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Performance of thin film composite membranes for ammonium removal and reuse of ammonium-enriched solution for plant growth

Marcus Ze Yuan Lim, Woon Chan Chong, Woei Jye Lau and Chai Hoon Koo

ABSTRACT

Ammonium is known to be one of the most significant pollutants in water bodies. The presence of ammonium in water is mainly originated from agricultural activities, domestic sewage and industrial effluent. This study evaluates the performance of two commercial thin film composite (TFC) membranes, i.e., NF270 and XLE from FilmTec™ for ammonium removal using synthetic wastewater and domestic sewage. The filtration experiment was conducted at different feed ammonium concentrations, humic acid concentrations, pHs and pressure. Results showed that the membrane rejection against ammonium increased dramatically with increasing ammonium concentration. However, the membrane flux was slightly compromised at higher ammonium concentration. With respect to pH, highest ammonium removal rate was able to be achieved at an optimum pH of 10. Besides, the permeation flux increased gradually with increasing feed pressure. From the results, the XLE membrane outperformed the NF270 membrane in terms of ammonium rejection. The retentate of XLE membrane filtration process was found to be useful as liquid fertiliser for plant growth. The results indicated that the TFC membrane process is not only able to produce permeate with an ammonium concentration below the acceptable limit of 10 mg/L but also able to produce retentate with enriched ammonium for plant growth.

Key words | ammonium removal, liquid fertiliser, sewage, sustainable management, thin film composite membranes

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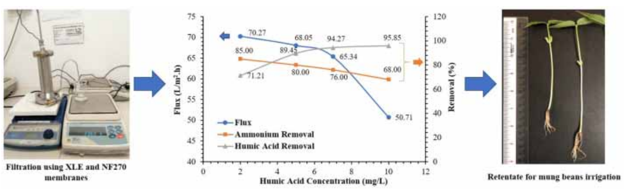
HIGHLIGHTS

- XLE membrane outperformed NF270 membrane in terms of ammonium rejection.
- Filtration conditions affected the ammonium rejection and permeability of the membrane.
- Retentate of membrane filtration was useful as liquid fertiliser for plant growth.
- The findings contribute towards the sustainable management of sewage treatment plant.

GRAPHICAL ABSTRACT



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INTRODUCTION

The inclining requirement for fresh and potable water is highly acknowledged due to the accelerated expansion of global population associated with the advancement of urbanization and industrialization. Water pollution and inadequacy of drinkable water access have posed a great threat towards the water security of living organisms on a global scale. Ammoniacal-nitrogen (NH_3-N) is one of the most significant pollutants in water bodies (Liu *et al.* 2017). The presence of the ammonium in water sources is mainly caused by agricultural activities, domestic sewage and rubber/food processing. The seeping of high concentrations of ammonium into the water bodies promotes the eutrophication process, which depletes the dissolved oxygen in water and threatens aquatic life (Chong *et al.* 2017).

As for the water pollution issues in Malaysia, a deteriorating trend can be observed for the poor river water quality detected in recent years. Fulazzaky *et al.* (2010) reported that water assessed in the Selangor River was in poor quality. The principal sources of the river pollution were identified and deemed to originate from industries, poultry farms and wet market. Al-Mamun & Zainuddin (2013) pointed out that water treatment plants (WTPs) in Cheras and Rawang in Selangor state had been forced to halt operations due to poor raw water quality and this has caused water disruption in the cities. In addition, the WTP of the Damansara River in Selangor state was forced to shut down due to polluted raw waters. A high level of NH_3-N in the river water that exceeded the drinking water intake standard of 1.5 mg/L was reported as the major pollutant contributing to the temporary shutdown of several WTPs in Johor and Selangor state over the years (Mahmood 2015; Shah 2019). Water supply disruption affects not only the resident's daily routines, but also causes economic losses. According to Abdul Aziz & Ishak (2018), one month of water supply disruption could lead to loss of 0.3–0.5% gross domestic product (GDP) of the country as this had affected the productivity of the industry and various sectors adversely. Therefore, measures must be taken by the water authority to ensure the water supply is sustainable.

As ammonium exists as a charged ion in an aqueous environment, the good characteristics of nanofiltration (NF) and reverse osmosis (RO) membranes are able to remove it promisingly. The recognition of NF and RO membranes has been vastly accepted around the globe for the promising results in producing fresh water. Kurama *et al.* (2002) reported that with the use of RO membranes (Desal-3B SE, Desalination Systems Inc.), high ammonium removal rate (96.9%) could be achieved with ammonium concentration in the permeate as low as 0.2 mg/L. As a comparison, NF membrane (N30F, DowFilmTec) was only able to remove 26.9% of the ammonium ions. Bódalo *et al.* (2005) also achieved excellent ammonium removal (98.99%) using another RO membrane (SEPA SS1C, Osmonics Inc.) when it was tested with feed solution containing 9,545 mg/L ammonium ions.

Sewage is primarily a mixture of organic substances and inorganic matter along with dead or live microorganisms. Previous studies reported that humic substances are responsible for the fouling of membranes where it could form a cake layer on the membrane surface, and hence deteriorate the membrane performance (Chong *et al.* 2019). However, the effect of humic substance present in the feed water on the TFC membrane performance in terms of ammonium rejection are rarely reported. In a typical water or sewage treatment plant, chlorine is dosed after filtration for ammonium reduction or disinfection purposes. However, the formation of nitrogenous disinfection by-products (N-DBPs) such as trihalomethanes, haloacetic acids, haloacetonitriles, bromochloroacetonitrile and trichloronitromethane are carcinogenic. The N-DBPs formed are positively correlated with the presence of dissolved organic nitrogen (DON) in the water (Ravindran *et al.* 2009; Xu *et al.* 2019; Xu *et al.* 2020). Removing these carcinogenic substances requires advanced treatment technology such as forward osmosis (Xu *et al.* 2018) and photocatalysis (Koe *et al.* 2020), but these technologies are not yet to be adopted at industrial scale. Hence, the separation of the DON from the water prior to the disinfection process is of utmost importance to reduce the formation of N-DBPs.

The retentate from membrane filtration might contain high concentrations of coonotaminants such as pathogens, heavy metals and organic pollutants (Cristina *et al.* 2020). The waste should be analysed carefully before it can be reused for plant growth. This is particular important to avoid the entry of toxic substances into the food chain. Jiang et al. (2018) found that the retentate of natural rubber wastewater from an ultrafiltration (UF) system contained an abundance of protein and could be used to produce fertiliser. Meanwhile, the retentate from the NF process was rich in quebrachitol and could be used in quebrachitol extraction. Obajdin & Košutić (2019) recommended reusing the retentate of a rendering plant from RO filtration for washing purposes, which could save up to 65% of the water consumption. A study by Körner et al. (2001) suggested that the *Lemna gibba* plant can be fed with wastewater containing high ammonium concentration with pH < 7.8. However, the plant's growth rate was reported to be slightly inhibited at very high ammonium concentration (200 mg/L).

The main objective of this work was to evaluate the performance of two commercial thin film composite (TFC) membranes; that is, NF270 and XLE, for ammonium rejection and permeation flux under various operating variables using synthetic wastewater and an industrial sewage treatment plant's effluent. The variables manipulated in this work were concentration of feed ammonium and humic acid, solution pH and operating pressure. Membrane filtration using NF and RO membranes was also performed using real sewage to determine the ammonium rejection, permeation flux and chemical oxygen demand (COD) removal. The retentate of the wastewater, comprising ammonium and humic substances, was recovered as a valuable liquid fertiliser to stimulate plant growth.

MATERIAL AND METHODS

Membrane characteristics

Two commercially available TFC membranes from FILMTEC™ – NF270 and XLE – were chosen in this study. Technical specifications of the NF270 and XLE membranes are presented in Table S1 (Supplementary Data). Both membranes consist of an active skin layer on the top, a microporous polysulfone layer in the middle and a polyester web as the structural support. The NF270 membrane is a semi-aromatic polyamide while the XLE membrane is made of fully aromatic polyamide (Do et al. 2012).

Filtration experimental setup

The filtration process was performed utilising an HP4750 dead-end stirred cell (Sterlitech™, USA). The permeability of the RO and NF membranes were evaluated in terms of permeation flux ($L/m^2 \cdot h$) at a pressure of 10 bar. The experiment was performed using distilled (DI) water or feed solution. The measurement of collected permeate was carried out at 5-min intervals with a weighing balance. Consequently, the computation of permeation flux can be done by the following equation:

$$J = \frac{Q_p}{A_m} \tag{1}$$

where J is permeation flux ($L/m^2.h$), Q_p is permeate flowrate (L/h) and A_m is membrane active surface area (m^2).

A sample of 100 mg/L of ammonium nitrogen stock solution was prepared by dissolving ammonium sulfate ($(NH_4)_2SO_4$) powder from Merck into DI water. The stock solution was preserved by keeping it in a refrigerator at 4 °C. The concentrations of ammonium in the feed solution and permeate were analysed by DR3900 spectrophotometer (HACH). The High range (HR) NH_3-N Salicylate Method was used as the standard measurement method. The wavelength for measurement was set at 655 nm for the determination of the NH_3-N. The rejection percentage, R (%) of ammonium was evaluated by applying Equation (2):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p is concentration of permeate (mg/L) and C_f is concentration of feed (mg/L).

Variation of filtration parameters

Different operating parameters such as pressure, ammonium feed concentration, solution pH and humic acid concentration are evaluated in the study. The feed solution pH was fixed at 7 for all the experiments, unless otherwise stated.

Operating pressure

By manipulating the pressure regulator connected to the gas cylinder, the desired operating pressure was obtained. Operating pressures of 8, 10 and 12 bar were adjusted in order to examine the effects of operating pressure on the membrane permeation flux and ammonium rejection. The feed solution used was fixed at 10 mg/L ammonium concentration at pH 7.

Ammonium feed concentration

100 mg/L ammonium nitrogen stock solution was diluted with DI water to obtain various concentration of 10, 20, 30 and 40 mg/L. For this study, operating pressure and solution pH were fixed at 10 bar and pH 7, respectively.

Solution pH

To study the effect of pH on the membrane performance, 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) was used for the pH adjustment. The applicable pH values were varied in the range of 2 – 10. A pH meter (Hanna HI-2550) was used for the pH measurement. For this study, operating pressure and ammonium nitrogen concentration were fixed at 10 bar and 10 mg/L, respectively.

Humic acid concentration

The concentration of HA was varied to examine the effect of natural organic matter (NOM) on the rejection of ammonium for the NF and RO membranes. HA from Merck was introduced into the ammonium nitrogen solution. For the preparation of a feed solution comprising HA, the powdered form of HA was dissolved in DI water with the aid of 0.1 M NaOH solution to produce a 0.1 g/L concentrated HA stock solution. The applicable concentrations of HA tested were varied at 2, 5, 7 and 10 mg/L. The solution pH was slowly adjusted to 7 using 0.1 M HCl prior to the rejection test. To determine the concentrations of HA in the feed solution and permeate, a UV-Vis spectrophotometer (Lambda 35, Perkin Elmer) was utilised in measuring the absorbance at 254 nm and the rejection efficiency was calculated using Equation (2).

Static adsorption test

The TFC NF and RO membranes of 0.2 g respectively were immersed in 50 mL of ammonium nitrogen solution for the static adsorption test. The test was conducted at pH values of 2 and 10 at a fixed ammonium concentration of 10 mg/L. A mechanical shaker operated at 150 rpm was used to shake the solution at room temperature for 24 h to achieve equilibrium adsorption. The ammonium adsorption was calculated using Equation (3):

$$Q_e = \frac{V(P_o - P_e)}{m} \tag{3}$$

where Q_e is ammonium adsorption (mg/g), P_o is concentration of the synthetic solution (mg/L), P_e is concentration of the residual solution (mg/L), V is volume of synthetic solution (L) and m is mass of membrane (g).

Membrane stability test

Initially, the NF270 and XLE membranes were immersed separately in strong acid (pH 1.5) and alkali solutions (pH 13.5). The permeation flux and ammonium rejection of the immersed membranes were tested weekly. After conducting the filtration tests, the membranes were re-immersed in their respective solutions. The same filtration tests were repeated weekly for up to 5 weeks.

Real sewage treatment

Real sewage sample was collected from an extended aeration pond in a local sewage treatment plant. The sewage had undergone a coagulation-flocculation process with the dosage of 60 mg/L of aluminium sulphate as the coagulant. The stirring process for the jar test was performed swiftly at 250 rpm for 3 min, continued with slow mixing at 30 rpm for 30 min. Next, the mixture was left idle for 30 min for the flocs to settle down. Subsequently, the supernatant formed was collected as the feed solution for the membrane filtration process. The feed solution was filtered using a UF membrane from Sepro Membrane (MWCO of 5000 Da) followed by the TFC membranes studied in this work. In addition to the ammonium, the COD of the wastewater was also studied. The COD was determined by the high range (HR) COD Reactor Digestion Method (Method 8000). DRB200 COD Reactor and HACH DR3900 spectrophotometer was employed for the COD test.

Metabolism test of plant with recovered retentate

Green mung bean seeds were selected as the samples in this study for the metabolism test to evaluate the effectiveness of the recovered retentate as liquid fertiliser for the plants. The metabolism test of the plants was assessed by the germination and growth of the green mung bean seeds. Green mung bean seeds were planted in a pot filled with 0.2 kg of potting soil and peat moss of the same amount. The green mung beans were irrigated with two different mediums; that is, DI water (for the control sample) and the retentate solution (ammonium concentration = 10.93 mg/L) obtained from the membrane filtration experiment. For each irrigation medium, three pots of green mung beans were planted to yield the average results. A 20 mL solution was used to irrigate the green mung bean seeds every day and adequate sunlight was readily available to the plants. The experiment ended once the initial trifoliate leaf of the controlled sample was developed. The metabolism and growth of the plants were determined by measuring the elongation and mass of the shoots and the roots of the plant (Ye *et al.* 2019).

RESULTS AND DISCUSSION

Effect of operating pressure on permeation flux and ammonium rejection

Figure 1(a) shows the overall trend of permeation flux of TFC membranes evaluated at different operating pressures. As the operating pressure inclined from 8 to 12 bar, the permeation flux increased gradually from 118.19 to 143.18 L/m^2·h and from 66.58 to 78.74 L/m^2·h for the NF270 and XLE membranes, respectively. The average permeability of NF270 and XLE membranes were 13.04 and 7.42 L/m^2·h·bar, respectively. The results were consistent with the findings by Racar *et al.* (2017). The increment of pressure would create a larger driving force, allowing more solvent to be transported through the membrane (Moradihamedani & Halim 2018). Since the NF270 membrane exhibits larger MWCO and is of greater hydrophilicity than the XLE membrane (see Table S1), it achieves higher permeation flux.

With respect to separation efficiency, the total ammonium rejection declined steadily from 40% to 31% and from 54% to 50% for the NF270 and XLE membranes, respectively when the pressure was increased from 8 to 12 bar. The XLE membrane achieved higher ammonium removal compared to that of the NF270 membrane due to its smaller and denser pore structures, which facilitated the solute retention (Diop *et al.* 2011). As the ammonium ions were adsorbed onto the membrane surface, a positively charged superficial layer was created. The negatively charged membrane surface attracted the ions of the opposite

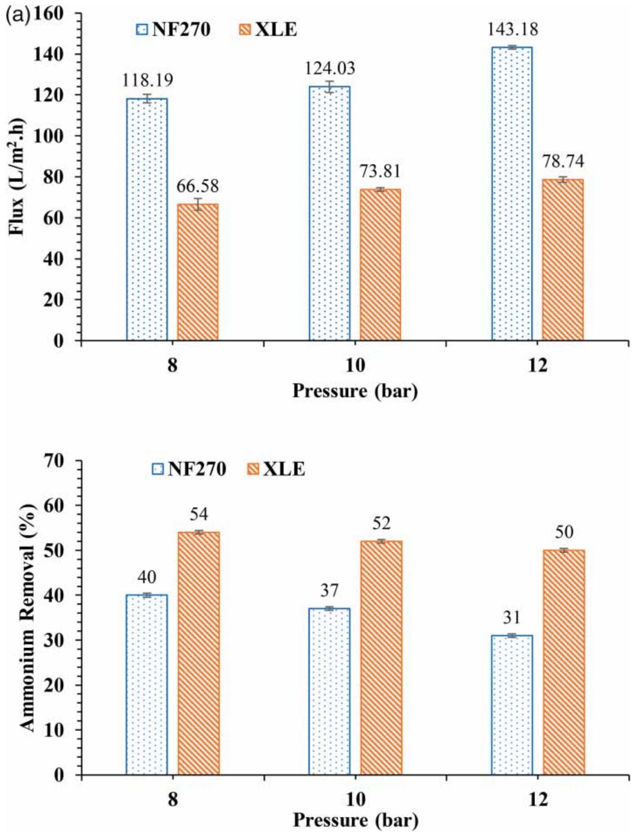
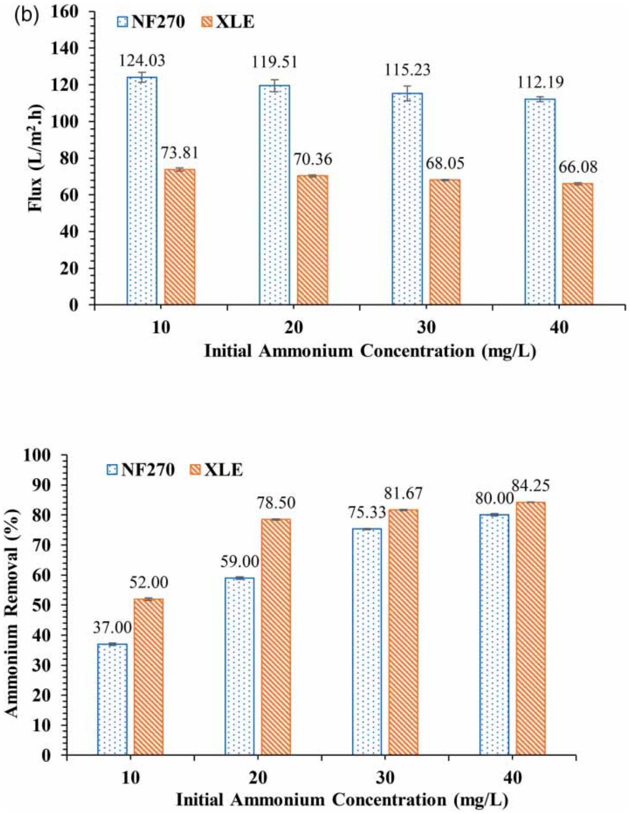


Figure 1 | (a) Effect of operating pressure on permeation flux and total ammonium removal (feed ammonium: 10 mg/L and pH: 7), (b) effect of initial ammonium concentration on permeation flux and total ammonium removal (pressure: 10 bar and pH: 7) and (c) effect of solution pH on permeation flux and total ammonium removal (feed ammonium: 10 mg/L and pressure: 10 bar) of NF270 and XLE membranes. *(Continued.)*



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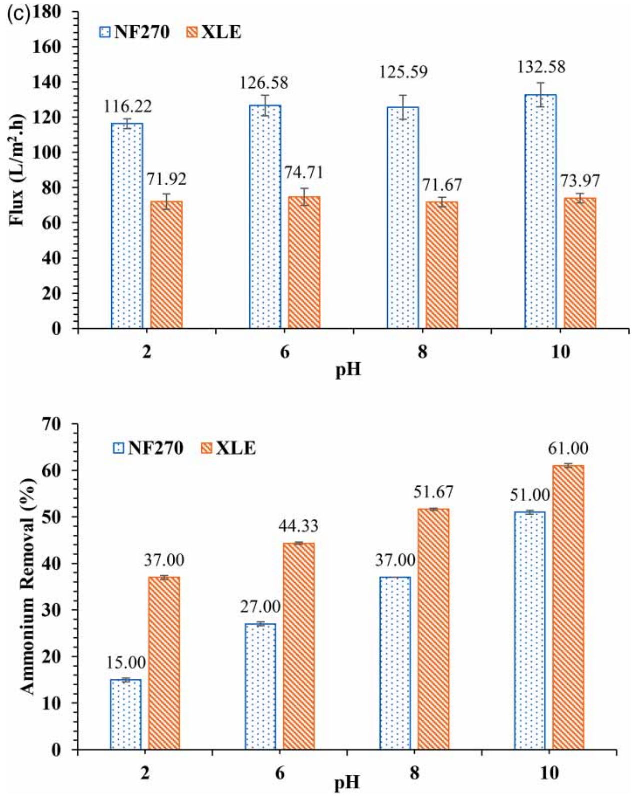

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charge. However, once the pressure inclined, the electrochemical forces were substituted by the pressure forces (Paugam *et al.* 2004). Therefore, the rejection of the ammonium ions was diminished, and more ions could permeate through the membrane.

Effect of initial ammonium concentration on permeation flux and ammonium rejection

Figure 1(b) presents the effect of initial ammonium feed concentration on the performance of NF270 and XLE membranes. As can be seen, the permeation flux of NF270 and XLE membranes decreased steadily from 124.03 to 112.19 L/m^2·h and from 73.81 to 66.08 L/m^2·h, respectively with increasing ammonium feed concentration inclined from 10 to 40 mg/L. The obtained results were consistent with the findings of Bódalo *et al.* (2005) whereby the permeation flux decreased by 16.67% as the ammonium feed concentrations increased from 0.055 to 9.545 kg/m^3 using a cellulose acetate RO membrane. The difference in the permeation flux between the membranes was correlated well to their respective pure water permeability. One of the reasons for the higher permeation flux of the NF270 membrane could be due to its larger MWCO compared to the XLE membrane. This reduced the transport resistance of water molecules and increased water permeability. Besides MWCO, Vrijenhoek *et al.* (2001) elucidated that the low permeation flux of the XLE membrane could be due to the excessive adsorption of ammonium onto the membrane surface, which resulted in a higher degree of fouling.

The reduced membrane permeation flux was seen to improve the ammonium rejection. It was found that the total ammonium rejection went up sharply from 37% to 80% and from 52% to 84.25% for the NF270 and XLE membranes, respectively when the initial ammonium concentration increased from 10 to 40 mg/L. The enhanced permeate quality at higher concentration of ammonium was likely due to the formation of an extra thin layer by the adsorption of ammonium onto the membrane surfaces.

As the layer of adsorbed ammonium thickened, fewer ammonium ions were allowed to pass through the membrane pores (Moradihamedani & Halim 2018). Therefore, the ammonium rejection was found to increase. Furthermore, higher ammonium concentration would create Donnan potential, reducing the diffusion of the ions into the membrane phase (Chai *et al.* 2019). As the ammonium feed concentration was increased up to 40 mg/L, the rejection of ammonium for both NF270 and XLE membranes were reported to be very similar. This could be due to the intensive fouling of an ammonium cake layer, which inhibited the permeability of ammonium ions through the membranes (Moradihamedani & Halim 2018).

Effect of feed solution pH on permeation flux and ammonium rejection

Figure 1(c) shows the effect of feed solution pH on the performance of TFC membranes with respect to permeation flux and ammonium rejection. It was noticed that as the feed solution pH increased from pH 2 to pH 10, the permeation flux experienced fluctuations in the range of 116.22 – 135.04 L/m^2·h for the NF270 membrane and 71.67 – 74.71 L/m^2·h for the XLE membrane. Overall, the NF270 membrane displayed higher permeation flux compared to the XLE membrane owing to its larger pore size. As little difference of permeation flux was found for the XLE membrane, it could be said that pH did not affect the membrane permeation flux. In other words, the performance of the XLE membrane was stable over a wide pH range. On the other hand, it was noticed that the NF270 membrane showed slightly higher permeation flux in alkaline conditions in comparison to acidic conditions. The results obtained was in agreement with the findings by Chai *et al.* (2019), where the permeability of the NF270 membrane inclined by approximately 40% when the pH changed from pH 1.5 to pH 13.5. This revealed that the NF270 membrane properties had been altered upon exposure to extreme acidic and alkali conditions. Some previous studies explained that the better permeability in alkaline conditions was most likely due to the increased negative surface charge of the membranes, which resulted in expanded and looser pore structures (Cancino-Madariaga *et al.* 2011). Hence, solvents could be more easily transported across the membranes.

The total ammonium rejection rose significantly from 15% to 51% for NF270 membrane and from 37% to 61% for the XLE membrane when the feed solution pH changed from pH 2 to pH 10. Cancino-Madariaga *et al.* (2011) also reported that membranes tended to have higher ammonium retention at higher pH values. The high rejection phenomenon at high pH could be explained by the difference between the ammonium charge and the isoelectric point of the membranes. The isoelectric points of NF270 and XLE membranes were approximately 3 and 4, respectively (Diop *et al.* 2011). Strong alkaline conditions would result in higher charge difference, promoting the ammonium ion rejection in the negatively charged membrane active layers. The attachment of the ammonium ions on the membrane surface formed a positively charged superficial layer, hence repelling the ammonium ions. The ammonium removal for the XLE membrane was found to be higher than that of the NF270 membrane. This could be explained by the higher permeability of ammonium ion flow through the pores of the NF270 membrane (Mouhoumed *et al.* 2014).

Effect of solution pH on the adsorption of ammonium

The amount of ammonium adsorbed onto both the NF270 and XLE membranes was higher in alkaline solutions (pH 10) compared to the acidic condition (pH 2), as presented in Figure 2. As the solution pH increased from pH 2 to

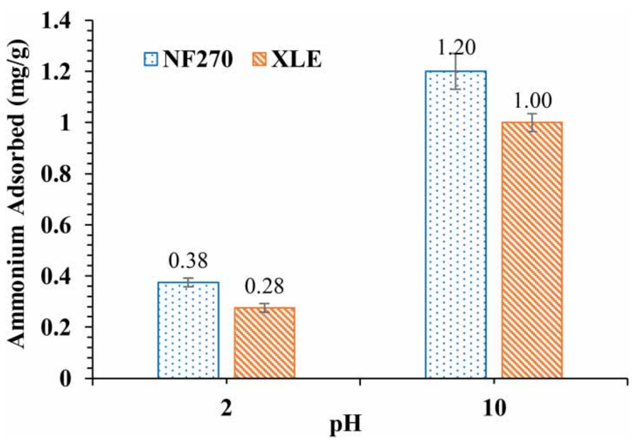

Figure 2 | Effect of pH on the adsorption of ammonium onto membrane structure (initial solution volume: 50 mL; feed ammonium: 10 mg/L; stirring period: 24 hours and mass of membrane tested: 0.2 g).

pH 10, the total ammonium adsorbed onto the NF270 membrane increased significantly from 0.38 to 1.20 mg/g. A similar adsorption phenomenon was also reported for the XLE membrane, in which the total ammonium adsorbed was increased from 0.28 to 1.00 mg/g.

A previous study by Dolar *et al.* (2012) indicated that the dilated pore structure of the micro-porous substrate of the membranes was the cause of the high ammonium adsorption in strong alkaline conditions. The facilitation of the ammonium transported into the internal adsorption sites of the membrane was also considered. The zeta potentials of NF270 and XLE membranes were approximately −100 and −60, respectively at pH 10 (Diop *et al.* 2011). The dissociation of carboxylic groups of the membranes in strong alkali resulted in a negatively charged chain (Chai *et al.* 2019). As the surface charge of the NF membrane was much more negative than the RO membrane, the likelihood of compounds entering the pores of NF membranes was higher (Mouhoumed *et al.* 2014).

Effect of solution pH on membrane stability

The long-term stability of the NF270 and XLE membranes were evaluated under extreme pH conditions and the results are presented in Figure 3. Although the increment of permeation fluxes for both pH values was minimal, as shown in Figure 3(a), a higher increment was noticed in strong alkali conditions compared to strong acid conditions. After the experiment was conducted for 5 weeks, it was observed that the permeation flux increased slightly with a total increment of 1.49% at pH 1.5 and 1.98% at pH 13.5 for the NF270 membrane. This could be explained by increment of membrane hydrophilicity and loosening of membrane pores at higher negative membrane surface charge due to the dissociation of carboxylic groups upon exposure to acid/alkali solution for long periods (Mänttäri *et al.* 2006). On the other hand, insignificant change in the permeation flux was observed for the XLE membrane. The increment of the permeation flux was less than 1% at both pH values. This could be due to the better pH resistance of the XLE membranes (Cancino-Madariaga *et al.* 2011).

The effect of extreme pH on the membrane stability with respect to ammonium rejection is presented in Figure 3(b). Gradual and noticeable decline was observed for the

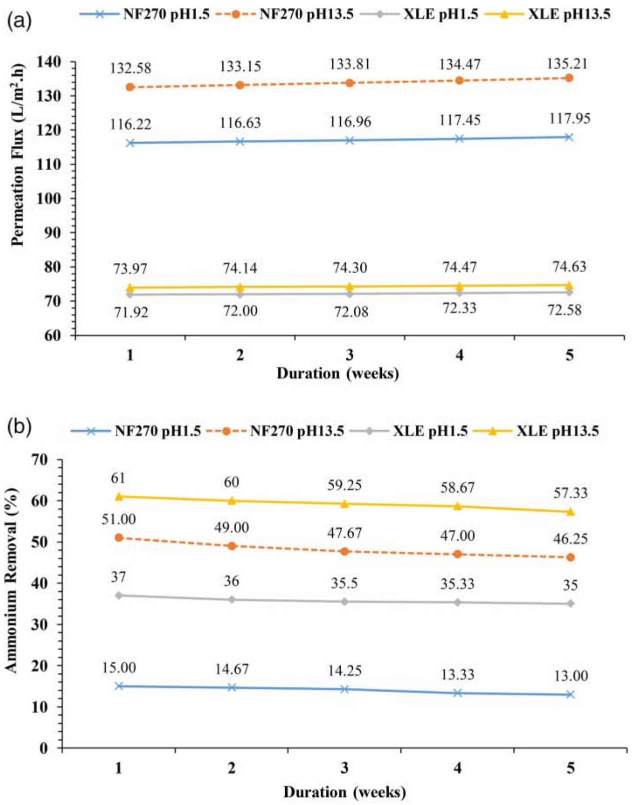

Figure 3 | Effect of strong pH (pH 1.5 and 13.5) on the stability of membranes with respect to (a) permeation flux and (b) ammonium removal (pressure: 10 bar and feed ammonium: 10 mg/L).

ammonium rejection for both the NF270 and XLE membranes. At pH 13.5, the rejection of NF270 and XLE membranes reduced by 9.31% and 6.02% in the fifth week, respectively. Meanwhile, the rejection of NF270 and XLE membranes reduced by 13.33% and 5.40%, respectively at pH 1.5. This showed that the extreme alkali and acidic conditions could deteriorate the membrane properties especially towards the NF membrane. To conclude the findings, it is not recommended to utilise these membranes at strong alkali and acid conditions as the ammonium rejection would be compromised to a certain extent over the time.

Effect of humic acid on membrane permeation flux and rejection

Owing to the better rejection rate of the XLE membrane for ammonium, this membrane was chosen for further evaluation by studying the impact of HA on the membrane water flux and rejection. Figure 4 shows the sharp fall of the permeation flux from 70.27 to 50.71 L/m^2·h (a decrement of 27.84%) as the HA concentration increased from 2 to10 mg/L. HA is generally known as a potential membrane foulant that could lead to permeate flux deterioration (Chong *et al.* 2019). Pore constriction and/or pore narrowing are the result of HA adsorption onto the membrane at low HA concentrations. However, as the HA concentration was increased to >5 mg/L, the deposition of the HA on the membrane surface resulted in the formation of a cake layer that intensively affected the membrane permeation flux (Chai *et al.* 2019).

Although organic fouling resulted in higher HA rejection, it compromised the rejection of ammonium. As the HA concentration increased from 2 to 10 mg/L, the HA rejection was significantly enhanced from 71.21% to 95.85%. Size exclusion effect was taken into consideration for the HA transporting through the membrane. Less than 18% of the HA was less than 10 kDa and the rest were of larger size (Chong *et al.* 2019). Therefore, the narrowing of pores and the formation of a cake layer enhanced the rejection of HA. According to Salama *et al.* (2013), ammonia is ionized to form ammonium ions at pH below 9.4 while existing as an ammonia molecule when the solution become more alkali. Concerning the ammonium rejection in this study, as the ammonia existed as ammonium ions at pH 7, the repulsion force of the membrane surface was affected by the reduced surface charge due to the presence of the HA cake layer. As a result, the total ammonium removal decreased from 85% to 68% with increasing HA concentration from 2 to 10 mg/L.

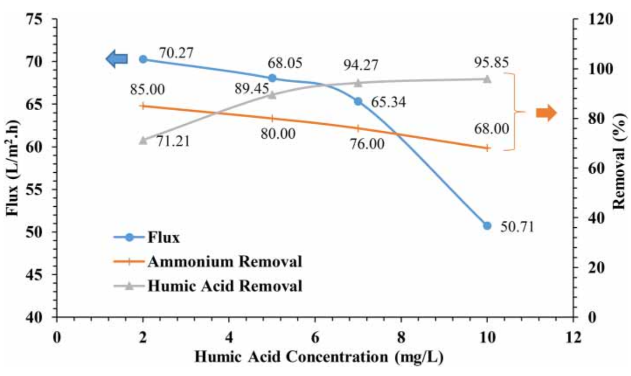

Figure 4 | Permeation flux, ammonium and HA rejection of XLE membrane against HA concentration (pressure: 10 bar; pH: 7 and feed ammonium: 10 mg/L).

NF270 and XLE membranes for sewage treatment

The initial ammonium concentration of the real sewage was 16.4 ± 0.08 mg/L, as presented in Table S2. After undergoing flocculation and UF pre-treatment, the ammonium concentration was reduced to 10.6 ± 0.08 mg/L. It was shown that the UF membrane was not able to reject the ammonium due to its larger membrane pore size. The final ammonium concentrations after the NF270 and XLE membrane filtration process were recorded at 6.3 ± 0.08 mg/L and 4.4 ± 0.08 mg/L, respectively. With respect to separation efficiency, NF270 and XLE membranes achieved 40.57% and 58.49% ammonium removal rate, respectively. The removal efficiency was quite consistent with the synthetic ammonium solution as discussed in Section 3.2. According to the Malaysia Environmental Quality Regulations 2009, the acceptable limit of ammonium for the discharge of industrial effluent is at 10 mg/L for Standard A. Therefore, the final ammonium concentration from the membrane separation processes was able to comply with the regulation.

With respect to COD level, it is reported that the COD value was reduced sharply from 114 to 50 mg/L and 27 mg/L after the NF270 and XLE membranes' filtration, respectively. The acceptable limit for the discharge of mixed effluent comprising COD is 80 mg/L for Standard A. Thus, the COD reduction achieved by both membranes was much lower than the acceptable limit. Concerning the permeation flux for the sewage, the permeation fluxes obtained were 87.21 and 41.14 L/m^2·h for the NF270 and XLE membranes, respectively. However, by comparing the permeation flux between sewage and the synthetic wastewater, it was noticed that the permeation flux for sewage was lower. This could be due to the presence of other ions and particulate matter that blocked the membrane pores and resulted in the greater flux reduction. This study showed that the treated sewage could achieve Standard A quality after the membrane treatment. Instead of discharging into water bodies, the reclaimed water could be used for non-potable uses such as washing, landscaping and water source for chemical mixing in the plant (Tan 2014).

Table S3 compares different treatment methods for ammonium removal from various water sources. The removal efficiency of ammonium using TFC membranes in this study are comparable with the previous studies. The stability of a forward osmosis system on ammonium ions removal is currently under study at lab scale. The membrane materials and orientations, as well as the charge imbalance between the wastewater and draw solution shall be investigated in detail before upscaling (Ferrari *et al.* 2019). According to Bernardi *et al.* (2018), adsorption of ammonium using chitosan as biodegradable adsorbent showed 100% removal efficiency for ammonium concentrations from 0.14 to 0.50 mg/L. However, the efficiency dropped to 55.35% when the ammonium concentration was increased to 2.15 mg/L. Tazkiaturrizki *et al.* (2018) utilised plants and microbials in wetland to degrade nitrogen and phosphorus. Although this method is simple and sustainable, it is only suitable for treatment plant which has a large piece of available land. Biological treatment using ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) are the most popular treatment methods for ammonium removal. Though, this treatment process requires close monitoring to make sure effective nitrification and denitrification processes take place during the treatment. Besides, the growth of the bacteria is sensitive to the variation of temperature (Liu *et al.* 2017). On the other hand, NF and RO membranes have high rejection towards various types of ions present in the wastewater. Although the membrane filtration system might require higher investment, this method is well established, stable, and promising.

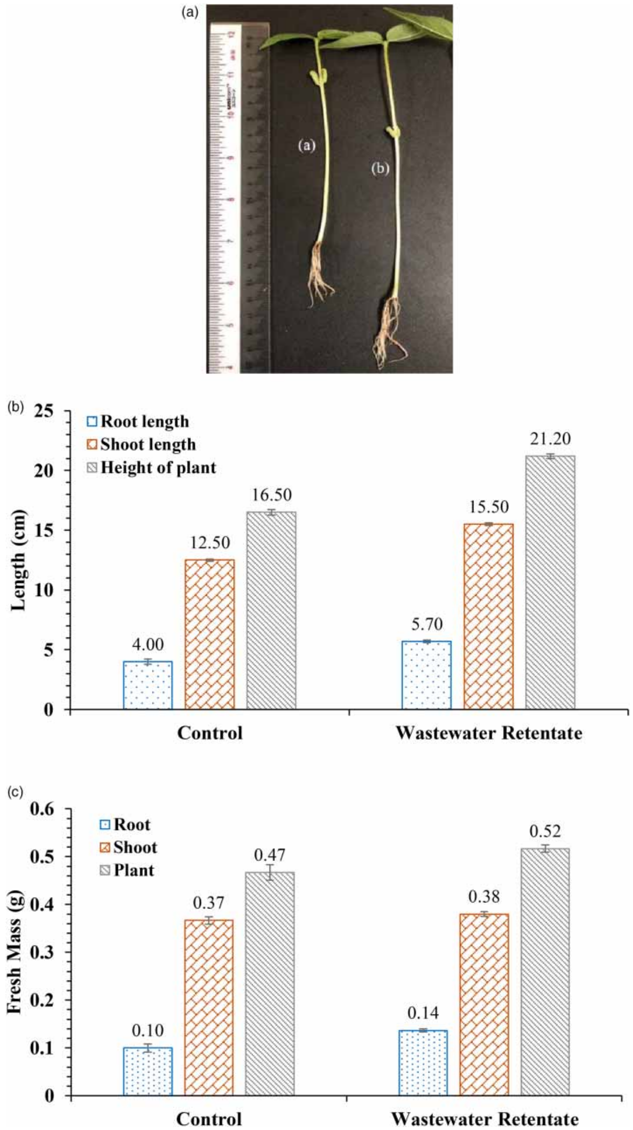

Figure 5 | (a) Germination and growth of green mung bean plants irrigated with pure water (left) and retentate (right), and growth of green mung bean plants according to (b) length of shoot, root and height of plant and (c) fresh mass of shoot, root and plant.

Plant metabolism test with recovered retentate

The retentate (concentrated stream) of the XLE membrane filtration process could be further utilised as liquid fertiliser for plant growth and the findings are presented in Figure 5. Other than ammonium, the wastewater obtained from sewage also contained phosphorus, potassium, humic substances and other micro-nutrients such as magnesium (Mg), manganese (Mn) and zinc (Zn) for plant growth (Cristina *et al.* 2020). Phosphorus is an important element that could contribute to the nuclei acid structure of plants for cell division and development of new plant tissue (Sharma *et al.* 2017). Potassium meanwhile helps in osmoregulation, photosynthesis and cell extension as well as improves plant's resistance against disease (Hasanuzzaman *et al.* 2018). Furthermore, humic substances enhance solubility of phosphorus in soils and stimulate plant elongation (Young *et al.* 2020).

As can be seen from the figure, the control sample displayed less propagation of lateral roots when compared with the plant that was irrigated with retentate. The outcome was in agreement with the study by Ye *et al.* (2019) where the leachate concentrate obtained from loose NF filtration process showed intensive propagation of the plant studied. This might be due to the presence of ammonium and organic substances in the water that promoted intensive leaf, shoot and root growth (Uysal & Kuru 2013).

As shown in Figure 5(b), the total length of the green mung bean plant increased from 16.5 (control sample) to 21.2 cm (sample irritated by retentate), showing a 26.5% increment. Meanwhile, the fresh mass of green mung bean plant was increased from 0.47 to 0.52 g upon utilisation of membrane retentate for irrigation, as shown in Figure 5(c). This recorded >10% of the mass growth of the plant. From previous studies, it was acknowledged that the effect of ammonium and humic acid concentration on the growth of shoot was positively associated with the growth of the root (Uysal & Kuru 2013; Ye *et al.* 2019). Therefore, the recovered retentate could be potentially used as liquid fertiliser for irrigation and contributes towards sustainable management of the sewage treatment plant.

CONCLUSIONS AND RECOMMENDATIONS

Approaches to eliminate ammonium in wastewater have become alarmingly crucial in recent years due to the strict regulation of permissible ammonium concentration in the effluent discharged. Filtration processes utilising TFC NF and RO membranes were demonstrated in this work as an alternative solution to remove ammonium ions from water source. The process conditions, such as operating pressure, solution pH, and HA concentration, posed great impact on the ammonium rejection and permeation flux.

As for the sewage treatment, our findings showed that both NF and RO membrane filtrations were able to meet the local discharge standard for both ammonium and COD, the XLE membrane showed higher separation efficiency than that of the NF270 membrane. As for the sustainable management of the wastewater concentrate, the recovered retentate was able to facilitate the growth of the green mung bean. To conclude, the XLE membrane surpassed the NF270 membrane in terms of ammonium rejection but the NF270 membrane managed to achieve higher permeation flux compared to the XLE membrane. The findings from this study could be helpful in the development of an ammonium treatment technique and liquid fertiliser from the sewage, which ultimately contribute towards the sustainable management of sewage treatment plant.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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