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Application of PTFE membrane for ammonia removal in a membrane contactor

Y. T. Ahn, Y. H. Hwang and H. S. Shin

ABSTRACT

The feasibility of a membrane contactor system for ammonia removal was studied. The mass transfer coefficient was used to quantitatively compare the effect of various operation conditions on ammonia removal efficiency. Effective removal of ammonia was possible with a Polytetrafluoroethylene (PTFE) membrane contactor system at all tested conditions. Among the various operation parameters, contact time and solution pH showed significant effect on the ammonia removal mechanism. The overall ammonia removal rate was not affected by influent suspended solution concentration unlike other pressure driven membrane filtration processes. Also the osmotic distillation phenomena which deteriorate the mass transfer efficiency can be minimized by preheating of influent wastewater. A membrane contactor system can be a possible alternative to treat high strength nitrogen wastewater by optimizing operation conditions such as stripping solution flow rate, influent wastewater temperature, and influent pH.

Key words | ammonia removal, membrane contactor, PTFE membrane

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INTRODUCTION

Phosphorus (P) and nitrogen (N) are the most commonly encountered contaminants to impair the quality of water sources. The intensive use of nutrient in agriculture or industry has led to an increase of eutrophication in lakes, estuaries and rivers, as well as the contamination of underground water reservoirs.

Especially, ammonia is a prevalent problem in the wastewater of many industries including agriculture. Because ammonia is contained in high concentration in manure, it must be treated or removed from water prior to being discharged into the water environment. Moreover, in anaerobic digestion (AD) for animal manure treatment, insufficient removal of ammonia-nitrogen has been reported as an important disadvantage of AD in several studies (Hafner & Bisogni 2009; Noike *et al.* 2004; Rousseau *et al.* 2008).

There are many conventional ways to remove ammonia from water but most of them produce a secondary waste stream that could cause a whole list of other problems. For example, conventional air stripping process releases ammonia gas to the atmosphere, and has been plagued by calcium carbonate precipitation resulting in clogging/fouling of the packing materials (Lei & Maekawa 2006).

Membrane contactors allow direct contact and mass transfer between gaseous and liquid phase without dispersing one phase into the other (Park *et al.* 2009). A typical use for these devices is the removal or dissolution of gases in water. Compared to conventional air stripping, ammonia stripping using membrane contactors is much faster because they provide a large contact surface area between wastewater and stripping solution.

Especially, ammonium can be recovered in the form of ammonium salt in a liquid/liquid membrane contactor system. Due to an increase in the global demand for nitrogenous fertilizer – from 10 Mt N in 1960 to 90 Mt N in 1998 (Mulder 2003) – control over the point sources of N and P shifted from removal to recovery, with a particular emphasis on improving the sustainability of agricultural activities.

In this study, a liquid/liquid membrane contactor system for high rate of ammonia removal and recovery was applied. The ammonia removal efficiency was also evaluated at different operating conditions.

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MATERIALS AND METHODS

Membrane

The tubular membrane used was made from PTFE having pore diameter of 0.4 μm, and 205.5 cm^2 of effective surface area.

Reactor configuration

Figure 1 shows the membrane contactor system used in this study. The membrane module consists of a PTFE tubular membrane encased in a polypropylene pressure vessel. The substrates were fed to the inside of the membrane and the strip solution was supplied on the shell-side. Sulphuric acid (10%, w/w) was used as a stripping solution and flew in the opposite direction of the feed solution.

The membrane's hydrophobic characteristic could prevent it from wetting caused by either ammonia or acid solutions. Ammonia diffused across the gas filled pores in the membrane, as described in Figure 2. As a result, the ammonia concentration decreased with respect to time. Samples were periodically collected from the acid reservoir and total ammonium concentration was analyzed.

Operation conditions

The feasibility of a membrane contactor as a high strength wastewater treatment was evaluated under different operating conditions. Influent pH was selected to figure out the effect of the free ammonia (FA) fraction on ammonia removal. The effect of initial ammonia concentration (250 and 1,000 mg/L), suspended solid concentration (0, 1,000 and 3,000 mg/L), flow rate of feed solution (10 and 20 mL/min) and strip solution (8 and 16 mL/min), and temperature difference between feed and strip solution (0, 13 °C) were also evaluated.

Figure 1 | Lab scale membrane contactor system for ammonia removal.

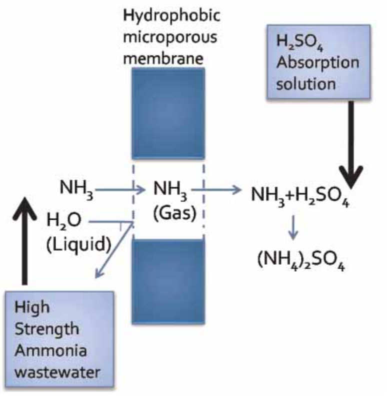


Figure 2 | Principle of ammonia removal in membrane contactor system.

Ammonia removal kinetics

Change of ammonia concentration with time was used to calculate the overall mass transfer coefficient (k_m) as follows (Semmens *et al.* 1990):

$$\ln\frac{C_0}{C} = \frac{Q_t}{V}(1 - e^{-\frac{k\alpha L}{v}}) \tag{1}$$

in which C_0 is the initial total ammonia concentration, Q is the total flow through the module, t is the time, V is the total volume of ammonia solution, and a, L, v are the area per volume, the membrane length, and the feed velocity in the module, respectively. Equation (1) was derived from mass balances of the module and the ammonia solution, assuming that the acid reservoir is big enough to neutralize all the ammonia.

RESULTS

pH

For efficient removal, the ammonia should be in its volatile form. Increasing pH or temperature to a point where all ammonium-nitrogen (NH_4^+-N) is in its volatile ammonia form (NH_3) ensures this. The expression for the FA fraction of the total reduced ammonia is derived from known equilibrium expressions and is presented in Equation (2) (Preez *et al.* 2005).

$$\mathrm{FA} = \frac{10^{\mathrm{pH}}}{e^{\frac{6{,}244}{273.15}} + 10^{\mathrm{pH}}} \tag{2}$$

At constant temperature, pH is the one factor which influences FA fraction. Therefore, pH is one of the most important factors determining overall reaction efficiency. According to Equation (2), high ammonia removal rate was expected at high pH. The ammonia removal rate is shown in Figure 3.

The ammonia removal rate increased with the increased free ammonia fraction in the feed solution in the pH range of 7 to 11. However, in the strong base condition ($pH > 11$), there was no significant change in ammonia removal since the free ammonia fraction was maintained to 1. Therefore, it was concluded that high pH of the feed solution was essential for effective ammonia stripping. All the following batch experiment was performed at pH 11 based on this preliminary test.

Influent concentration

Biological processes can be applied to remove ammonia and other contaminants from water and wastewater. However, the high concentration of ammonia has an inhibitory effect on biological wastewater treatment processes. By using the membrane contactor, which is one of the conventional physico-chemical processes, selective dissolved pollutants can be removed. To verify the effect of influent concentration on membrane contactor operation the ammonia removal rate was observed at different initial ammonia concentrations of 250 mg/L and 1,000 mg/L.

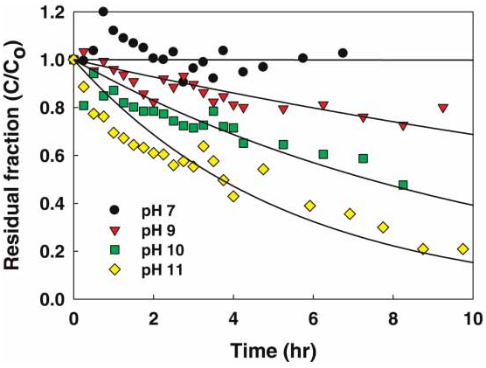


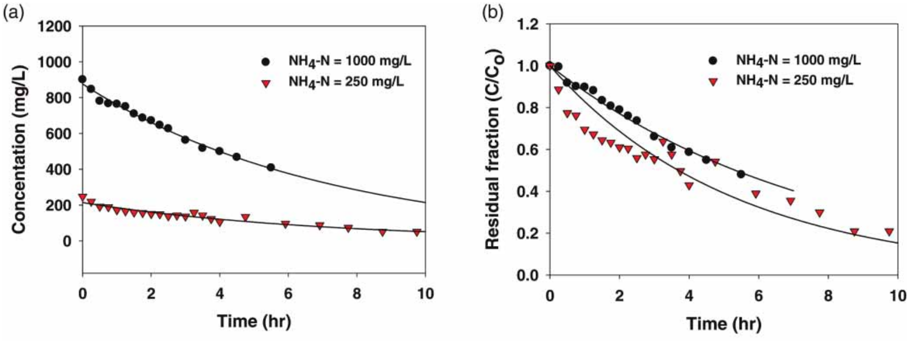
Figure 3 | Ammonia removal time profile at various solution pH conditions.

The amount of removed ammonia was increased with the increased influent ammonia concentration (Figure 4). Meanwhile, the mass transfer coefficient (k_m) decreased from 8.9×10^{-3} m/h to 7.0×10^{-3} m/h as the ammonia concentration increased from 250 mg/L to 1,000 mg/L. The decrease in the mass transfer coefficient indicated that much higher surface area and/or contact time between feed stream and strip solution stream were required for the high ammonia removal.

Suspended solid

It is well known that suspended solid concentration has a negative effect on the membrane filtration process. Membrane fouling is the main drawback of the application of the membrane filtration process such as membrane bioreactors in wastewater treatment. However, the driving force of mass transfer across the membrane is not a pressure in a membrane contactor system. Therefore, the effect of suspended solid on operation is less than other pressure driven membrane filtration processes. To evaluate the effect of suspended solid on the ammonia removal rate, mixed liquor taken from a full scale activated sludge process was added to the feed solution.

Figure 5 shows the effect of suspended solid on ammonia removal. Total ammonia removal at 3,000 mg-SS/L was less than that of suspended solid free operation. Also, the mass transfer coefficient was decreased to 5.4×10^{-3} m^3/h at 3,000 mg-SS/L. However, the inhibitory effect of suspended solid was less significant than pH. Therefore, it



concentration

residual fraction

Figure 4 | Effect of initial concentration on ammonia removal in the membrane contactor.

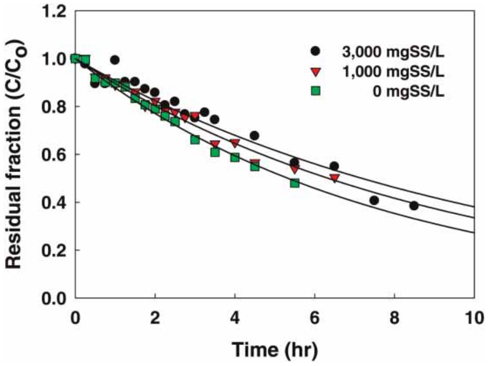


Figure 5 | Effect of suspended solid concentration on ammonia removal in the membrane contactor.

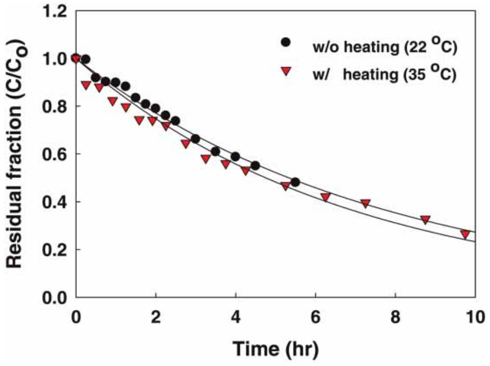


Figure 6 | Effect of operating temperature on ammonia removal in the membrane contactor.

is recommended to operate at high pH condition when treating wastewater containing high suspended solid.

Osmotic distillation

Osmotic distillation (OD) is an evaporative membrane contactor process which is a coupled process in membrane absorption used for treating wastewater containing high strength ammonia (Wang & Shi 2003). Due to the difference of vapour pressure between feed stream and strip solution stream, water molecules leak from the feed solution into the strip solution through the membrane pores.

It was clear that the coupled OD brought negative effects on ammonia removal in membrane contactor system. Removed ammonia could not be concentrated in the strip solution effectively due to the undesired transfer of water molecules with osmotic distillation phenomenon. Therefore, the OD effects should be minimized to ensure successful operation of the membrane contactor process. Pre-heating of feed solution is one of the possible solutions to minimize the OD effect. Due to the high vapour pressure of heated strip solution, water could not pass through the membrane from the feed solution. To verify this theory the strip solution was heated to 35 °C which was selected as model temperature in mesophilic conditions (feed solution: 22 °C)

As shown in Figure 6, the ammonia removal rate increased to 7.3×10^{-3} m/h (4.4%) due to temperature difference. This result indicated that the effect of osmotic distillation on ammonia removal was not significant.

In the case of the control experiment, the volume of feed solution increased as osmotic distillation phenomena did (Table 1). On the other hand, the volume of feed solution decreased in the case of heating. Therefore, the osmotic distillation phenomena were suppressed by temperature increase, even though it was not significant.

Flow rate

A large surface area of the membrane module can guarantee successful removal of ammonia in a membrane contactor system as the ammonia removal mechanism is evaporation through the membrane pore. The operation with high flow rate is one of the alternative ways to increase the contact between the strip solution and wastewater stream. The flow rate was increased to twice that of the control experiments for both feed solution and strip solution.

As the flow rate increased for both of feed and strip solutions, the ammonia removal efficiency increased slightly as described in Figure 7. Especially, increase of strip solution flow rate showed great enhancement of ammonia removal rate. It might be due to strip solution that was saturated at low flow rate. Therefore, the supply of fresh strip solution and high membrane surface area were essential for efficient membrane contactor operation.

The mass transfer coefficients under various operation conditions are summarized in Table 2. Mass transfer coefficient increased with the low influent ammonia concentration, suspended solid-free condition, suppression of osmotic distillation by temperature difference, and high flow rate for both the strip and feed stream. Among these various operation conditions, higher flow rate led to great enhancement of mass transfer. It meant that the most important factor for efficient ammonia removal in membrane contactor was the contact time, which could be also attained

Table 1 | The effect of osmotic distillation in membrane contactor operation

	Initial volume (mL)	Final volume (mL)	Volume change (mL)
Control	940	965	+25
Heating	940	930	−10

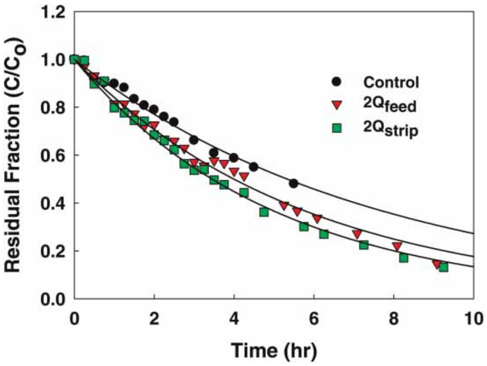


Figure 7 | Effects of feed and stripping solution flow rate on ammonia removal in the membrane contactor.

Table 2 | Summary of mass transfer coefficient under various operating conditions

	NH$_{3\ in}$	**SS**	**ΔT (°C)**	**Q$_{feed}$ (mL/min)**	**Q$_{strip}$ (mL/min)**	**Mass transfer coefficient. (× 10^{-3} m/h)**
Influent NH$_3$-N	250	0	0	10	8	8.9
	1,000	0	0	10	8	7.0
SS	1,000	1,000	0	10	8	5.8
	1,000	3,000	0	10	8	5.4
Temperature	1,000	0	13	10	8	7.3
Flow condition	1,000	0	0	20	8	9.7
	1,000	0	0	10	16	11.0

by the use of a membrane having a large surface area. Therefore, using a hollow-fiber module with a large surface area was suggested for membrane contactor operation. Alternatively, operation at high flow rate condition could be considered for effective ammonia removal.

The influent SS concentration was not a significant factor for ammonia removal in this study, which allows the application of membrane contactor system to real wastewater. High pH showed better performance, because high pH increased the free ammonia fraction which could be removed in the membrane contactor. Therefore, the optimization of various operation conditions was required to maximize ammonia removal.

CONCLUSION

In this research, the feasibility of a membrane contactor system for ammonia removal was studied. Ammonia was effectively removed in a PTFE membrane contactor system even with high suspended solid concentration. Among the various operation conditions, flow rate showed the most critical impact on ammonia removal by increasing the mass transfer coefficient over 50%. The ammonia removal rate could be maximized by optimizing operation conditions and changing the membrane configuration. Therefore, a membrane contactor system could be a solution for treating high strength ammonia wastewater.

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