater. *Sep. Sci. Technol.* 42(3): 493-515. https://doi.org/10.1080/01496390601120789.

[36] K. Häyrynen, E. Pongrácz, V. Väisänen, N. Pap, M. Mänttäri, J. Langwaldt, R. L. Keiski. 2009. Concentration of Ammonium and Nitrate from Mine Water by Reverse Osmosis and Nanofiltration. *Desalination.* 240(1-3): 280-289. https://doi.org/10.1016/j.desal.2008.02.027.

[37] B. Cancino-Madariaga, C. F. Hurtado, R. Ruby. 2011. Effect of Pressure and pH in Ammonium Retention for Nanofiltration and Reverse Osmosis Membranes to be Used in Recirculation Aquaculture Systems (RAS). *Aquac. Eng.* 45(3): 103-108. https://doi.org/10.1016/j.aquaeng.2011.08.002.

[38] L. Paugam, S. Taha, G. Dorange, F. Quéméneur. 2003. Influence of Ionic Composition on Nitrate Retention by Nanofiltration. *Chem. Eng. Res. Des.* 81(9): 1199-1205. https://doi.org/10.1205/026387603770866380.

[39] T. Schütte, C. Niewersch, T. Wintgens, S. Yüce. 2015. Phosphorus Recovery from Sewage Sludge by Nanofiltration in Diafiltration Mode. *J. Membr. Sci.* 480: 74-82. https://doi.org/10.1016/j.memsci.2015.01.013.

[40] C. Niewersch, K. Meier, T. Wintgens, T. Melin. 2010. Selectivity of Polyamide Nanofiltration Membranes for Cations and Phosphoric Acid. *Desalination.* 250(3): 1021-1024. https://doi.org/10.1016/j.desal.2009.09.097.

[41] J. J. Lee, Y.C. Woo, H.-S. Kim. 2014. Effect of Driving Pressure and Recovery Rate on the Performance of Nanofiltration and Reverse Osmosis Membranes for the Treatment of the Effluent
from MBR. *Desalin. Water Treat.* 54(13): 3589-3595. https://doi.org/10.1080/19443994.2014.923196.

[42] M. L. Salazar-Peláez, J. M. Morgan-Sagastume, A. Noyola. 2017. Fouling Layer Characterization and Pore-blocking Mechanisms in an UF Membrane Externally Coupled to a UASB Reactor. *Water S. A.* 43(4). https://doi.org/10.4314/wsa.v43i4.05.

[43] A. Zakmout, F. Sadi, C. A. M. Portugal, J. G. Crespo, S. Velizarov. 2020. Tannery Effluent Treatment by Nanofiltration, Reverse Osmosis and Chitosan Modified Membranes. *Membranes (Basel).* 10(12). https://doi.org/10.3390/membranes10120378.

[44] A. I. Schäfer, A. G. Fane, T. D. Waite. 2000. Fouling Effects on Rejection in the Membrane Filtration of Natural Waters. *Desalination.* 131(1-3): 215-224. https://doi.org/10.1016/s0011-9164(00)90020-1.

[45] X. Du, Y. Shi, V. Jegatheesan, I. U. Haq. 2020. A Review on the Mechanism, Impacts and Control Methods of Membrane Fouling in MBR System. *Membranes (Basel).* 10(2). https://doi.org/10.3390/membranes10020024.

[46] L. Zhu. 2015. Rejection of Organic Micropollutants by Clean and Fouled Nanofiltration Membranes. *J.Chem.* 2015: 1-9. https://doi.org/10.1155/2015/934318.

[47] A. M. Ravazzini, A. F. van Nieuwenhuijzen, J. H. M. J. van der Graaf. 2005. Direct Ultrafiltration of Municipal Wastewater: Comparison between Filtration of Raw Sewage and Primary Clarifier Effluent. *Desalination.* 178(1-3): 51-62. https://doi.org/10.1016/j.desal.2004.11.028.

[48] V. Yangali-Quintanilla, A. Sadmani, M. McConville, M. Kennedy, G. Amy. 2009. Rejection of Pharmaceutically Active Compounds and Endocrine Disrupting Compounds by Clean and Fouled Nanofiltration Membranes. *Water Res.* 43(9): 2349-62. https://doi.org/10.1016/j.watres.2009.02.027.

[49] C. M. Galanakis, G. Fountoulis, V. Gekas. 2012. Nanofiltration of Brackish Groundwater by using a Polypiperazine Membrane. *Desalination.* 286: 277-284. https://doi.org/10.1016/j.desal.2011.11.035.