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The potential of a polysulfone (PSF) nanofiltration membrane as the end stage treatment technology of aquaculture wastewater

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ABSTRACT

Aquaculture produces considerable quantities of organic matter, ammonia, and phosphorus during cultivation processes. Aquaculture waste left without proper treatment may cause deterioration to the water quality inside the pond or receiving water. The polysulfone (PSF) membranes were prepared via a dry/wet phase inversion technique and were analyzed to determine their potential for aquaculture wastewater treatment. The results indicate that the tailored membranes have a good quality permeate which can retain up to 66% ammonia, 85% total ammonia (TAN) and 95% phosphorus with high flux permeability (0.499–0.712 L/m^2.h). This promising result was observed at pH 6 with a 6-bar applied pressure. It was also found that by altering the pH, the membrane surface charge changed. Furthermore, membrane surface charge plays an important role in the enhancement of membrane performance. This study indicates that membrane technology has high prospective as a tertiary treatment for aquaculture wastewater and helps to elevate aquaculture production quality.

Keywords: Ammonia; Aquaculture; Polysulfone membrane; pH; Surface charged

1. Introduction

Aquaculture is superficially presented as a clean industry. Nevertheless, as with other forms of intensive animal production, intensive aquaculture systems can produce large quantities of polluting wastes. Aquaculture wastes consist primarily of uneaten fish feeds, fecal and other excretory wastes, which are sources of nutrient pollution such as carbon-based organic matter, nitrogen and phosphorous compounds. Ammonia can promote undesirable algal growths in the water bodies. Furthermore, a relatively small amount of ammonia exceeding the maximum lethal concentration in the water can be detrimental to the aquatic life. High nutrient levels can stimulate blooms of phytoplanktons or algae populations. When algae die in large numbers, their subsequent degradation can drastically reduce oxygen levels in water, stressing or killing fish and other organisms. Oxygen depletion may not be the most harmful effect of nutrient-stimulated phytoplankton growth: blooms of toxic algae species can produce huge fish kills, contaminate shellfish, and potentially even pose a health hazard to humans. Preliminary evidence suggests that such blooms may be promoted by nutrient pollution from various sources.

Many studies have been conducted to examine the aquaculture wastewater treatment efficiency of differ-

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ent types of biofilters: trickling filters, submerged filters, rotating media filters, fluidized bed filters, low-density media filters [1–5] and continuous bioreactors using immobilized alginate beads [6] have all been evaluated in pilot scale treatment systems with varying degrees of success. The defects of biofilters are also obvious, which include excessive sludge production, unstable performance, and nitrate accumulation.

Although several attempts have been made to develop a process for removal of dissolved nitrogen compounds in the water, no commercial process for ammonia removal is currently available [7]. All the preliminary and secondary treatment reduces the BOD levels of the sewage. Tertiary treatment is employed when specific wastewater constituents not removable by secondary treatment must be removed. This includes removal of nitrogen, phosphorus, additional suspended solids, refractory organics, heavy metals and dissolved solids.

Nanofiltration (NF) membrane is an emerging technology classified between those of ultrafiltration and reverse osmosis membranes leading to a wide range of applications. These include water softening, removal of natural organic matter, drinking and industrial water production, food processing and wastewater treatment. Since the applications are diverse, the feed solutions have different compositions, pH values as well as foulant contents. Nanofiltration membranes have been used for separation of aqueous solutions containing electrolytes. Both steric (sieving) and electrostatic (Donnan) partitioning effects between the membrane external solutions are separation mechanism involved in NF membrane. This mechanism allows NF membranes to be effective for separation of a range of organic molecule mixtures (neutral or charged) and salts [8,9]. Thus, the membrane has special performance and properties [10].

Membrane technology has the potential as an alternative option to lessen wastewater pollution. In line with the current technological development, most researchers employ commercial membrane in their studies. These commercial membranes are basically manufactured in module packaging and can only meet certain applications. Hence, a major experimentation is necessary to select the appropriate membrane which can comply with the performance standards.

In conjunction to this notion, this research is very significant to provide the information on the preparation condition and characterization details which are very functional as the tertiary stage in treating aquaculture wastewater. Based on the results, this study presents a comprehensive understanding of the optimum condition of a high selective membrane usable to treat ammonia and phosphorus in aquaculture wastewater. This research also provides a platform to produce a high-perm selective membrane with potential improvement on the membrane performance.

2. Materials and method

2.1. Materials

Polysulfone (PSF) purchased from Amoco was selected based on the chemical and physical attributes of this PSF, which include good thermal and chemical stability, mechanical strength as well as excellent oxidative resistance. The N-methyl-2-pyrrolidone (NMP) used in this experiment was sourced from MERCK Schuchardt, Germany and water was used as the non-solvent.

2.2. Dope and membrane preparation

The membranes were prepared via dry/wet phase inversion technique. The dope was prepared by liquidating 20.1% PSF in 74.4% NMP by adding 5.5% water. The dope was poured onto the glass plate and cast with 150 μm thickness. The membranes were subsequently immersed in the coagulation bath with water medium for 24 h before they were transferred into the methanol solution for another six hours to remove all residues. The fabricated membranes were left to dry in the ambient temperature.

2.3. Characterization of wastewater and membrane

2.3.1. Wastewater samples

The aquaculture wastewater samples were obtained from the fish wastewater at the hatchery pond of the Department of Fisheries, Universiti Malaysia Terengganu (UMT). The volume of water inside the pond is 0.71 m^3 consisting of 10–15 catfish with age ranging from five to six month with an average weight of 0.4 kg each. The sample was taken at the discharge point after pass through a sand filter. The raw aquaculture wastewater characteristics are presented in Table 1. The wastewater quality characteristics were analyzed by using the standard method and digestion technique determined by a Hach spectrophotometer (Hach 2500 Model).

Table 1
Characteristics of the aquaculture wastewater

Characteristics	Concentration
pH	6.81
Turbidity, NTU	101
Total suspended solids, mg/L	65.9
Ammonia nitrogen, mg/L	82.7
Phosphorus, mg/L	71.7
Total ammonia nitrogen (TAN), mg/L	75
Biological oxygen demand (BOD), mg/L	7.4
Nitrate, mg/L	0.455
Nitrite, mg/L	5.29
Copper, mg/L	0.14
Zinc, mg/L	1.05
Manganese, mg/L	6.81

2.3.2. Membrane performance analysis

The experiments were carried out in a dead-end permeation cell SterlitechTM HP4750 stainless steel. The tailored membranes were cut into circular shapes 14.6 cm^2-wide and placed in the dead-end permeation cell. The feed pressure imposed onto the membrane using nitrogen gas was controlled within the range of 6–10 bar. The pure water flux is calculated by Eq. (1):

$$J_v = \frac{V}{t \cdot A \cdot \Delta p} \quad (1)$$

where V is the volume (L) of permeate collected; J_w is the water flux (L/m^2.h); ΔT is the sampling time (h); and A is the membrane area (m^2). The permeability coefficients calculated by the statistical linear regression of volume flux J_v vs. applied pressure, $J_v = P_m \Delta P$. The salt solution was conducted using NaCl solution by using a Cyberscan 510 conductivity meter. The rejection percentage was calculated using Eqs. (2) and (3), which involved the value of feed (C_f), permeate (C_p) and retentate (C_r) conductivity.

Percentage of rejection:

$$R_{obs} = 1 - \left(C_p / C_b\right) \quad (2)$$

$$C_b = \left(C_f + C_r\right) / 2 \quad (3)$$

Subsequently, the fabricated membrane was analyzed by using aquaculture wastewater samples. The collected permeate was analyzed by using Hach method via spectrophotometer. The percentage of rejection was computed using Eq. (4) below.

$$R(\%) = \left[1 - \left(C_p\right) / \left(C_f\right)\right] \times 100\% \quad (4)$$

where C_f and C_p are concentrations of solute in the feed and permeate respectively.

2.3.3. Morphology structure

The membrane structures were characterized using the Scanning Electron Microscopic (SEM) model JSM 6360 LA. The specimens were characterized due to its membrane morphology such as the skin layer, pores structure, and surface porosity. The samples were fractured in liquid nitrogen to produce unformed structure on the cross-section surface.

2.3.4. Surface charged analysis

The zeta potential value measurement of fabricated membranes was conducted via an Electrokinetic Analyzer (EKA) unit available at the Environmental Technology Laboratory of UMT. Two pieces of membrane samples from each formulation were cut into 12.7 cm × 5.1 cm dimensions and mounted into rectangular-shaped measuring cell. Potassium chloride (KCl) at a concentration of 0.01 M was used to obtain the streaming potential value across the membrane surface. The output of the EKA unit was in terms of ZP value in mV.

3. Results and discussion

3.1. Pure water permeability

The pure water permeability (PWP) analysis was conducted by using distilled water with applied pressure between 6–10 bar. The PWP data are depicted in Fig. 1. It illustrates that the PWP is inversely proportional with the applied pressure. A linear function was obtained whereby the flux increased as the feed pressure was increased. This linear function showed that the produced membrane were stable in producing flux.

3.2. Sodium chloride (NaCl) rejection performance

The NaCl separation performance seemed to be deteriorating with the increase of pressure as tabulated in Table 2. The NaCl rejection percentage was in the range of 29.49–20.76%. With the increase of pressure applied, the rejection percentage decreased. According to [11], the maximal rejection value could not be reached at high membrane pressure. This stimulated the reduction of the NaCl rejection with the increase of applied pressure. A low applied pressure caused a lower flux to pass through

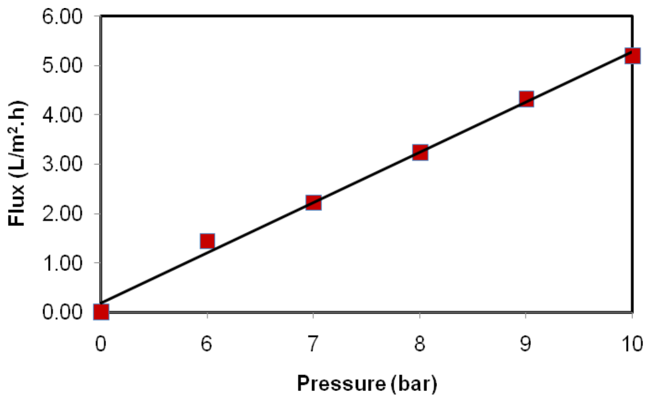

Fig. 1. Pure water permeation vs. pressure.

Table 2
NaCl separation data

Pressure (bar)	Flux (L/m^2.h)	Rejection (%)
6	2.23	29.49
7	2.25	27.15
8	2.35	24.69
9	2.56	23.55
10	2.77	20.76

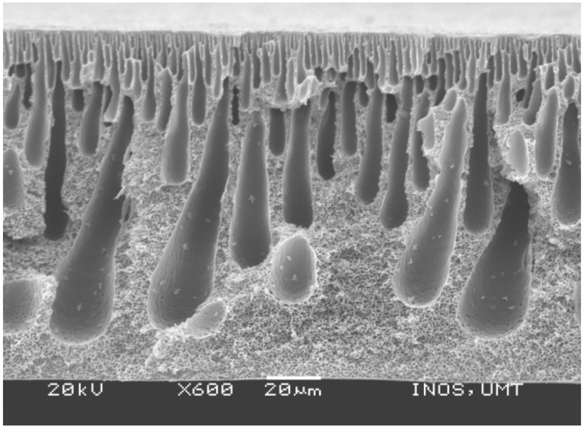

Fig. 2. SEM image of fabricated membrane.

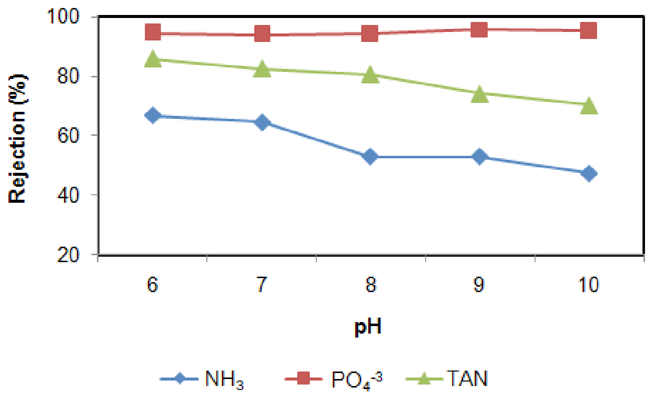

Fig. 3. Rejection of TAN, NH_3 and PO_4^{3-} at different pHs.

the membrane which caused high rejection percentage. However, it can be clearly seen that the fluxes increased with the increase of pressure. Increasing the pressure applied would increase the flux rate, thus increasing the transmission of the NaCl ions, which in the end resulted in a lower rejection at high pressure applied.

3.3. Membrane morphology

In order to analyze the membrane morphology, the cross-section of the NF membranes was observed via scanning electron microscopy as illustrated in Fig. 2. It can be seen that the tailored membrane had an asymmetric structure consisted of dense top layer and porous support structure and was occupied by a fingerlike structure lead from top to bottom of the sub layer. The bottom part of the support layer demonstrated a denser sponge structure.

3.4. Evaluation of separation performance of aquaculture wastewater

As can be seen in Table 1, there were 11 parameters of the wastewater characteristic analyzed. However, only three of the parameters [total ammonia nitrogen (TAN), phosphorus (PO_4^{3-}) and ammonia (NH_3)] were selected for further analysis based on the fact that their excessive existence in the environment promotes a severe environmental problem. The concentration for these parameters was comparatively higher than the standard quality requirement for aquaculture wastewater. Therefore, membrane treatment had been applied to treat this aquaculture wastewater since conventional treatment had previously been proven to have some downsides such as high production of sludge as well as large land area requisite.

3.4.1. Effect of pH

The separation process in the NF membrane is a combination of sieving and diffusion of molecules through the selected layer of the membrane. The surface charges play an important role in the separation by NF than other pressure-driven membrane processes, thus if two NF membrane surfaces have different surface charge patterns, they should show different ion retention at different pHs [12].

In aquaculture wastewater treatment, pH plays an important role in partitioning TAN producing NH_3 and NH_4^+. Hence, pH is strongly suspected to be the key parameter for the removal of TAN and NH3. Fig. 3 illustrates the rejection of TAN, ammonia and phosphorus at different pHs in the range of 6–10.

Fig. 3 represents the retention of TAN and the fraction of TAN, which is presented as free ammonia (NH_3) by NF21-E. At pH 6, the retention of TAN was 85%. It is noted that at pH 7, the retention of TAN correspondingly decreased. As the pH value was raised to 10, the TAN rejection decreased to 70%. The remarkable phenomenon may be due to the fact that some of the NH_4^+ may have been converted in the attempt to reach the equilibrium [13] thereby increasing the free ammonia (NH_3) concentration in the feed. As stated previously, this occurrence was probably linked to the influence of pH to the surface charge. The pH dependence on zeta potential is demonstrated in Fig. 4. The remaining NH_4^+ has been positively charged, thus when the ions interacted with the negatively charged membrane, they were attracted to each other and tended to decrease the TAN retention.

Furthermore, at pH 6, the ammonia retention was 66%. However, as the pH elevated to 7, the retention of ammonia started to decrease. At pH 8, the ammonia rejection notably decreased to 53% and when the pH increased to 10, the rejection of ammonia reduced to 47%. This could be attributed to the weak interaction of the free ammonia with the membrane surface since it has no charge. Likewise, upon reaching equilibrium, the free ammonia concentration increased. Since ammonia has no charge and is very small, it has less difficulty diffusing through the membrane.

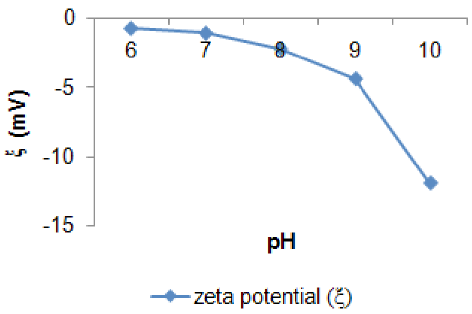

Fig. 4. The zeta potential of NF21-E at different pHs.

In Fig. 4, the results show that the surface of the PSF membrane in contact with the KCl solution at different pHs presented a small negative charge, which enabled the decrease of the hydrophobic character of polysulfone [14]. The charge can be slightly decreased by specific adsorption of anions. The pH dependence for zeta potential is as illustrated in Fig. 4. In the pH range of 6–10, the membrane is negatively charged. The anion adsorption also played a major role in the charge formation of the nanofiltration membrane [15]. The surface would be positive at low pH values. The solutes with higher anionic charged density or with low cationic-charged densities are rejected easily [10]. As the pH increased, the membrane had a negative charge. In this case, the dominant form of nitrogen compound is free ammonia (NH_3), an uncharged molecule difficult to be rejected by membrane [16]. This explains the findings that the retention of NH_3 was lower.

However, for alkali pH, the TAN retention decreased as the pH increased. The negative charge of the membrane grew when the pH increased, which was similar to the finding reported by [17]. TAN has high cationic-charged density, thus when it interacted with the negatively-charged membrane, the ions tended to draw towards each other, which consequentially promote the transmission of TAN through the membrane and reduce the TAN rejection percentage.

The phosphorus retention remained higher (up to 95%) and did not present any clear tendency with respect to the pH, which was similar to the finding reported by [13]. This could be due to the phosphorus ions (PO_4^{3-}) that contain a high anionic charged density. The rise in the pH leads to the rise of the membrane's negative charge and as a consequence, the retention of phosphorus remains high at every pH.

Ensuing from that, the zeta potential could be used to characterize the membrane. In fact, small differences in the membrane material due to fabrication process as well as hydration state of the polymeric membrane material may modify the streaming potential values, as reported by [18].

The finding showed that the membrane electrostatic properties can be managed by altering the pH since there is a strong interaction between the solute and the membrane surface charged. The optimum performance was achieved at pH 6 with high rejection of phosphorus and considerable retention of TAN and ammonia. This outcome is in line with the finding reported by [19,20] who stated that the maximal rejection is reached in more acidic condition.

4. Conclusion

The optimization process of aquaculture wastewater treatment was determined pertaining to the membrane separation performance. From the results, it can be concluded that the best condition for aquaculture wastewater treatment is at pH 6, which considerably retains the optimum retention of TAN (85%), ammonia (66%) and phosphorus (95%). These findings indicate that the membrane technology has promising prospect as end stage treatment process in aquaculture wastewater treatment, which serves as a more efficient aquaculture wastewater treatment as well as helps to improve the environmental quality.

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Symbols

C_b — Bulk concentration, mol m^{-3}
C_f — Concentration on the feed side of membrane, mol m^{-3}
C_p — Concentration in permeate, mol m^{-3}
C_w — Wall concentration, mol m^{-3}
J_v — Flux, ms^{-1}
R_{obs} — Observed rejection, %
V — Stirring speed, rad.s^{-1}

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