Potential of nanofiltration and low pressure reverse osmosis in the removal of phosphorus for aquaculture
C. P. Leo, M. Z. Yahya, S. N. M. Kamal, A. L. Ahmad and A. W. Mohammad

ABSTRACT
Aquaculture activities in developing countries have raised deep concern about nutrient pollution, especially excess phosphorus in wastewater, which leads to eutrophication. NF, NF90, NF450 and XLE membranes were studied to forecast the potential of nanofiltration and low pressure reverse osmosis in the removal of phosphorus from aquaculture wastewater. Cross-sectional morphology, water contact angle, water permeability and zeta potential of these membranes were first examined. Membrane with higher porosity and greater hydrophilicity showed better permeability. Membrane samples also commonly exhibited high zeta potential value in the polyphosphate-rich solution. All the selected membranes removed more than 90% of polyphosphate from the concentrated feed (75 mg/L) at 12 bar. The separation performance of XLE membrane was well maintained at 94.6% even at low pressure. At low feed concentration, more than 70.0% of phosphorus rejection was achieved using XLE membrane. The formation of intermolecular bonds between polyphosphate and the acquired membranes probably had improved the removal of polyphosphate at high feed concentration. XLE membrane was further tested and its rejection of polyphosphate reduced with the decline of pH and the addition of ammonium nitrate.

Key words | aquaculture, low pressure reverse osmosis, nanofiltration, phosphorus

INTRODUCTION
Excess phosphorus in wastewater leads to eutrophication, causing degradation of aquatic habitats, mass mortality of aquatic populations and imbalance of aquatic ecosystems. Raw domestic wastewater generally contains between 6 and 8 mg/L of total phosphorus; while concentration in municipal wastewater can be reduced to 3 or 4 mg/L of phosphorus after conventional treatment (Ragsdale 2007). As for industrial sources, phosphates usually originate from fertilizer manufacturing plants, food industry and also pulp and paper mills. In developing countries, agriculture and aquaculture activities provoke phosphorus pollution due to the disposal of animal manure, excess fertilizer and soil erosion. Approximately 10.5–15.2 million tons of phosphorus have been produced worldwide annually from these industrial, agriculture and aquaculture activities (UNEP 2005).

Aquaculture is the cultivation of marine and freshwater organisms such as fish, shellfish and even plants, ranging from land-based to open-ocean production. Aquaculture production has continuously shown a strong annual growth rate of 6.1%, from 34.6 million tons in 2001 to 55.7 million tons in 2009 (FAO 2011). The bloom of aquaculture especially in developing countries has raised deep concern about nutrient pollution. This is because aquaculture effluents are known to be a significant source of nitrogen and phosphorus pollution for the receiving streams (Gowen et al. 1990). Research based on trout facilities reported that 30–84% of the total phosphorus discharged from fish farms originates from uneaten food and carcass debris (Foy & Rosell 1991; Bergheim et al. 1993; Cho & Bureau 2001). Phosphorus generated from fish farming is either discharged with the effluent or settled at the bottom of the pond (Lefrançois et al. 2010). Typical phosphorus concentrations in wastewater from aquaculture facilities range from 0.06 to 80 mg/L (Mortula & Gagnon 2007).

Stringent water quality standards for phosphorus in wastewater have been initiated in many developed countries. A total phosphorus limit of 1–2 mg/L has been applied under European regulations (Lesjean et al. 2005).
while a guideline value of 0.3 mg/L has been implemented in Sweden (Tykesson & la Cour Jansen 2005). The United States Environmental Protection Agency has also stated that phosphates content in effluent should not exceed 0.05 mg/L for streams discharged into lakes or reservoirs (Ragsdale 2007). Thus, phosphorus removal technologies such as physical, chemical and biological techniques are currently of great interest. Physical treatment involves the filtration of particulate phosphorus while chemical treatment involves the precipitation of phosphorus. The latter method is more effective in phosphorus removal, but the use of a great amount of chemicals and the production of sludge remain the major disadvantages (Mook et al. 2012). Biological treatment has been widely studied for aquaculture wastewater because microorganisms can accumulate large amounts of phosphorus in the form of polyphosphate granules under aerobic conditions. Although enhanced biological phosphorus removal has shown more than 90% removal of phosphorus-rich effluent (60–100 mg P/L), the process remains operationally unstable with sudden reductions in phosphorus removal. Conventional methods for removing nitrogenous compounds from aquaculture effluent such as fluidized sand biofilters have only exhibited 41% phosphorus removal, while the wetlands have shown not more than 71% phosphorus removal (Lin et al. 2002; Davidson et al. 2008).

For small aquaculture facilities, biological treatment may not be suitable because of its complexity, cost and time involved (Mortula & Gagnon 2007). A simple pressure driven process, membrane filtration shows great potential for aquaculture industry. Phosphorus removal using membrane separation has been studied by few researchers but the studies mainly focused on wastewater from pulp and paper mills (Leo et al. 2011) or municipal waste (Acero et al. 2010a, b) that contain low phosphorus concentration. Separation performance of nanofiltration and low pressure reverse osmosis membranes in phosphorus-rich solution remains uncertain. In this work, phosphorus-rich solution is filtered using nanofiltration and low pressure reverse osmosis membranes in order to evaluate the potential of phosphorus reduction using membranes. Comparisons were made not only based on the phosphorus rejection, but the permeability and flux decay ratio were also accounted for. Membranes were characterized to understand the differences in the separation behavior. Besides the initial phosphorus content, the effects of solution pH and nitrogenerous compounds on membrane performance were studied as well.

**MATERIAL AND METHODS**

The contact angle between the water and the membrane surface was measured with a contact-angle measurement apparatus after the membranes were dried overnight. The instrument used was a Rame-Hart model 200 standard contact angle goniometer with DROPimage Standard Software with an accuracy of ±0.1°. The media used for contact angle measurement were ultrapure water and air at ambient temperature (22–23 °C). Zeta potential of the membrane surface was determined using ZetaCad (CAD Instruments, France). The membranes were immersed in aqueous solution containing phosphorus for 24 h before measurement.

Membrane permeability was determined using ultrapure water at room temperature. Permeation studies were carried out using a dead-end stirred cell, Sterlitech HP4750 (Sterlitech Corporation, WA) with an active membrane area of 14.6 cm². Permeability of the membranes was tested in the pressure range of 3–12 bar after compaction under nitrogen gas. Sodium tripolyphosphate (Sigma Aldrich) was then added to the ultrapure water in order to study the separation performance of the commercial membranes. The phosphorus content of permeate was measured using HACH spectrophotometer DR5000. To study the effects of pH, acid hydrochloride, HCl (Merck) was added to the feed solution containing phosphorus. Additionally, ammonium nitrate (Sigma Aldrich) was also added to the feed solution in order to investigate the effects of nitrogen content which may exist in aquaculture wastewater. The filtration experiments were repeated at least three times using fresh membranes. The flux decay patterns were analyzed to compare the fouling potential of membrane samples. Flux decay ratio was used to compare the membrane performance.

\[ \text{Flux decay ratio} = \frac{\text{Flux of pure water, } J_0 - \text{Flux of solution, } J}{\text{Flux of pure water, } J_0} \]  

(1)

**RESULTS AND DISCUSSION**

**Membrane characterization**

Phosphorus occurs in wastewater as organically bound phosphates, orthophosphates (H₂PO₄⁻, HPO₄²⁻, PO₄³⁻) and polyphosphates. Polyphosphates including sodium tripolyphosphate (Na₅P₃O₁₀), sodium hexametaphosphate (Na₆(PO₃)₆), and tetrasodium pyrophosphate (Na₄P₂O₇)
can gradually hydrolyze into orthophosphate. The hydrolysis of sodium tripolyphosphate \( \text{(Na}_5\text{P}_3\text{O}_{10}) \) into orthophosphate, however, is incredibly slow in near neutral solution (pH 7–8) without the presence of microbial catalysis. The predicted half-life of tripolyphosphate is in the order of years (Zinder et al. 1984). Thus, removal and reuse of polyphosphate such as sodium tripolyphosphate with molecular weight (MW) of 367.8 g/mol using nanofiltration membranes with molecular weight cut off (MWCO) of 200–300 Da or with low pressure reverse osmosis membranes is highly potent after pretreatment of aquaculture wastewater. In addition, nanofiltration or reverse osmosis can be used to recover polyphosphate in the activated sludge from the enhanced biological phosphorus removal system.

Several types of nanofiltration membranes were selected based on the supplier’s recommendation. Separation characteristics of the selected membrane (NF, NF90, NF245 and XLE) were tabulated in Table 1. The information was obtained from the membrane supplier, Filmtech™. NF and NF245 membranes are commonly used for water softening and they are able to remove 99.0% of MgSO\(_4\) with concentration of 2,000 ppm, but NF245 membrane offers higher permeability compared to NF membrane. NF90 membrane is designed for removal of salts, nitrate, iron and organic compounds such as pesticides and herbicides while XLE membrane offers lower operating pressure for municipal and industrial water applications.

From the measurement of water contact angle on membrane samples, NF245 and NF membranes showed low water contact angle while NF90 and XLE membranes exhibited great water contact angle (Table 2). Membranes with low water contact angle are preferable in aqueous filtration as hydrophilic membranes generally demonstrate great water permeability and slight fouling of organic compounds. A lower water contact angle indicates greater surface hydrophilicity which allows hydrogen bonding with water instead of hydrophobic organic foulants. The highest water permeability was achieved using hydrophilic NF membrane as shown in Table 2. Based on the previous report (Dolar et al. 2012), the pore-size distribution of NF membrane is bimodal specifically showing small pores sized around 1.04 nm and large pores sized between 1.3 and 2.1 nm. The large pores may have further contributed to the great permeability of NF membrane. XLE membrane with lower water contact angle showed higher water permeability than NF90 membrane even though the reported pore size of XLE membrane (0.89 nm) is slightly smaller compared to NF90 (0.90 nm) (Dolar et al. 2012). NF245 membrane with the lowest water contact angle in this study, however, displayed much lower water permeability than NF membrane. Water permeability of NF245 membrane is only slightly higher than XLE and NF90 membranes. Besides surface energy, membrane roughness and porous structure actually affect water contact angle on the membrane surface.

### Table 1 | Membrane separation characteristics reported by Filmtech™

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Permeate flux (m(^3)/m(^2).day)</th>
<th>Separation performance</th>
<th>Feed conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF</td>
<td>1.08–1.61</td>
<td>99.0% removal of MgSO(_4)</td>
<td>2,000 ppm MgSO(_4) feed; 896 kPa feed pressure; 25 °C</td>
</tr>
<tr>
<td>NF90</td>
<td>0.76 (NaCl)</td>
<td>85–95% removal of NaCl</td>
<td>2,000 ppm NaCl or 2,000 ppm MgSO(_4); 483 kPa feed pressure; 25 °C</td>
</tr>
<tr>
<td>NF245</td>
<td>2.12–2.93</td>
<td>99.0% removal of MgSO(_4)</td>
<td>2,000 ppm MgSO(_4) feed; 896 kPa feed pressure; 25 °C</td>
</tr>
<tr>
<td>XLE</td>
<td>1.34–1.67</td>
<td>98.7% removal of NaCl</td>
<td>2,000 ppm NaCl; 862 kPa feed pressure; 25 °C</td>
</tr>
</tbody>
</table>

### Table 2 | Membrane characteristics

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (°)</th>
<th>Zeta potential (mV)</th>
<th>Permeate flux (m(^3)/day.bar)</th>
<th>Decay ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.5 mg/L TP</td>
<td>75 mg/L TP</td>
<td>0.5 mg/L TP</td>
</tr>
<tr>
<td>NF</td>
<td>17.2</td>
<td>–7.70</td>
<td>–41.33</td>
<td>0.2483</td>
</tr>
<tr>
<td>NF90</td>
<td>83.4</td>
<td>–7.46</td>
<td>–29.70</td>
<td>0.1158</td>
</tr>
<tr>
<td>NF245</td>
<td>11.0</td>
<td>–10.10</td>
<td>–34.53</td>
<td>0.1583</td>
</tr>
<tr>
<td>XLE</td>
<td>70.9</td>
<td>–4.14</td>
<td>–44.76</td>
<td>0.1271</td>
</tr>
</tbody>
</table>
A membrane with low contact angle may show low permeability due to low porosity or small pore size. In general, in the literature the observed water permeability pattern is similar to the reported flux pattern during the separation of inorganic salt (Dolar et al. 2012) but different from the supplier’s information (Table 1). NF exhibited the highest flux followed by XLE and NF90, in agreement with Dolar and co-workers’ work (Dolar et al. 2012). Nevertheless, NF245 showed relatively low water permeability compared to the supplier’s data. The dissimilarity may be due to different compaction pressure and experimental setup. There is also the possibility that NF membrane experienced fouling in salt separation, thus showing much lower permeability than NF245 membrane in the supplier’s data compared to the measured water permeability in this study.

Nanofiltration membranes are slightly charged in aqueous solution due to the dissociation of surface functional groups or the adsorption of charged solutes. The liquid layer covering the membrane surface exists as Stern layer where the adsorbed charged solutes are strongly associated, followed by a diffuse layer where the adsorbed charged solutes are less firmly bound. Zeta potential is the potential between the diffuse layer and bulk solution, giving an indication of the membrane charge effects during nanofiltration. Zeta potential of the acquired membranes in this study was measured and presented in Table 2. All the membrane surfaces are generally negatively charged in polyphosphate solution. Membrane samples also commonly showed relatively low zeta potential value in the aqueous solution containing low concentration of polyphosphate but high zeta potential value in the polyphosphate-rich solution. Phosphorus concentration obviously affects the membrane surface charge which controls the rejection of polyphosphate. Besides sieving effects, the rejection of polyphosphate is expected to be improved by the enhancement of electrostatic effects at high concentration of phosphorus.

**Phosphorus removal**

As shown in Figure 1(a), all the selected membranes removed polyphosphate more than 90% from phosphorus-rich solution (75 mg/L) at 12 bar. Using XLE membrane, phosphorus content could be reduced to 3.45 mg/L which is close to the European regulations (1–2 mg/L). Multistage filtration is suggested for stringent water standards. The separation performance of XLE membrane was well maintained at 94.6% at 3 bar but only 65.4% of phosphorus rejection was achieved using NF membrane at the very low operating pressure of 3 bar. Phosphorus removal ability of NF90 membrane is slightly affected by pressure but not NF245 membrane. A change of rejection as high as 16.3% was observed for NF245 membrane at 3 bar. This observation may be related to the membrane characteristics, particularly pore-size distribution and surface energy as the charged solutes could be removed by sieving and Donnan effects.

XLE membrane not only exhibited the highest zeta potential value, but also much smaller pore size compared to the other membranes. Although surface energy of NF membrane is higher than NF245 and NF90 membranes, the large secondary pores reported by others (Dolar et al. 2012) obviously have encouraged the passage of polyphosphate molecules. Supplier data and the literature do not contain much information on the pore-size distribution or MWCO of NF245 membrane. NF245 membrane with higher zeta potential exhibited slightly lower phosphorus removal compared to NF90 membrane at low pressure.
NF245 membrane removed slightly more phosphorus than NF90 membrane at high pressure. According to Ratanatamskul et al. (1996), transmembrane pressure affects anion rejection of nanofiltration membrane significantly if the membrane pore size is less tight. Hence, it is proposed that MWCO of NF245 membrane is relatively higher than MWCO of NF90 membrane. Similar explanation may also be applied for the variation of phosphorus rejection of NF membrane under increased pressure.

During the filtration of phosphorus solution containing low concentration of sodium tripolyphosphate (0.5 mg/L), XLE membrane remained the most appropriate membrane for phosphorus removal as shown in Figure 1(b). Phosphorus content as low as 0.118 mg/L could be achieved, fulfilling water standards in Sweden but not in the United States. More than 70.0% phosphorus rejection was achieved using XLE membrane for pressure not lower than 6 bar. Beyond 6 bar, the separation performance NF245 membrane was well maintained above 65.0% which is higher than NF90 membrane. NF membrane showed unacceptable separation ability with only phosphorus removal range of 14–58.4%. The observed phosphorus removal at low feed concentration contradicted the literature (Mohammad et al. 2007; Leo et al. 2011) as anion rejection generally improved with the reduction of feed concentration. As reported by other researchers, Donnan potential for electric repulsion becomes more effective when fewer anions are available in the feed concentration. The contradiction can be only explained by the formation of intermolecular bonds between polyphosphate and membranes as reported by Ahmadiannamini et al. (2010). In their work, the rejection of HPO$_4^{2-}$ anion was improved at high salt concentration, which was probably due to the irreversible crosslinking of poly(diallyldimethylammonium) chloride (PDDA) with phosphate.

NF and NF90 membranes are expected to be easily fouled among the tested membranes. This is because nearly 40% of membrane flux decayed during the removal of polyphosphates using NF and NF90 membranes (Table 2). The fouling potential of these membranes is relatively independent of surface energy. Although surface electrostatic properties and zeta potential promote fouling, fouling mechanisms also involve pore constriction, intermediate pore blocking, complete pore blocking and cake formation which depend on more factors such as hydropobicity and membrane pore size. Zeta potential of NF membrane in polyphosphate-rich solution is high but its water contact angle is relatively low. Thus, the high decay ratio of NF membrane was probably contributed to by electrostatic interaction between NF membrane and sodium tripolyphosphate. Unlike NF membrane, the high decay ratio of NF90 membrane was induced by the low hydropobicity instead of the electrostatic interaction. NF245 and XLE membranes show impressive removal of polyphosphate with acceptable decay ratio as observed in Table 2. NF245 membrane exhibited only near 10% of flux decay ratio, most likely due to its high hydophobicity.

**Further separation study of XLE membrane**

XLE membrane was further studied for phosphorus removal due to the excellent rejection of polyphosphate.
With pH adjustment, the separation performance of XLE membrane was greatly reduced as shown in Figure 2. Less than 70% of polyphosphate was rejected in acidic or near neutral solution; even concentration of sodium tripolyphosphate was as high as 75 mg/L. The rejection of polyphosphate increased with increasing pH, which is similar to the variation of zeta potential measured at varied pH (Figure 2). The zeta potential value of XLE membrane is compatible with the literature (Xu et al. 2006; Azari & Zou 2012), reporting an increment in the negative effective membrane charge at higher pH. The significant increment of rejection and membrane charge at pH 9 may be attributed to the dissociation of sodium tripolyphosphate as the reported $pK_a$ value for sodium tripolyphosphate was 9.25 (Hoshino et al. 2005).  

Besides pH, a small amount of ammonium nitrate induced significant loss of phosphorus removal using XLE membrane. Concentration of ammonium nitrate as low as 0.05 mg/L in polyphosphate-rich solution with 75 mg/L of sodium tripolyphosphate caused nearly 15.3% reduction in phosphorus rejection as shown in Figure 3. Similar reduction was observed when 2 mg/L of ammonium nitrate was added to the solution containing 0.05 mg/L of polyphosphate. The highest phosphorus rejection of 61.9% was achieved using XLE membrane. The dramatic reduction of membrane separation performance may be explained by the membrane charge shielding caused by the great amount of cation. Besides that, anion selection based on hydrated size may contribute to the reduction of polyphosphate removal (Paugam et al. 2004).

**CONCLUSION**

XLE membrane with lower water contact angle showed higher water permeability than NF90 membrane even though the reported pore size of XLE membrane (0.89 nm) is slightly smaller compared to NF90 (0.90 nm). All the selected membranes removed polyphosphate more than 90% from phosphorus-rich solution (75 mg/L) at 12 bar. The separation performance of XLE membrane was well maintained at 94.6% for concentrated feed and more than 70.0% of phosphorus rejection was achieved using XLE membrane for diluted feed. The formation of intermolecular bonds between polyphosphate and membranes probably has improved the removal of polyphosphate at high feed concentration. XLE membrane was further studied and it was observed that the rejection of polyphosphate increased with increasing pH. This observation concurs with the variation of zeta potential measured at varied pH. With the addition of ammonium nitrate, separation performance of XLE membrane was significantly reduced. The reduction may be explained by the membrane charge shielding due to the great amount of cation and anion selectivity. Low pressure reverse osmosis membrane, XLE, has great potential in polyphosphate separation after removing nitrate from aquaculture wastewater. The concentrated phosphorus solution is useful as fertilizer.

**ACKNOWLEDGEMENTS**

The authors would like to thank Universiti Sains Malaysia for the financial support for this research (Short Term...
Grant 304/PJKIMIA/60311016). The authors also wish to express their appreciation to Ms Low Ee Mee for proof-reading this manuscript.

REFERENCES


Ragsdale, D. 2007 Advanced Wastewater Treatment to Achieve Low Concentration of Phosphorus. EPA 910-R-07-002, United States Environmental Protection Agency, Seattle, WA.


Tykesson, J. L. & la Cour Jansen, J. 2005 Experience from 10 years of full-scale operation with enhanced biological phosphorus removal at Oresundsvetket.


First received 19 July 2012; accepted in revised form 25 September 2012