

The Effect Of Initial Concentration And Ph
Of Wastewater In Ammonia Removal Using Membrane Contactor In
Counter-Current Mode

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Abstract

This study shows the application of hollow fiber membrane contactor (HFMC) for ammonia removal from its solution using super hydrophobic polypropylene membrane. In this study, the waste water solution was flow in shell side while the absorbent solution in lumen fiber side in counter-current mode. Sulfuric acid (98% v/v) was used as absorbent fluid. The HFMC module consists of 3000 fibers packed in 2-in diameter cylinder of Polyvinyl chloride (PVC) with fiber's effective length of 25 cm. As shown on the results of this study, super hydrophobic Polypropylene hollow fiber membrane contactor work effectively in removing ammonia from waste water. The highest amount of ammonia that can be removed was obtained for initial concentration of 800 ppm which is 620.12 mg/L. In this study, the highest overall mass transfer coefficient is achieved at waste water pH of 12 which is 0.004 m.s⁻¹.

Key Words: ammonia removal; hollow fiber membrane contactor; membran contactor.

1. INTRODUCTION

Ammonia as one of possible pollutant substance that can be found in waste water from industrial activities or municipal wastewater. The accumulation of dissolved ammonia in waste water has severe effects to aquatic organism, mostly fish (Ashrafizadeh et al., 2010). 0,01 ppm of ammonia in water will have negative effects on fish (Mandowara et al., 2011). It is therefore, waste water treatment is a mandatory for industrial waste before release to environment. Further treatment by removing dissolved gas, such as ammonia, will allowed the plant to re-use the water. The treatment for ammonia removal can be carried out by physical, chemical or biological means. Some conventional methods have been used to separate ammonia from purge gas. Traditionally, packed towers or scrubbing using spray device are common equipment in petrochemical plant. Using

conventional method for removing ammonia in low concentration is not suitable (Mandowara et al., 2011). Recently, membrane technology can be used to capture toxic gas or removing dissolved gas from its solution. One of important membrane process which can be used for those purposes is membrane contactor. Membrane contactor is porous membrane that can keep contact between phases such as liquid-liquid or gas-liquid (Gabelman et al., 1999). The most common membrane contactor found in industry application is hollow fiber membrane contactor (HFMC). This kind of contactor has high surface area per unit volume. HFMC offers advantageous point due to its modularity in scale-up for larger capacity, independently adjustment in flowrate for both phases and problem free from flooding and foaming. On contrary with conventional liquid-liquid contactors, such as packed column or tray tower, maximizing contacting area to provide large interface area can be achieved just by enlarge the size of tower or column. Additional tower will cost additional energy and space area in plant. Removing ammonia by biological treatment having problem in handling sudden increase of ammonia concentration in feed stream, needs large space for pond. For ammonia concentration over 300 mg/L, conventional biochemical needs longer time to complete bioconversion process (Ashrafizadeh et al., 2010). Hollow fiber membrane contactor can be easily combine with other process to get higher overall performance in removing ammonia from its solution, such as ozonation process (KartohardjonoPutri et al., 2012), Advance Oxidation Process in Hybrid Plasma-Ozone Reactor (KartohardjonoHandayani et al., 2012) and combine with anaerobic digester as submerged reactor (Lauterböck et al., 2012). As a consequence for those improvement, the systems utilize more energy and need additional equipments to run the process. In this study, the performance of hollow fiber membrane contactor (HFMC) with super hydrophobic membrane of polypropylene (PP) in removing ammonia from solution was observed. The aim of this study are to investigate the effects of pH of waste water and initial concentration of dissolved ammonia in ammonia removal using HFMC module in counter-current flow arrangement.

2. EXPERIMENT

The hollow fibers membranes contactor (HFMC) module that used was consists of 3000 fibers of super hydrophobic microporous hollow fiber membrane. Fibers were made of polypropylene (PP) with 235 μm of inside diameter and 541 μm of outside diameter and then inserted in to modules made off Polyvinyl chloride (PVC). The module has effective fiber length of 25 cm. The reagents and material used were ammonium sulfate crystal (Merck), demin water from Brataco, sodium hydroxide (Merck) to increase the pH of synthetic waste water and sulfuric acid (H_2SO_4 98% v/v) as absorbent solution. Synthetic solution of waste water were prepared by adding measured weights of ammonium sulfate to demin water for concentration of 100, 200, 400 and 800 ppm. The pH of waste water was

adjusted with sodium hydroxide or sulfuric acid which added as needed. The absorbent solution was a solution of sulfuric acid of pH 1. The solution pH in recirculation tank was measured by pH meter (Eco tester pH 2). Waste water was pumped from recirculation tank using peristaltic pump (LongerPump^(R) WT600-2J) through flowmeter to shell side of Hollow Fiber Membrane Contactor (HFMC) module. Absorbent solution was flow in through the HFMC module in lumen side of the fiber by gravity force. The flow is in counter-current mode and both waste water and absorbent flow were measured using flow meter (Anderson Eurotech Z-3000). At time $t = 0$, solution in recirculation tank was taken for measuring as the initial concentration of ammonia in waste water. Along the experiments, samples in recirculation tank were taken for every 15 minutes and the ammonia concentration was measured by Nessler's reagent colorimetric method using ammonia meter Martini Instrument Mi-405. Schematic of the experimental configuration as shown in Figure 1.

The efficiency of ammonia removal, R , is calculated by equation (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Ammonia concentration was plotted over time to calculate the overall mass transfer coefficient, K using equation (2) (Semmens et al., 1990):

$$\ln \frac{C_0}{C_t} = \frac{Q_t}{V} \left[1 - \exp \left(\frac{K a L}{v_l} \right) \right] \quad (2)$$

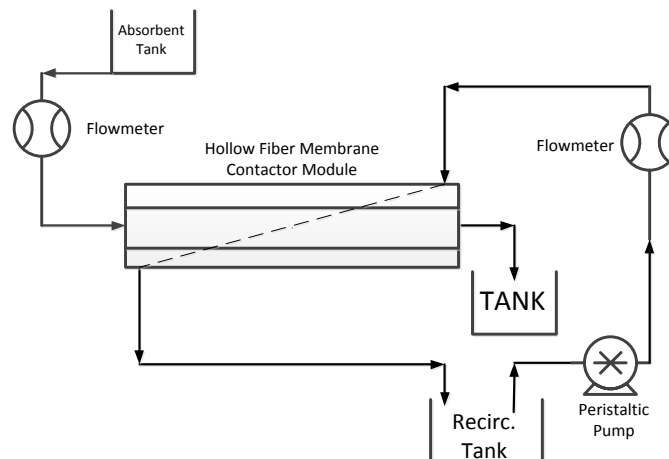


Figure 1. Schematic of Experimental Configuration

where:

- C_0 = initial total ammonia concentration [mg/L]
- C_t = total ammonia concentration at time t [mg/L]

- Q = total flow through the module [$\text{m}^3 \cdot \text{s}^{-1}$]
 t = time [s]
 V = volume of solution in recirculation tank [L]
 v_l = waste water velocity in the membrane contactor module [$\text{m} \cdot \text{s}^{-1}$]

Plotting $\ln(C_0/C_t)$ vs t will yielded a straight line, and the overall mass transfer coefficient, K , can be calculated using equation (3) and (4)

$$\text{slope} = \frac{Q}{V} \left[1 - \exp\left(-\frac{K a l}{v_l}\right) \right]$$

(3)

$$K = \frac{v_l}{a l} \ln \left[1 - \left(\text{slope} \frac{V}{Q} \right) \right]$$

(4)

where:

- a = fiber surface area per volume [$\text{m}^2 \cdot \text{m}^{-3}$]
 K = overall mass transfer coefficient [$\text{m} \cdot \text{s}^{-1}$]
 l = lenght of fiber [m]

3. RESULTS AND DISCUSSION

3.1. Influence of initial concentration of ammonia in waste water on Rejection (%). The waste water solution was feed in shell side of HFMC module and recirculated back to the module by peristaltic pump after collected at recirculation tank at the outlet port of the module (figure 1). The variation of ammonia concentration reduction in waste water on time for different initial ammonia concentration are shown in figure 2. For initial concentration of 800 ppm, the ammonia concentration reduce significantly compare to others initial concentration, from 933.28 to 313.16 mg/L which means 620.12 mg/L of dissolved ammonia has been removed. Compare to 400, 200 and 100 ppm, the amount of dissolved ammonia that removed were 148.48, 240.16 and 133,8 mg/L respectively. It can be understood, since the membrane contactor operation based on concentration difference as driving force (Mansourizadeh et al., 2009), the highest overall concentration reducing will be acheived by initial concentration of 800 ppm. The ammonia rejection (R) as function of time for various initial waste water concentration is shown on figure 3. In term of rejection (R), the trends of rejection shows increasing over time for every variation of initial concentration. Longer time will increasing the amount of ammonia that can be removed.

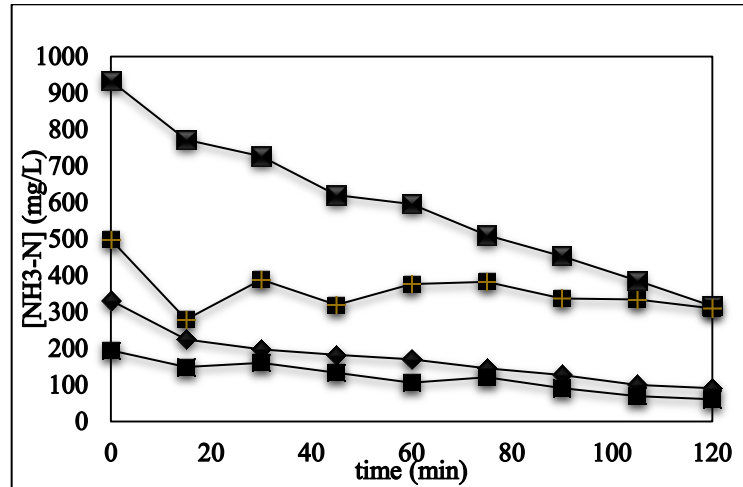


Figure 2. Ammonia concentration vs time for various initial concentration of ammonia in wastewater. (Legends: 800 ppm (■), 400 ppm (+), 200 ppm (◆) and 100 ppm (x)).

The ammonia rejection (R) as function of time for various initial waste water concentration is shown on figure 3. In term of rejection (R), the trends of rejection shows increasing over time for every variation of initial concentration. Longer time will increasing the amount of ammonia that can be removed. Since Rejection is expressed as percentage ratio of the difference between concentration at specified time to initial concentration at time = 0 over initial concentration at $t = 0$, the results show there are no clear influence of initial concentration on percentage of Rejection (R).

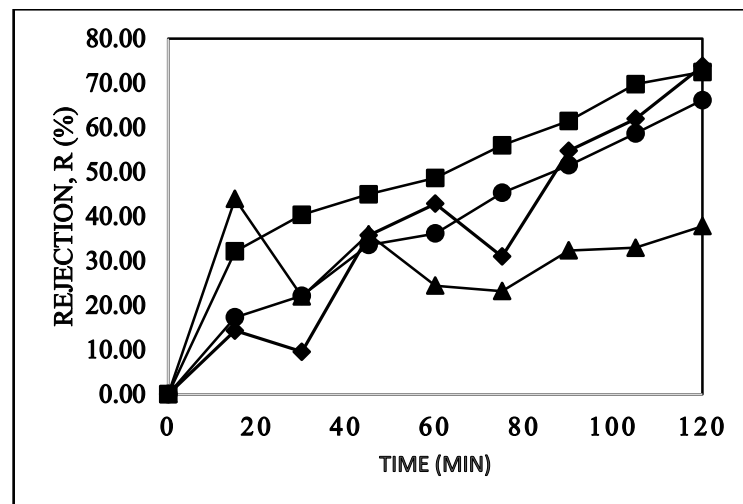


Figure 3. Ammonia Rejection, R (%) as function of time (min) for various initial concentration of waste water. (Legends: ◆ 100 ppm; ■ 200 ppm; ▲ 400 ppm; ● 800 ppm)

3.2. The effect of pH and initial concentration of waste water on reducing amount of ammonia and Overall Mass Transfer Coefficient (K). When ammonia dissolved in water, it will be exists in two form, free ammonia (NH_3) and ammonium ions (NH_4^+). The composition of this forms depends on pH and temperature of its solution (Mandowara et al., 2011; Nosratinia et al., 2014), on high pH (base) the free form of ammonia will be more dominant than ionic form (ammonium ion). From the experiments (figure 4), the amount of ammonia can be removed from its solution were 68.9% for pH 10, 72.47% for pH 11 and 96.6% for pH 12. The highest removal was achieved when the solution of ammonia was 12. On that condition of pH, the composition free ammonia (NH_3) in solution will be greater than ammonium ions. In terms of mass transfer, the overall mass transfer coefficient (K) as variation of pH (figure 5) is relevant with the result achieved as shown on figure 4. Since the highest amount of ammonia removed was on pH 12, the highest overall mass transfer coefficient will also be achieved on pH 12 with $0.004004136 \text{ m.s}^{-1}$ while $0.002776 \text{ m.s}^{-1}$ and 0.00267 m.s^{-1} for pH 10 and pH 11 respectively.

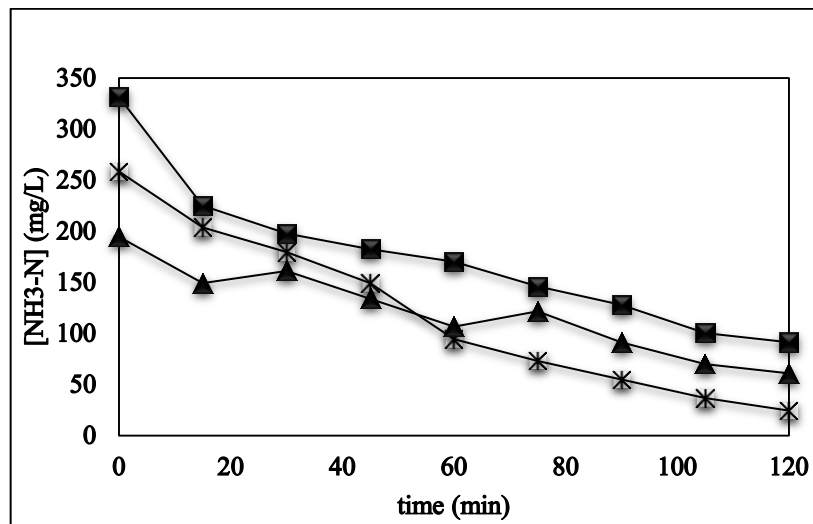


Figure 4. Effect of pH of wastewater on ammonia concentration over time.
(Legends: pH 10 (▲), pH 11 (■) and pH 12 (x))

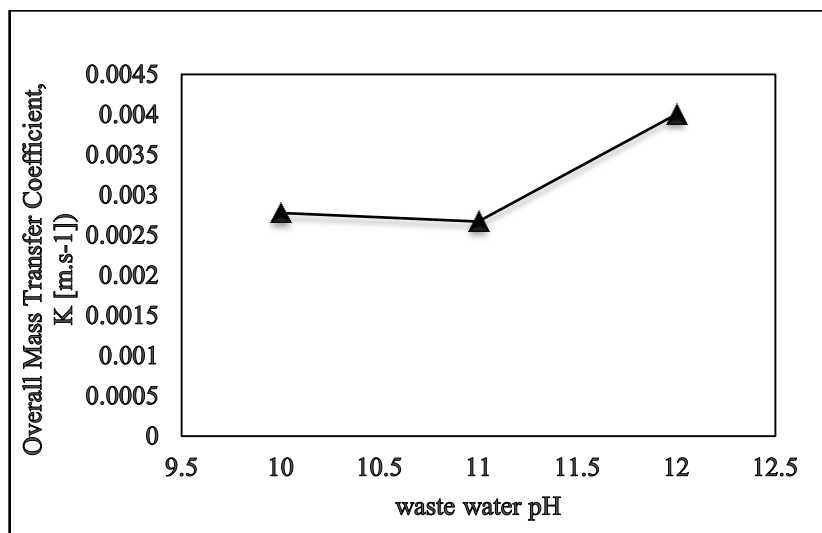


Figure 5. Effect of waste water pH on Overall Mass Transfer Coefficient, K

4. CONCLUSIONS

The following conclusions can be outline from the results of this study are:

1. Ammonia removal from waste water can be carried out by means of hollow fiber membrane contactor.
2. The application of high value of pH for waste water can enhance the ammount of ammonia removal and also give higher value for Overall mass transfer coefficient (K).
3. The highest ammount of ammonia that can be removed was obtained for initial concentration of 800 ppm which is 620.12 mg/L.
4. In this study, the highest overall mass transfer coefficient is achieved at waste water pH of 12 which is 0.004 m.s⁻¹.

5. ACKNOWLEDGEMENT

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