COMBINATION OF OZONATION AND ABSORPTION THROUGH MEMBRANE CONTACTOR TO REMOVE AMMONIA FORM WASTEWATER

Sutrasno Kartohardjono*, Milasari Herdiana Putri, Setijo Bismo
Department of Chemical Engineering, Universitas Indonesia
Kampus Baru UI, Depok 16424
sutrasno@che.ui.ac.id

Abstract

Ammonia in wastewater is a major pollutant produced in industrial and agricultural wastewaters. Ammonia is often removed by conventional technologies such as pack tower aeration, biological treatment or adsorption as ammonium ion onto zeolites. In many cases, conventional methods are very costly and inefficient, and therefore, there is a need for an alternative separation technique for more efficient removal of ammonia from wastewaters. The aim of this study is to investigate the performance of the combination of ozonation and absorption through membrane processes to remove ammonia from wastewater using natural hot spring water (NHSW) as absorbent. Experimental results show that operating variables such as time and pH of absorbent solution are found to remarkably influence the removal process efficiency. Based on experimental results ozonation can improve ammonia removal efficiency through the hollow fiber membrane contactor. Ammonia removal efficiencies and overall mass transfer coefficients increase with decreasing pH of absorbent solution.

Keywords: Ammonia, mass transfer, membrane, ozonation, removal efficiency

Abstrak

Amonia di dalam air limbah merupakan polutan utama yang berasal dari air limbah industri dan pertanian. Amonia kebanyak disisihkan dengan teknologi konvensional seperti aerasi di menara isian, pengolahan secara biologi atau penyerapan sebagai ion amonium pada zeolit. Dalam banyak hal, metode konvensional sangat mahal dan kurang efisien, sehingga diperlukan teknik separasi alternatif untuk proses penyisihan amonia dari air limbah yang lebih efisien. Tujuan dari studi ini adalah untuk menyelidiki kinerja kombinasi proses ozonasi dan proses absorbsi melalui membran untuk menyisihkan amonia dari air limbah menggunakan absorben berbahan dasar air dari sumber air panas. Hasil eksperimen memperlihatkan bahwa variabel operasi, seperti waktu dan pH larutan penyerap, sangat mempengaruhi efisiensi proses penyisihan amonia. Berdasarkan hasil eksperimen, ozonasi dapat meningkatkan efisiensi penyisihan ammonia melalui kontaktor membran serat berlubang. Efisiensi penyisihan amonia dan koefisien perpindahan massa keseluruhan naik dengan turunnya pH larutan penyerap.

Kata kunci: Amonia, perpindahan massa, membran, ozonasi, efisiensi penyisihan

*corresponding author

1. Introduction

Ammonia in wastewater is a major pollutant produced in industrial and agricultural wastewaters (El-Bourawi et al., 2007). Ammonia is classified as a corrosive substance which can damage body tissue. Ammonia even at very low concentrations can cause problems especially in aquatic life due to nitrogen release in the water streams causing a decrease in dissolved oxygen required, toxic effects on fish, reduced disinfection efficiency and accelerated corrosion of metals and construction materials (Ashrafizadeh and Khorasani, 2010). Ammonia removal is very important in reusing wastewaters in the industry. Ammonia is often removed by conventional technologies such as pack tower aeration, biological treatment or adsorption as ammonium ion onto zeolites. The applicability of ammonia removal processes generally depends upon several factors such as contamination level, plant safety and regulatory consideration, and availability of a heating source and chemicals (Xie et al., 2009). In many cases, conventional methods are very costly and inefficient (Bonmatı´ and Flotats, 2003), and therefore, there is a need for an alternative separation technique for more efficient removal of ammonia from wastewaters.

The use of hollow fiber membrane as a liquid-liquid contactor is one techniques being developed in the process of ammonia removal from wastewaters. This technology is still relatively new compared with other conventional technologies. The development of hollow fiber membrane contactor provides an attractive alternative for ammonia removal from waste waters. Hollow fiber membrane contactors employ ammonia concentration difference between wastewater side and absorbent solution side as a driving force for ammonia transfer across the membrane. To prevent direct contact between the two phases, the wastewater is passed on the shell side of the contactor, whilst the absorbent solution is passed on the lumen fibers. There are many studies have been conducted to remove ammonia from wastewater using hollow fiber membrane contactor through various methods such as liquid-liquid contactor (Ashrafizadeh and Khorasani, 2010; Norddahl et al., 2006; Hasanoglu et al., 2010), membrane distillation (Ding et al., 2006), sweep gas membrane distillation (Xie et al., 2009) and vacuum membrane distillation (El-Bourawi et al., 2007). This study will utilize hollow fiber membrane module and ozonator to remove ammonia from wastewater. The aim of this study is to investigate the performance of the combination of ozonation and absorption through membrane processes to remove ammonia in its aqueous solutions using natural hot spring water (NHSW) as absorbent.

2. Methodology

The mechanism of ammonia removal from the feed side to the absorbent solution side in membrane contactor is illustrated in Figure 1. The hydrophobic hollow fiber separates two liquid phases; the feed that is aqueous phase containing ammonia on the shell side and the absorbent solution; a diluted solution of acid on the lumen side. The membrane pore are filled with air as the membrane is hydrophobic, which is not wetted by the aqueous solutions. First, ammonia (NH_3) diffuses from the bulk of the feed side of the feed-membrane interface. NH_3 volatilizes through the feed-membrane interface, diffuses across the air-filled pore of the membrane, and finally it reacts immediately with an absorbent solution on the interface to form non-volatile compound, $(NH4)_{ax}$, where X is sulfate ion or other anions consists in acid solution such as chloride and nitrate ions. Thus, the concentration of ammonia in the receiving solution is essentially zero. Total ammonia removal could be theoretically possible under this configuration, since the driving force for this liquid–gas–liquid membrane contactor operation is the difference in ammonia partial pressure between the feed side and the absorbent solution (Hasanoglu et al., 2010).

Ammonia transfer through the hollow fiber membrane contactor occurs due to complex ionization. Ammonia in aqueous solution exists in two forms: volatile ammonia molecules NH_3 and NH_4^+ ions as expressed in Eq. 1. Only the volatile ammonia molecules can be removed by membrane contactor. Ammonia treatment processes seek to maximize the volatile ammonia component. The amount of ammonia that can be removed depends largely on the pH and temperature (El-Bourawi et al., 2007).
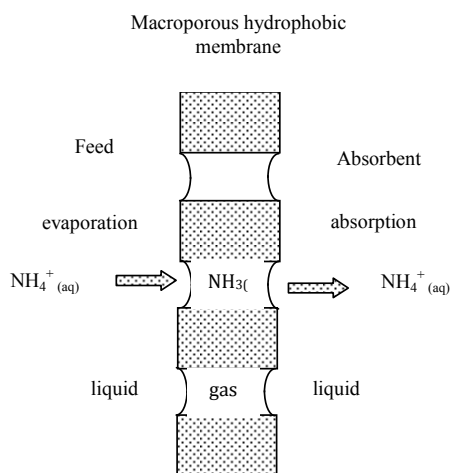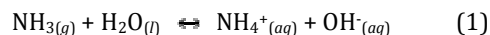
Macroporous hydrophobic
membrane

Figure 1. The mechanism of ammonia removal from the feed side to the absorbent solution side in the membrane contactor (Hasanoglu et al., 2010)

Increasing pH reverses the ammonia dissociation reaction to produce more volatile ammonia in the aqueous solution. Increasing temperature also favors production of volatile ammonia in the aqueous solution. This is because the solubility of ammonia decreases with increasing temperature, resulting in a higher total vapor pressure. It has been reported that increasing the pH improved the overall mass transfer significantly up to pH 10 while a further increase to 11 resulted in only a slight improvement (Ashrafizadeh and Khorasani, 2010). In this study ozonator was employed to increase the production of volatile ammonia in the aqueous solution before it was absorbed by the absorbent

solution in the membrane contactor. It is expected that ozone can shift the equilibrium reaction as shown in Eq. (1) to the production of ammonia.

$$NH_{3(g)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \qquad (1)$$

The fibers used in the experiments were microporous hydrophobic polypropylene membranes of about 2.0 mm OD, 0.2 mm wall thick and 40 cm length. Figure 2 shows a schematic diagram of the experimental setup for a combination of ozonation and membrane processes. The membrane fibers were potted using acrylic in the contactor and it's inside diameter is 1.2 cm and consists of 16 fibers. The feed solution was pumped continuously through shell side of the contactor; meanwhile, absorbent solution was flowed through the fibers' lumen. The feed is then sent to the ozonator before entering the wastewater reservoir for further circulating for 2 hours. During the experiment, waste water samples from the reservoir were taken every 30 minutes for ammonia analysis using Ammonia Meter Palintes 1000. The experiments are conducted at atmospheric pressure. The ammonia removal efficiency (R) from the experiment is determined as follows:

$$R\% = \frac{C_0 - C_t}{C_0} x100\% \qquad (2)$$

where C_0 is the ammonia concentration in the feed solution (mg/L) at initial condition and C_t is the ammonia concentration at time t.
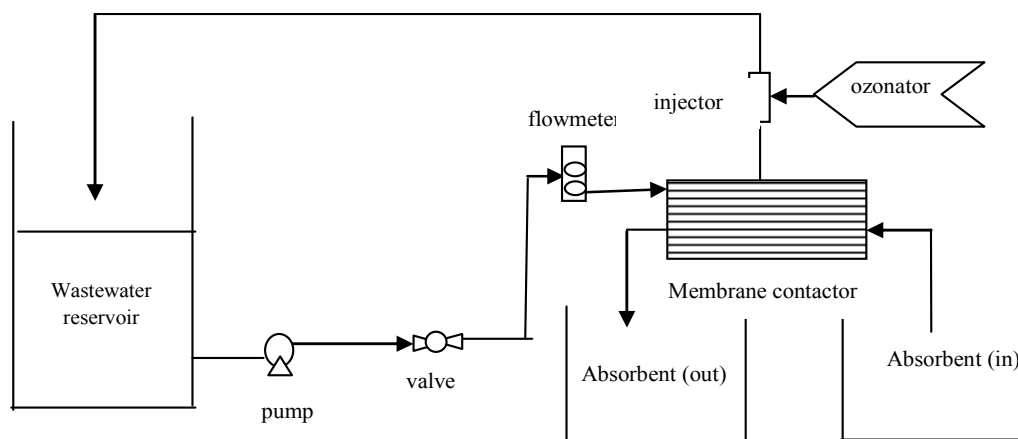

Figure 2. Schematic diagram of experimental setup

Furthermore, the overall mass transfer coefficient, K_{OV}, for the ammonia removal process, can be determined using the following equation (Norddahl et al., 2006).

$$K_{OV} = \frac{V}{At} \ln\left(\frac{C_0}{C_t}\right)$$ (3)

where V is the initial liquid volume of the feed solution and A the membrane area, respectively.

3. Results and Discussions

The NHSW used in the experiment was taken from Ciater – Subang, West Java, Indonesia. The chemical analysis of NHSW used in this study is shown in Table 1.

Table 1. Chemical Analysis Of Natural Hot Spring Water (NHSW) (Kartohardjono et al., 2011)

Parameter	Contents (mg/L)	Measurement Methods
Ca	30.8	SNI.06-6989-12-2004
Mg	28.9	SNI.06-6989-12-2004
Nitrate (NO_3^-)	2.46	SNI.01-3554-2006, point 2.8
Sulfate (SO_4^{2-})	291	SNI.06-6989-20-2004
Chloride (Cl^-)	9.03	SNI.06-6989-19-2004
Fluoride (F^-)	2.83	SNI.06-6989-29-2005
Cyanide (CN^-)	0.002	SNI.01-3554-2006
Hydrogen sulfide	<0.002	APHA.4500D-2005
Phosphate	0.07	APHA 4500 PO4 2005
Iron (Fe)	12.9	SNI.06-6989-4-2004
Mangan (Mn)	1.71	SNI.06-6989-5-2004
Sodium (Na)	30.54	AAS
Potassium (K)	26.35	AAS
Magnesium (Mg)	15.28	AAS
Calcium (Ca)	76.29	AAS
Cadmium (Cd)	0.004	APHA.3120B-2005
Chromium (Cr)	0.03	APHA.3120B
Copper (Cu)	< 0.002	APHA.3120B
Nickel (Ni)	< 0.002	APHA.3120B

In the ammonia removal experiment through combination of ozonation and membrane processes the pH of absorbent solution were varied into 2.0, 1.0 and 0.7, whilst circulation rate of wastewater is kept at 5.0 L per minute (Lpm) and the pH of wastewater is kept around 11.0. Removal efficiencies were analyzed to see the process performance of ammonia removal from wastewater. The ammonia removal experiments were also conducted through a single process of ozonation and membrane absorption.

Effects of various operation modes on ammonia removal efficiency at a pH of absorbent solution 1.0 are shown in Figure 3. Ammonia removal efficiencies through a combination of ozonation and membrane processes show the highest values, whilst ozonation process gives the lowest values. The ozonation process gives the lowest values of removal efficiencies due to slow reaction occurs between ozone and ammonia as shown in Eq. 4. In this case the feed solution is in a base condition (pH $\approx$ 11.0) so that the equilibrium reaction in Eq. 1 shift to the production of ammonia. The reaction rate constant for the reaction is around 20.0 $M^{-1}s^{-1}$ and $t_{1/2}$ = 96 hours at pH=7 and ozone concentration of 1 mg/L (Langlais and Brink, 1991).

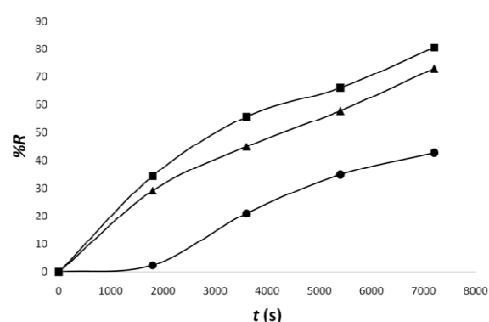$$4\,O_3 + NH_3 \rightarrow NO_3^- + 4O_2 + H_3O^+$$ (4)

Figure 3. Variation of ammonia removal efficiency, %R, and time, t, at pH of absorbent solution 1.0 and wastewater circulation rate of 5 Lpm for combination of ozonation and membrane processes (■), membrane process (▲) and ozonation process (●)

The pH of absorbent solution is one of important factor in ammonia removal via a combination of ozonation and membrane processes. The effect of absorbent's pH on the ammonia removal efficiency is illustrated in

Figure 4. Experimental results show that the lower the *p*H of absorbent solution the better the ammonia removal efficiencies at the same wastewater circulation rate as shown in Figure 4. At the lower *p*H, absorbent solutions will promote more acid leading to enhancements of mass transport from the membrane surface at absorbent side and result in higher removal efficiencies. The hydrophobic membrane isolated the two aqueous solutions and the ammonia from feed solution diffused across micropores in the membrane wall, but water could not pass through the hydrophobic membrane. As a result, the ammonia in the feed solution decreased by reaction forming ammonium salt in the acid solution.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \qquad (5)$$

The highest removal efficiency achieved in the experiment is around 91% at *p*H absorbent of 0.7 and the wastewater circulation rate of 5 Lpm.
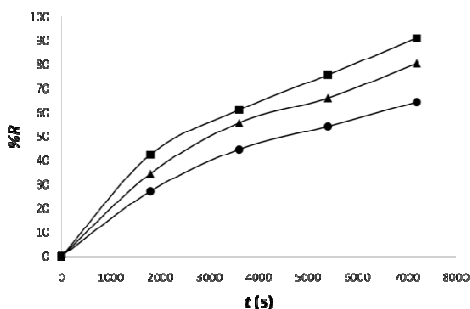
Figure 4. Variation of ammonia removal efficiency, *%R*, and time, *t*, at wastewater circulation rate of 5 Lpm for combination of ozonation and membrane processes at *p*H of absorbent solution 0.7 (■), 1.0 (▲) and 2.0 (●)

Figure 5 gives plots of all data from the experiments to see the effects of modes of operation and *p*H of absorbent solution. It is clear that in the same mode of operation the lower the pH the better ammonia removal efficiency. Figure 5 also shows that combination process ozonation and absorption to the membrane process give a better result compare to the membrane process alone. Overall mass transfer coefficient, K_{OV} for each *p*H of absorbents are shown in Figure 6. K_{OV} was calculated using Eq. (3) and their values are presented in

Figure 6. It can be seen from Figure 6 that the overall mass transfer coefficients were affected in a similar manner with ammonia removal efficiencies by their response to the *p*H of absorbent solution. Experimental results show that the lower the *p*H of absorbent solution the better the mass transfer coefficients as shown in Figure 6.
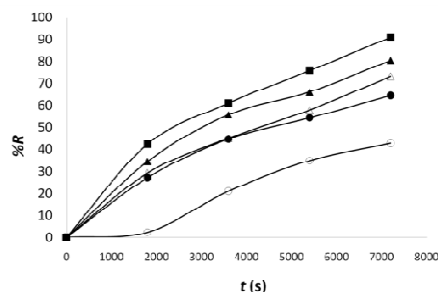
Figure 5. Variation of ammonia removal efficiency, *%R*, and time, *t*, at wastewater circulation rate of 5 Lpm for combination of ozonation and membrane processes at *p*H of absorbent solution 0.7 (■), 1.0 (▲) and 2.0 (●), membrane process at *p*H of absorbent solution 1.0 (Δ) and ozonation process (0)
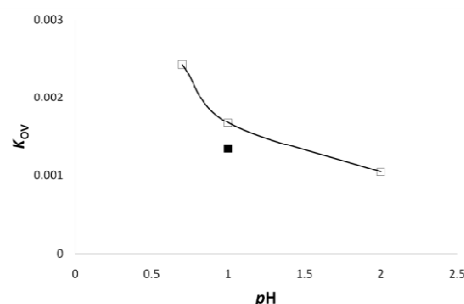
Figure 6. Variation of overall mass transfer coefficients, K_{OV}, and *p*H of absorbent solution, *p*H, at wastewater circulation rate of 5 Lpm for combination of ozonation and membrane processes (□) and membrane process (■)

4. Conclusions

Experiments have been conducted to remove ammonia from wastewater through ozonation, membrane and combination of ozonation and membrane processes. Experimental results show that hollow fiber membrane contactor has potential application for ammonia removal from wastewater. Operating variables such as time and pH of absorbent solution are found to

remarkably influence the removal process efficiency. Based on experimental results ozonation can improve ammonia removal efficiency through the hollow fiber membrane contactor. Ammonia removal efficiencies and overall mass transfer coefficients increase with decreasing pH of absorbent solution. The highest removal efficiency achieved in the experiment is around 91% at pH absorbent of 0.7 and the wastewater circulation rate of 5 Lpm.

Acknowledgement

References

Ashrafizadeh, S. N.; Khorasani, Z., Ammonia removal from aqueous solutions using hollow-fiber membrane contactors, *Chemical Engineering Journal*, **2010**, 162(1), 242-249.

Bonmatı́, A.; Flotats, X., Air stripping ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, *Waste Management*, **2003**, 23(3), 261-272.

Ding, Z.; Liu, L.; Li, Z.; Ma, R.; Yang, Z., Experimental study of ammonia removal from water by membrane distillation (MD): The comparison of three configurations, *Journal of Membrane Science*, **2006**, 286(1-2), 93-103.

El-Bourawi, M. S.; Khayet, M.; Ma, R.; Ding, Z.; Li, Z.; Zhang, X., Application of vacuum membrane distillation for ammonia removal, *Journal of Membrane Science*, **2007**, 301(1-2), 200-209.

Hasanoğlu, A.; Romero, J.; Pérez, B.; Plaza, A., Ammonia removal from wastewater streams through membrane contactors: Experimental and theoretical analysis of operation parameters and configuration, *Chemical Engineering Journal*, **2010**, 160(2), 530-537.

Kartohardjono, S.; Beauty, D.; Andika, R.; Bastian, R.; Bismo, S., *Ammonia Removal from Aqueous Solution through Hollow Fiber Membrane Contactor Using Natural Hot Spring Water (NHSW) as Absorbent*. in The 12th International Conference on Quality in Research (QIR), Bali, 4-7 July 2011, p. A2.3.

Langlais, B.; Reckhow, D. A.; Brank, D. R., *Ozone in Water Treatment : Application and Engineering*; Lewis Publishers: Boca Raton, Florida, 1991.

Norddahl, B.; Horn, V. G.; Larsson, M.; du Preez, J. H.; Christensen, K., A membrane contactor for ammonia stripping, pilot scale experience and modeling, *Desalination*, **2006,** 199, 172-174.

Xie, Z.; Duong, T.; Hoang, M.; Nguyen, C.; Bolto, B., Ammonia removal by sweep gas membrane distillation, *Water Research*, **2009**, 43(6), 1693-1699.