Recovery of both Volatile Fatty Acids and Ammonium from Simulated Wastewater: Performance of Membrane Contactor and Understanding the Effects of Osmotic Distillation

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Abstract

Membrane Contractor (MC) is a separation method that has had growing interest because of its recovery performance and comparably lower energy consumption. Herein, a two-stage recovery MC system was investigated to recover volatile fatty acids (VFAs) and ammonium from simulated wastewater. The MC achieved the total VFA recovery of 77% ± 3%, 82% ± 5%, and 74% ± 8%, with 0.1, 0.3, and 0.5 M NaOH permeate solutions, respectively. The 0 M NaOH permeate recovered only 38% ± 2% of the VFAs due to the osmotic distillation occurring in the opposite direction (permeate to feed) of the VFA transport. Despite the initial pH of the feed solution, osmotic distillation was similar when the permeate was maintained at 0.5 M NaOH. The vapor pressure changes at each sampling period showed high correlation with the water transported ($R^2=0.958$). Ammonium recovery was not significantly different when the pH was maintained while increasing the molarity of the H_2SO_4 permeate, likely due to the high vapor pressure of ammonia gas. Multi-criteria decision analysis was used to determine the optimal operation conditions for MC operation. The results of this study would encourage further exploration of MC technologies for efficiency recovery of VFA and ammonium from wastewater.

Keywords: Membrane separation; resource recovery; volatile fatty acid; ammonium; anaerobic digestate, wastewater treatment

1.1 Introduction

Anaerobic digestion (AD) is a waste treatment technology capable of recovering energy in the form of biogas. Factors that determine the efficacy of the AD process include waste feed source, digester temperature, and microbial community composition (*1, 2*). Among the key compounds of interest in digestate, both volatile fatty acids (VFAs) and ammonia can be separated and then recovered with reuse value in the agricultural, textiles and food industries (*3, 4*). They abundantly co-exist in environments where anaerobic process or fermentation is occurring. Ammonia (pKa~9.23) is a reduced nitrogen species of weak base and commonly found in wastewater and sludge (*5*). VFAs (e.g., acetic (pKa~4.76), propionic (pKa~4.88), and butyric (pKa~4.82) acid at 25°C) are weak acids that are produced during acidogenesis from biological degradation of carbohydrates (*6*). Despite the robustness of AD, there are many toxins that negatively affect the treatment process (*7*). For example, a high ammonium concentration can significantly alter the carbon-nitrogen ratio which inhabits microbial degradation of long-chained carbon molecules to simple carbon structures (*8, 9*). This can result in the accumulation of VFAs in the digestate and low biogas production because microorganisms cannot properly carry out acetogenesis and methanogenesis reactions (*10*). Increased ammonium concentrations have been shown to directly affect the transport of K^+ across the cell membrane for the purpose of maintaining intercellular pH levels (Xing, 2021). It is possible that this change causes the microbial community to diversify its composition to still carry out methane production. However, in cases where this is not evident it presents an opportunity for the digestate to have increased amounts of VFAs and ammonium for subsequent recovery, for example using membrane technologies.

Membrane based technologies such as membrane distillation (MD), electrodialysis (ED) and reverse osmosis (RO) have been employed to recover useful resources from wastewater, and factors such as energy consumption, recovery efficiency and efficacy, and technology durability are used to assess a technology's applicability (*11*). MD operation requires a temperature gradient between a feed solution and a permeate solution which promotes water vapor transport from the hot to the cold source (*12*). It was reported that nutrients such as ammonia can have a higher flux at a higher temperature of 60°C (0.82 ± 0.02 g m^{-2} h^{-1}) compared to that at a lower temperature of 20°C (0.26 ± 0.03 g m^{-2} h^{-1}) during the MD treatment (*13*). Typical ED treatment takes advantage of an applied voltage to increase the migration of anions and cations across ion exchange member towards different compartments, resulting in the concentrated solutions of cations or anions (*14*). Previous ED studies have reported ammonia recovery efficiency of 95.8-100% (*15*) and 95% recovery for acetic acid (*16*). The main challenges that arise with ED and MD approaches are the increased inputs of electrical and thermal energy to drive resource recovery. Although RO is typically used as a desalination technology, it has also shown potential for ammonia recovery via concentration or gas permeation depending on the feed pH (*17*). For example, 95% of ammonium was concentrated when the solution $pH < 9$ but 63% of ammonia gas was able to pass the RO membrane when $pH > 9$ (*18*). The demand for a high pressure that causes acute fouling however would let RO to be less considered for resource recovery compared to other technologies.

Evolved from MD, membrane contactor (MC) has received a growing interest for resource recovery because of its low energy consumption and comparably good recovery efficiency (*19*). MC has been studied to remove carbon dioxide from air sources (*20, 21*), and other compounds such as sulfur dioxide (*22*), alcohols (*23*), ammonia (*24*) and VFAs (*25*) as its applicability has become broader. Specifically for ammonia and VFAs, MC works if a pH gradient exists so that the gaseous form is released from the feed solution and then absorbed in the aqueous form in the permeate solution. For example, the mass flux rate of acetic acid decreased from ~11.03 to ~2.45 g m^{-2} h^{-1} when the solution pH was adjusted from 3 to 5.45, suggesting the immobility of acetic acid in its ionic form at the higher pH level, and the increased acetic acid recovery was observed for the increased NaOH absorption solution normality (*26*). One factor that has been overlooked in many MC studies is water vapor transport via osmotic distillation because of vapor pressure difference between the feed and permeate solutions (*27*). Recent studies have begun to report water flux (*28, 29*), but the further understanding of the implications that osmotic distillation may have on VFA and ammonia recovery is still necessary. Modeling ammonia recovery using MC has been pursued in a few studies (*30-33*), but many of these models lack the consideration of how water vapor transport affects recovery of volatile compounds as well as economic feasibility of using MC.

In this study, the effects of permeate composition and pH adjustment on osmotic distillation and resource recovery via MC were investigated. We proposed a two-step recovery process using a hollow fiber membrane module where switching pH would allow VFAs recovery in a NaOH absorption solution and then ammonium recovery in a H_2SO_4 absorption solution. The operation mode used in this study was direct contact, liquid-liquid MC with no temperature gradient between the feed and permeate solution, thereby minimizing the temperature influenced water vapor transport, which is common in MD processes. This will highlight the effects of osmotic distillation. Acetic, propionic, and butyric acids are used to better identify the effects

VFAs have on the MC separation and osmotic distillation. A synthetic solution was used in order to effectively compare the recovery of VFA and ammonium during the different iterations of the study. The specific objectives of this study included: (1) demonstrating the feasibility of two-step recovery of VFAs and ammonia; (2) optimizing operation conditions for maximum VFA and ammonium recovery; (3) developing a model to predict VFA recovery, ammonium recovery, and water movement based on operation conditions; and (4) conducting initial evaluation of economic feasibility of recovering VFAs and ammonium using MC. System optimization based on the order of recovery was then investigated after all individual experiment iterations were compared using multi-criteria decision making.

2. Method & Material

2.1 Membrane Contractor Set Up & Operation

A hollow fiber membrane module (St. Louis, USA) was used for the membrane contactor experiment. The initial volumes of the feed and permeate solutions were equal at 400 mL before pH adjustments. The detailed operation conditions are shown in Table 1 that outlines the initial pH and solute molarity for the feed and permeate solutions. The feed solution composed of 2000 mg L^{-1} acetic acid, 750 mg L^{-1} propionic acid, 750 mg L^{-1} butyric acid, and 3.68 g L^{-1} $(NH_4)_2HPO_4$, and other elements (per liter of deionized (DI) water): 0.15 g NH_4Cl, 0.5 g NaCl, 0.015 g $MgSO_4$, 0.02 g $CaCl_2$, 0.1 g $NaHCO_3$. The pH adjustments were made with H_2SO_4 and/or NaOH solutions under continuous stir mode with pH probe inserted into the solution. The basic and acidic permeate solutions were prepared om a stir plate until the solute was completely dissolved in the water. The feed and permeate solutions were recirculated through the membrane module at 20 mL min^{-1}. The VFA recovery tests were operated in a batch mode of 24 hours with sample collection at 0, 3, 6, 12, and 24 h. The ammonium recovery tests were operated in a batch mode of 6 hours with samples taken at 0, 1, 2, 3, and 6 h. Membrane cleaning was performed before MC operation for VFA and ammonium separation. The membrane was cleaned by (i) backwash with DI water, (ii) backwards flushing with acid/ base, (iii) acid/base soak, and (iv) forward flushing with DI water. Before VFA separation, an acid solution (0.10 M H_2SO_4) was used on the feed side of the membrane and a base solution (0.05 M NaOH) was used on the permeate side for membrane cleaning step (ii) and (iii). Before ammonium separation, a base solution (0.10 M NaOH) was used on the feed side of the membrane and an acid solution (0.05 M H_2SO_4) was used on the permeate side for membrane cleaning step (ii) and (iii). All solutions were prepared using a stir plate until the solute was completely dissolved. All tests were performed in triplicate under room temperature (~24 ºC).

2.2 Measurement and Analysis

A digital balance (Scort Pro, Ohous, Columbia, MD, USA) was used to measure the permeate solution mass. LoggerPro data collection software was used to record mass of the permeate at 2-minute intervals. Water flux (J_w, L h^{-1}) was calculated according to Eq. 1:

$$J_w = \frac{\Delta m}{\Delta t} \tag{1}$$

where Δm (g) is the change in mass of the feed solution that is converted to liters and Δt is the change in time (h^{-1}).

The VFA and NH_4^+ transport and recovery were calculated using Eq. 2-3:

$$J_S = \frac{C_f V_f - C_i V_i}{\Delta t} \tag{2}$$

$$\% = \frac{C_f V_f - C_i V_i}{C_i V_i} \tag{3}$$

where C_f and C_i (mmol L^{-1} and mg L^{-1}) represent the final and initial concentration, respectively, of VFA and NH_4^+. The V_f and V_i (L) variables represent the final and initial volumes of the feed solution, respectively.

Specific flux (g L^{-1}) was calculated according to Eq. 4:

$$\text{Specific flux} = J_S/J_w \tag{4}$$

VFAs were analyzed using gas chromatography equipped with a flame ionization detector (Focus GC, Thermo Scientific; GC-FID). The ammonium concentration was analyzed using cation chromatography equipped with IonPac CS12A (Dionex Easion, Madison, WI, USA). Electrical Conductivity (Mettler-Toledo, Columbus, OH, USA) and pH (Oakton Instruments, Vernon Hills, IL, USA) were measured using benchtop conductivity and pH meters.

2.3 Modeling

To understand water permeation during the MC treatment, the vapor pressures of the feed and permeate solutions were calculated. Raoult's Law was used to calculate the theoretical vapor pressure ($P_{solution}$) of each solution according to Eq. 5-8

$$P_{solution} = P_{water} - \sum_{1}^{n} \chi_{solvent} P_{solvent}^{o} + \sum_{1}^{n} \chi_{solvent} P_{solvent}^{o} \tag{5}$$

$$\chi_A = \frac{n_A}{n_A + n_B} \tag{6}$$

$$K_a = \frac{[H^+][VFA^-]}{[VFA]} \tag{7}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{8}$$

where P_{water} (mmHg) is the vapor pressure of pure water (23.8 mmHg at 25°C), χ_A is the mole fraction of the solvent, $P_{solvent}^{o}$ (mmHg) is the initial vapor pressure of the solvent, n_A and n_B

represent the moles of the solvents and solutes, K_a represents the disassociation constant of the acids to determine the state of VFAs based on pH and K_b represents the disassociation constant of the base to determine the state of ammonium based on pH in the solution.

The vapor pressure gradient between the feed and permeate solution was calculated according to Eq. 9:

$$\Delta(P_{feed} - P_{permeate}) = \frac{(P_{feed} - P_{permeate})_f - (P_{feed} - P_{permeate})_i}{2} \qquad (9)$$

where P_{feed} and $P_{permeate}$ (mmHg) are the vapor pressure of the feed and permeate solutions, respectively, and the P_f and P_i are the vapor pressure gradients of the final and initial samples, respectively.

3. Results & Discussion

3.1 VFAs recovery dependence on NaOH and pH

VFAs were successfully recovered using the MC with NaOH in the permeate solution. In details, the recovery of acetic acid was less affected by NaOH and exhibited similar efficiency of 76 ± 3%, 79 ± 6%, and 70 ± 9% with the 0.1 M, 0.3 M and 0.5 M of NaOH, respectively (Fig. 2A). The MC achieved more recovery of propionic acid (80 ± 3%, 86 ± 2%, and 80 ± 8%) and butyric acid (86 ± 8%, 92 ± 2%, and 89 ± 5%) with three tested NaOH solutions. The phenomenon that higher recovery of higher-chained VFAs was also reported in the previous studies that utilized gas permeable membranes for VFAs separation and recovery (*25*). In the absence of NaOH in the permeate solution (0 M), the MC recovered 36 ± 2%, 39 ± 2%, and 45 ± 2% of three different types of VFAs, with a total VFAs recovery efficiency of 38 ± 2% in a period of 24 hours. Despite a lack of alkaline solution in the permeate, the highly acidic feed (pH=3) should have resulted in some VFAs being able to cross the gas permeable membrane.

The previous finding that increasing the molarity permeate solutions yield greater recovery across gas permeable membrane (*26*) was not clearly observed in the present study.

Because of water osmosis, the 0.5 M and 0.3 M NaOH adsorption solutions extracted 100 ± 5 mL and 60 ± 8 mL of water from the feed solution, respectively (Fig. 2B). That is, some water was moving in the same direction as VFAs from the feed to the permeate solution. On the contrary, when the adsorption solution did not contain NaOH, 30 ± 9 mL of water transported in a reverse direction from the permeate to the feed, because the pure water permeate (0 M NaOH) had a higher vapor pressure due to the lack of solutes than the feed solution. This reversal water movement in the opposite direction of VFAs migration might have created some resistance to VFAs migration and contributed to the significantly lower VFAs recovery (38 ± 2%) ($p<0.05$) than that with the 0.1, 0.3, and 0.5 M NaOH (77 ± 3%, 82 ± 5%, and 74 ± 8%) (Fig. 2C).

To further understand the effects of osmotic distillation, the permeate solution containing 0.5 M NaOH was maintained while the pH of the feed solution was adjusted from 3 to 6. After the MC treatment, the total VFAs concentration in the feed was 5.30 mM, 15.36 mM, 40.91 mM, and 53.14 mM, at the pH of 3, 4, 5, and 6, respectively (Fig. 3A). A higher VFAs concentration at a higher feed pH was because of VFAs being more ionized at the higher pH level and thus rejected by the gas permeable membrane. Interestingly, these results occurred under relatively high water transport compared to the tests where the pH was maintained and the permeate solution molarity was adjusted. The water displaced increased from 91.5 ± 2.9 mL (pH=6), to 101.8 ± 0.9 mL (pH=5), 103.5 ± 1.7 mL (pH=3), or 110.8 ± 9.8 mL (pH=4) (Fig. 3B). The total VFAs recovered was significantly lower at pH=5 (28 ± 4%) or pH=6 (16 ± 2%) because of the solution pH exceeding the pKa for each VFA (Fig. 3C). The pH and EC of the feed and permeate solutions had little effect on the VFA recovery (Figure S1-2).

Specific VFAs flux corroborated the observation that VFAs transport is a separate phenomenon from osmotic distillation. When the permeate solution was maintained at 0.5 M NaOH, the water flux decreased from 5.26 mL h^{-1} at 3 h to 3.65 mL h^{-1} after 24 h of the MC treatment (Fig. 4). The test under the condition of 0.1 M NaOH and pH=3 showed that VFAs could transport across the membrane despite water movement. The reason for water transport during MC has yet to be defined to any particular variable. However, experimental observations suggest that the vapor pressure difference between the feed and permeate solutions is likely the driving force for water transport. In the presence of individual VFAs, the water transport showed high correlation (R^2=0.958) to the vapor pressure gradient (Fig. 5). As the theoretically calculated vapor pressure increased, more water moved from the feed to the permeate. Reverse water transport was observed when the vapor pressure of the permeate was higher than that of the feed (pH=3, pure water permeate). A small range (0.126-0.173 mmHg) of vapor pressure gradient difference with an average of 0.154 ± 0.015 mmHg was determined for the operation modes using 0.5 M NaOH as a permeate, because the amount of VFAs in the gaseous state did not alter the solutions vapor pressure compared to the amount of base that did significantly decrease the permeates vapor pressure. Additionally, the transport of water across the membrane due to the differences in vapor pressure could inhibit maximum recovery of the VFA. This was evident in the case where osmotic distillation from the permeate to the feed decreased the VFA transport across the membrane. Limiting the amount of water transport would also decrease the dilution of the permeate which could complicate reuse of the VFAs.

3.2 Ammonium recovery and the effects of permeate volume

Ammonium recovery was mainly dependent on the initial pH of the feed solution instead of the H_2SO_4 molarity of the permeate (adsorption solution). The water displaced also had direct correlation to the permeate solution. As the H_2SO_4 molarity in the permeate increased from 0.1 to 0.5 M, the water displaced from the feed to the permeate increased from 19.1 ± 6.4 to 54.2 ± 8.1 mL (Fig. 6A). Similar to the VFA recovery, the displaced water was due to osmotic distillation based on the vapor pressure gradient between the feed and the permeate. Ammonium recovery efficiencies of 64 ± 6% (0.1 M of H_2SO_4), 70 ± 1% (0.3 M), and 73 ± 18% (0.5 M) were obtained in the first hour of MC separation (Fig. 6B), benefited from the high vapor pressure of NH_3 gas when the pH of the feed solution was adjusted to 12 using NaOH. After 6 hours of the MC operation, the recovered ammonium using 0.1 M, 0.3 M and 0.5 M H_2SO_4 permeate solutions was 71 ± 6%, 75 ± 2%, and 81 ± 7%, respectively. The difference of recovery efficiency between 1-hour and 6-hour operation suggested that most of recovery occurred in a relatively short period of time and thus the extended MC operation might not be necessary (which would help decrease the operation related expense). Indeed, less than 10% of the recovered ammonium was obtained in the last 5 hours of the treatment time. Changes in pH for feed pH=9-10 explain the decrease in recovery (Figure S3). Additionally, less water was displaced with the lower molarity permeate solutions, suggesting that the vapor pressure gradient was lower than the higher molarity permeate solution tests.

Water displacement increased as the feed pH was adjusted from 9 to 12 due to the increased vapor pressure gradient. Only 25.4 ± 1.9 mL of the feed water transported into the permeate at the feed pH of 9, much lower than 54.6 ± 7.5 mL at the pH=12, related to the NH_4^+/NH_3 ratio (Fig. 7A): the solution having more NH_4^+ present at lower pH levels would lower the vapor pressure and thus result in less water transport; in contrast, higher pH levels mean more NH_3 is present which increases the vapor pressure resulting in a greater vapor pressure gradient and more water transport. The pH and EC of the feed and permeate also adjusted as ammonium moved across the membrane (Figure S4). Ammonium recovery obtained after 6 hours of operation was 30 ± 7%, 63 ± 4%, 70 ± 3%, and 81 ± 7%, at pH=9, 10, 11 and 12, respectively. Clearly, a higher permeate pH could drive more NH_3 to transport across the gas permeable membrane. Compared to the H_2SO_4 permeate solution tests, ammonium recovered went from 17 ± 4% to 30 ± 7% (pH=9) and 44 ± 7% to 63 ± 4% (pH=10) from the first to last hour, respectively. Higher recovery was observed initially for pH=11 and pH=12, indicating that less time is necessary for ammonium recovery at higher pH levels despite the molarity of the permeate solution. Additional benefits of less acid usage and less energy demand could be beneficial to the overall MC recovery process.

The specific flux of ammonium between the tests where the permeate solution was maintained (0.5 M H_2SO_4) decreased from 59.9 g NH_4^+-N L^{-1} at pH=11 to 16.4 g NH_4^+-N L^{-1} at pH=9. When the pH of the feed was maintained at pH=12, the specific flux of ammonium trended downward with an increase in permeate solution molarity. The highest specific ammonium fluxes were 59.9 g NH_4^+-N L^{-1} (0.5 M H_2SO_4 and feed pH=11), 52.7 g NH_4^+-N L^{-1} (permeate: 0.1 M H_2SO_4 and feed pH=12), and 47.7 g NH_4^+-N L^{-1} (permeate: 0.5 M H_2SO_4 and feed pH=10) (Fig. 8). An evident trend was not observed based on pH or molarity. A point to highlight however is that similar recovery at the different starting feed pH levels may suggest that adjusting to the highest pH or generating a higher molarity permeate might not be necessary. This would decrease the need for dilution of the permeate and cost for operation. In addition, the water transport rate for the conditions when the feed pH=12 for the 0.1 M, 0.3, and 0.5 M permeate solutions increased from 5.1 ± 3.4 to 6.3 ± 3.6 mL h^{-1}, 9.0 ± 3.2 to 13.0 ± 3.5 mL h^{-1} , and 10.1 ± 3.4 to 12.8 ± 1.5 mL h^{-1} , respectively, from the first hour to the second hour of the MC operation. This is likely due to the decrease of the permeate vapor pressure after the rapid recovery of ammonium. A similar transport rate trend (4.3 ± 3.9 mL h^{-1} to 6.2 ± 4.8 mL h^{-1}) was observed when the permeate was 0.5 M H_2SO_4 and the pH=11 in the feed. In the case where the ammonium recovery happened more slowly due to a lower NH_4^+/NH_3 ratio (pH=9 and 10) at pH levels closer to pK_a=9.23, lower water transport was observed. However, higher water recovery occurred when the feed pH=10 compared to feed pH=9 that did not yield greater ammonium transport, suggesting that the pH of the solution had a greater effect than osmotic distillation. This ultimately means that each operating conditions optimal recovery requires less time because of NH_3 having a high vapor pressure at higher pH levels.

3.3 Economic Factors and Decision Analysis

Economic feasibility of the proposed two-stage recovery system should be considered when determining optimal operating conditions. The cost of each operation condition is related to the amount of acid (H_2SO_4) and base (NaOH) necessary to (1) adjust the pH of both feed and (2) generate permeate solutions to trap the resources (Table S1). These values were determined based on market value of the chemicals at the time of data collection. The cost increased as the feed pH decreased in the VFA recovery mode or the feed pH increased in the NH_4^+ recovery mode, as well as for increasing molarity permeate solutions. The cost of each combination of VFA and NH_4^+ recovery was then compared to the recovery percentages observed during the MC experiments (Fig. 9). The recovery of ammonium had the lowest Quartile range (66.5%-78.0%) for variables that would determine operation conditions. The decreased range of recovery efficiencies is likely due to the high vapor pressure of ammonia gas. After the pH exceed the pKa, the ammonia effectively moved across the hollow fiber membrane with little adverse effects as the pH was increased. The VFA recovery ranged from the 1st Quartile to the 2nd Quartile is 35.9% to 74.8%, respectively, suggesting that operational decisions are more important to the MC efficacy separation for VFA recovery compared to ammonium recovery. In contrast to ammonium recovery, VFAs have lower vapor pressures and do not completely disassociate in solution. This means that VFAs in the solution would be available for recovery in their gases state compared to stronger acids. The use of acid and base for pH change and permeate generation also showed a wide range from $0.27 to $1.19 for the various configuration of VFA and ammonium recovery that were possible based on combining operation modes. The balance between VFA recovery, ammonium recovery, and cost are not well explained by the variability to understand which operation modes would be most favorable. Additional analysis is warranted to identify optimal conditions based on economic feasibility and resource recovery efficacy.

Multi-criteria decision analysis was used to determine the optimal operating conditions based on VFA recovery, ammonium recovery and cost of operation. The 42 number of possible combinations were evaluated using 4 variables (v_1=Cost, v_2=VFA recovery, v_3=NH_4^+ recovery v_4=VFA/ NH_4^+ ratio) for 4 situations (S_1- equal variable weight, S_2- cost variable heavily considered S_3- cost variable mildly considered , S_4- cost variable lowly considered). The different situations were able to evaluate the cases where recovery performance and cost were of equal importance, as well as a range of importance of either variable. The 42 combinations were listed from the highest score to the lowest score for each of the 4 situations. After compiling the operation combinations, multiple combinations were favorable in more than 1 situation due to high rankings after applying variable weights (Table 2). The only combination recovery steps that made it into the top of the analysis of the 4 situations was NH_4^+ (pH=12, 0.1 M H_2SO_4; pH=3, 0.1 M NaOH). This is considered the most optimized coupling because regardless of the variable weights, it resulted in the top 5 of all possible combinations of VFA and NH_4^+ recovery conditions. In addition, this is due to the low cost necessary to generate the permeate solutions in both VFA and NH_4^+ recovery modes. Situation 2 is the only situation where a different operation mode was favored because of a lack of a NaOH permeate solution. Overly considering cost however may not be a strong evaluation due to such low consideration of performance. While not considered in the multi-criteria decision analysis, limiting the dilution of the permeate due to osmotic distillation would allow for a more concentrated source of each resource. To determine if there are any advantages of recovering VFA or NH_4^+ first, additional MC separation tests were completed. The recovery of acetic acid (1st: 71 ± 4% vs. 2nd: 70 ± 4%), propionic acid (1st: 77 ± 4% vs. 2nd: 76 ± 3%) and butyric acid (1st: 81 ± 3% vs. 2nd: 81 ± 3%) was the similar regardless of the recovery order and minimal lost (Fig. 10). The NH_4^+ recovered was higher at 81 ± 7% as the second step compared to 73 ± 3% as the first step based on the amount of ammonium available. However, the absolute amount revealed that NH_4^+ lost was lower when it was recovered first. This suggests that the 1-hour recovery of ammonium should take place initially before the 24-hour VFA recovery.

3.4 Perspectives

Utilizing MC for recovery of volatile fatty acids and ammonium is potentially a promising method because of the decreased energy demand compared to MD. Challenges around recovery time, operational cost, and performance decline due to fouling would need to be addressed to improve the technologies implementation. First, VFAs in their gaseous state have a much lower vapor pressure than ammonia which results in a long recovery time that is over 24 times slower. This could be solved through design where MC retention time for VFA recovery is greater than that for ammonia. Absorption of VFAs utilizing amine-functional groups has shown to have recovery times less than 280 minutes (*34*) and could potentially be applied in membrane fabrication to increase recovery rate during MC operation. VFA selectivity could also be explored based on the membrane fabrication. Second, the use of acids and bases can increase cost of the operation for both VFA and ammonium recovery. Addressing this issue is highly necessary to increase the economic feasibility of MC separation. Producing acid and based using electrolysis has shown to be an effective approach for recovery of many resources from wastewater (*35*) but would increase the energy intensiveness. Using renewable energy such as solar energy that is becoming more popular in wastewater treatment plants may help address the energy need by electrolysis that provides onsite acid/base production. Third, membrane fouling is an inevitable issue. This issue could be further evident when using MC to separate VFA and ammonium from AD from a real digester. The presence of other wastewater constituents such as microbes and toxic gases could exacerbate the fouling in the membrane. Additionally, the two-stage recovery MC process requires acidification and alkalization of the wastewater, the effects of membrane fouling might be decreased during operation changes (*36*). Understanding long term effects of VFA and ammonium recovery could help increase the financial feasibility inclusive of membrane requirements. For instance, using less acid and base to achieve recovery with less osmotic distillation could increase the chances of biological fouling in membrane pores (*37*). Using AD effluents as the feed solution would be an important next step to fully understand performance implications of MC for real world application. This could be averted using different membrane fabrication and modification techniques that has been explored in membrane fouling literature.

4. Conclusions

This study has demonstrated a two-stage MC system for effective recovery of both VFAs and ammonium. The VFAs were recovered from the feed solution most effectively when the pH was less than the pKas of the VFAs. Recovery of VFAs was hindered in cases when the vapor pressure of the permeate solution was higher than the feed solution. A high correlation (R^2=0.958) was observed between the vapor pressure difference and water transport across the hollow fiber membrane. This suggests that permeate solutions can be determined based on the composition and characteristics of the feed solution. Ammonium recovery occurred much faster than VFA recovery due to its higher vapor pressure. Multi-criteria decision analysis also identified the most optimal operating conditions when considering the cost and recovery performance of each operating condition. VFAs recovered with an initial feed pH=3and 0.1 M NaOH absorption solution and ammonium recovered with an initial feed pH=12 and 0.1 M H_2SO_4 absorption solution was the optimal recovery conditions for the two-stage recovery.

Future research should seek to address the challenges about VFA/NH_4^+ recovery coordination, operation costs, performance prediction, and membrane fouling due to long term operation.

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Table 1. Operation Conditions for MC experiments. The VFA Recovery experiments varied permeate molarity (A) and initial feed solution pH (B). The NH_4^+ Recovery experiments varied initial feed solution pH (A) and varied permeate molarity (B).

	Condition	pH (Feed)	Permeate Solution (NaOH)		Condition	pH (Feed)	Permeate Solution (H_2SO_4)
VFA Recovery (A)	(i)	3	0.5 M	NH_4^+ Recovery (A)	(i)	9	0.5 M
	(ii)	3	0.3 M		(ii)	10	0.5 M
	(iii)	3	0.1 M		(iii)	11	0.5 M
	(iv)	3	0 M		(iv)	12	0.5 M
VFA Recovery (B)	(i)	3	0.5 M	NH_4^+ Recovery (B)	(i)	12	0.5 M
	(ii)	4	0.5 M		(ii)	12	0.3 M
	(iii)	5	0.5 M		(iii)	12	0.1 M
	(iv)	6	0.5 M				

Table 2. Multiple Criteria Decision Analysis for 4 Situations (S) with 4 decision variables (v) normalized between 0 and 1. S_1- Equal variable weight, S_2- Cost variable heavily considered S_3- Cost variable mildly considered , S_4- Cost variable lowly considered. v_1=Cost, v_2=VFA recovery, v_3=NH_4^+ recovery v_4=VFA/ NH_4^+ ratio

	S_1 (v_1=0.25, v_2=0.25, v_3=0.25, v_4=0.25)	**S_2** (v_1=0.70, v_2=0.10, v_3=0.10, v_4=0.10)	**S_3** (v_1=0.40, v_2=0.20, v_3=0.20, v_4=0.20)	**S_4** (v_1=0.10, v_2=0.30, v_3=0.30, v_4=0.30)
1	$^{A}NH_4^+$:pH=12,0.1M VFA: pH=3,0.1M	$^{E}NH_4^+$:pH=12,0.1M VFA: pH=3,0M	$^{A}NH_4^+$:pH=12,0.1M VFA: pH=3,0.1M	$^{C}NH_4^+$:pH=12,0.5M VFA: pH=3,0.1M
2	$^{B}NH_4^+$:pH=12,0.3M VFA: pH=3,0.1M	$^{A}NH_4^+$:pH=12,0.1M VFA: pH=3,0.1M	$^{B}NH_4^+$:pH=12,0.3M VFA: pH=3,0.1M	NH_4^+:pH=12,0.5M VFA: pH=3,0.3 M
3	$^{C}NH_4^+$:pH=12,0.5M VFA: pH=3,0.1M	NH_4^+:pH=12,0.3M VFA: pH=3,0 M	$^{E}NH_4^+$:pH=12,0.1M VFA: pH=3,0M	NH_4^+:pH=12,0.5M VFA: pH=3,0.3 M
4	$^{D}NH_4^+$:pH=11,0.5M VFA: pH=3,0.1M	NH_4^+:pH=10,0M VFA: pH=3,0 M	$^{C}NH_4^+$:pH=12,0.5M VFA: pH=3,0.1M	$^{B}NH_4^+$:pH=12,0.3M VFA: pH=3,0.1M
5	NH_4^+:pH=12,0.1M VFA: pH=3,0.3M	NH_4^+:pH=11,0.5M VFA: pH=3,0 M	$^{D}NH_4^+$:pH=11,0.5M VFA: pH=3,0.1M	$^{A}NH_4^+$:pH=12,0.1M VFA: pH=3,0.1M

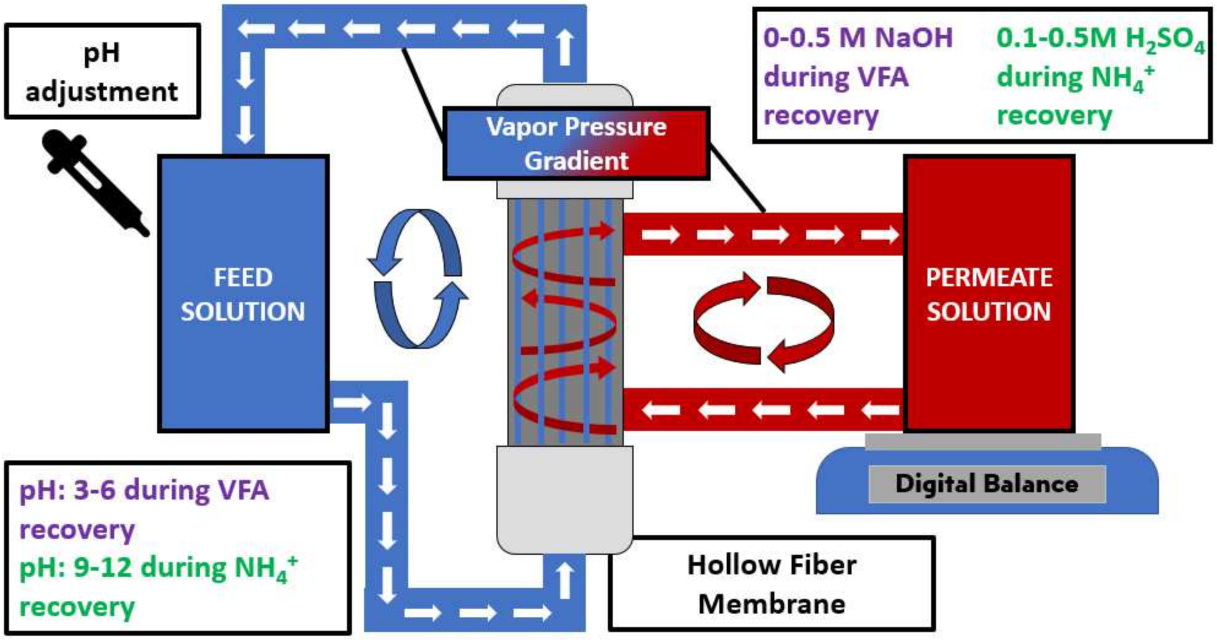

Figure 1. Schematic and experimental description for membrane contactor set up

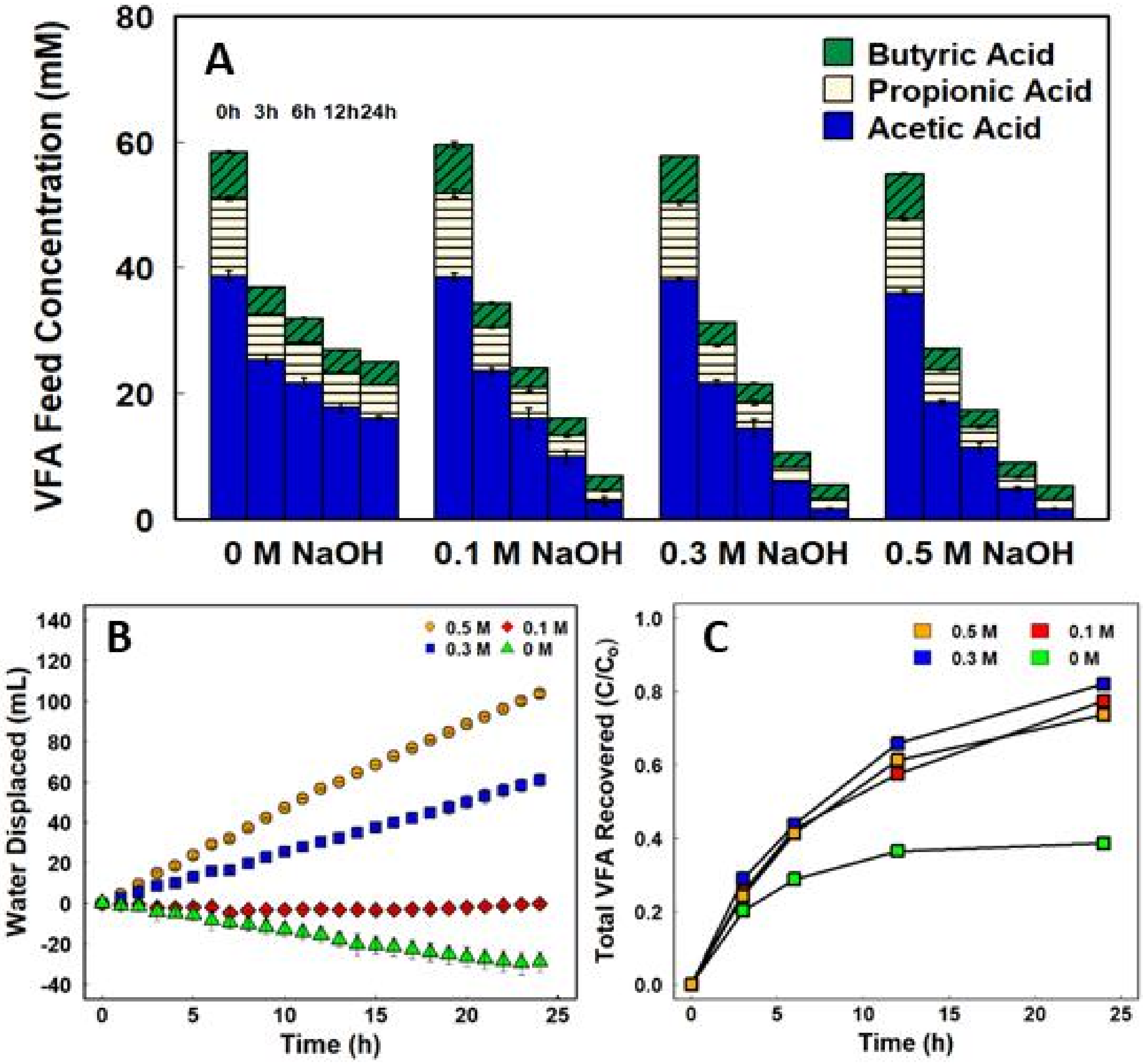

Figure 2. VFA separation using various NaOH molarities as the permeate while maintaining feed pH=3: (A) Feed VFA distribution at each sampling time, (B) water displacement, and (C) total VFA recovery

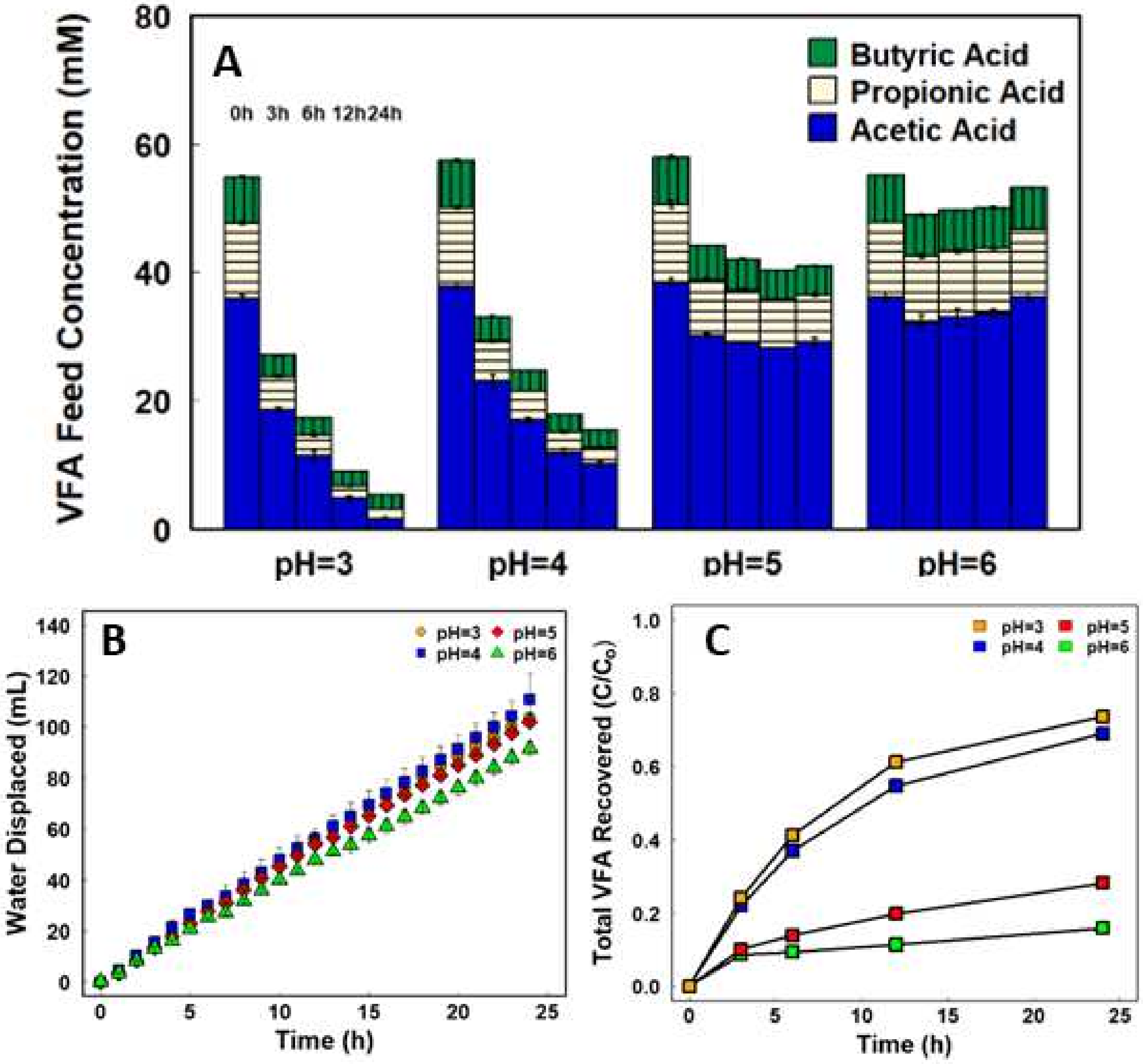

Figure 3. VFA separation using various initial feed pH levels while maintaining 0.5 M NaOH permeate: (A) Feed VFA distribution at each sampling time, (B) water displacement, and (C) total VFA recovery

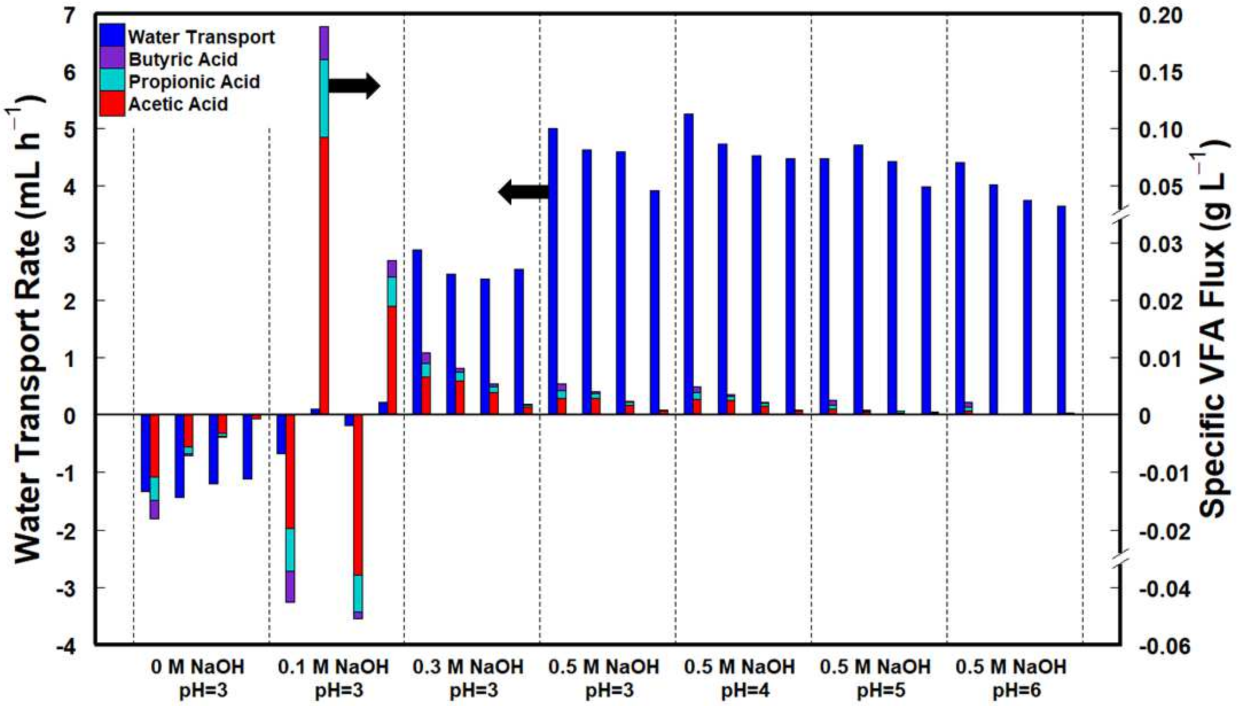

Figure 4. Water transport and specific VFA flux for MC operation modes

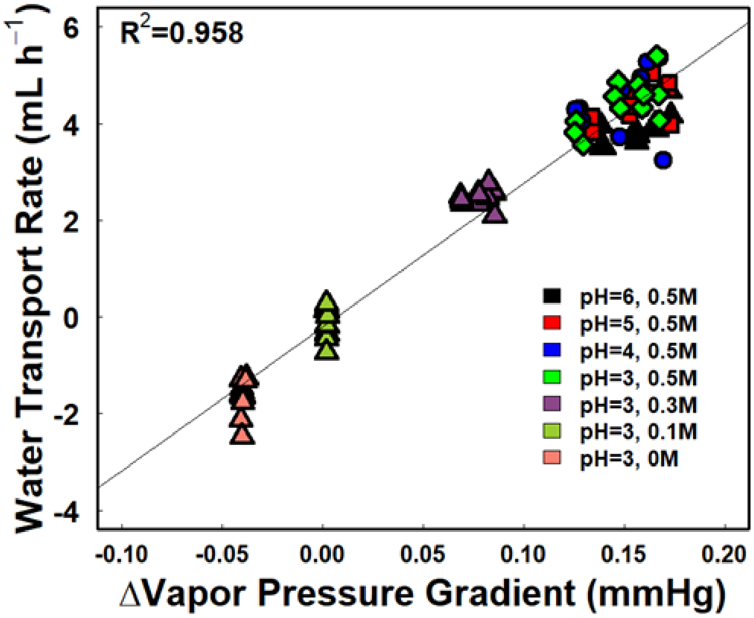

Figure 5. Water transport during each sampling period for each iteration of the MC separation of VFAs

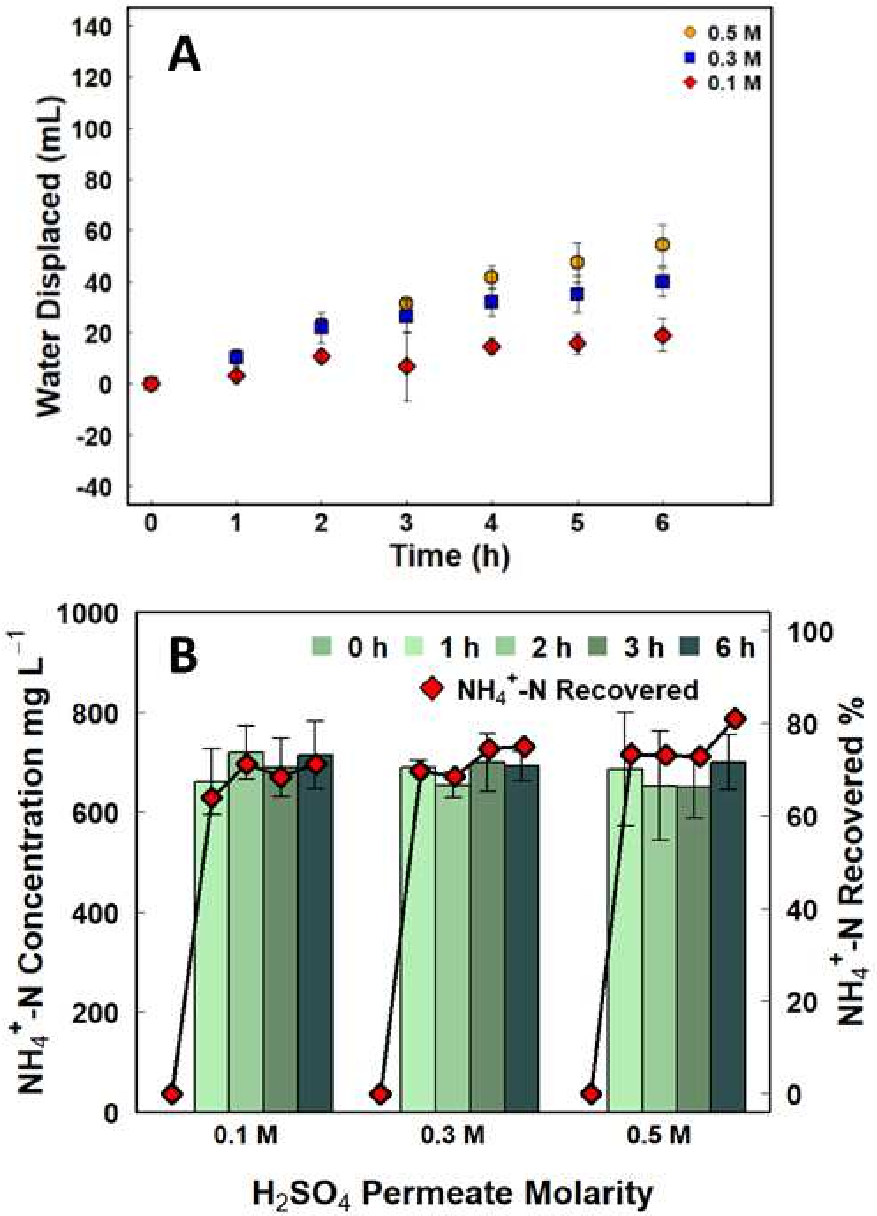

Figure 6. Ammonium separation using different H_2SO_4 solutions as the permeate while maintaining initial feed pH=12: (A) water displacement and (B) NH_4^+ concentration and recovered amount in the permeate

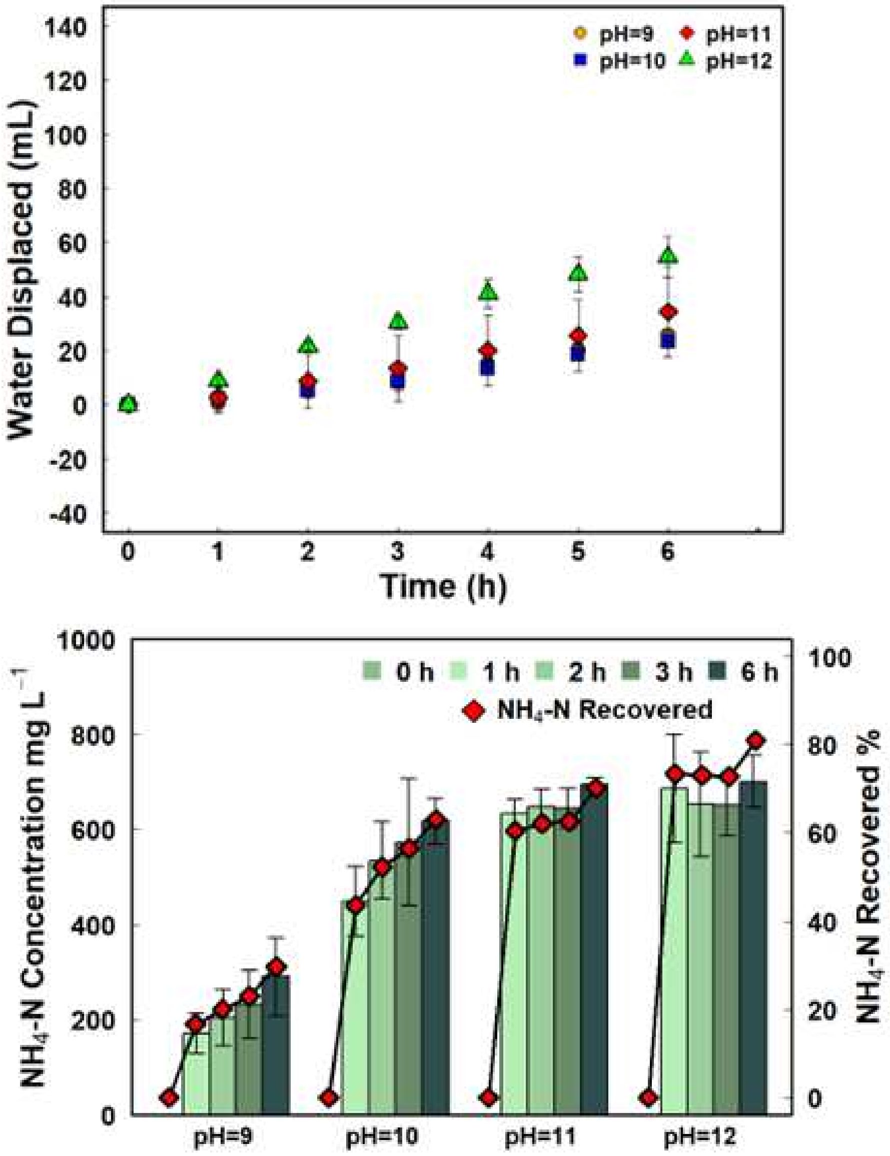

Figure 7. Ammonium separation using different initial feed pH levels while maintaining 0.5 M H_2SO_4 permeates: (A) water displacement and (B) NH_4^+ concentration and recovered amount in the permeate

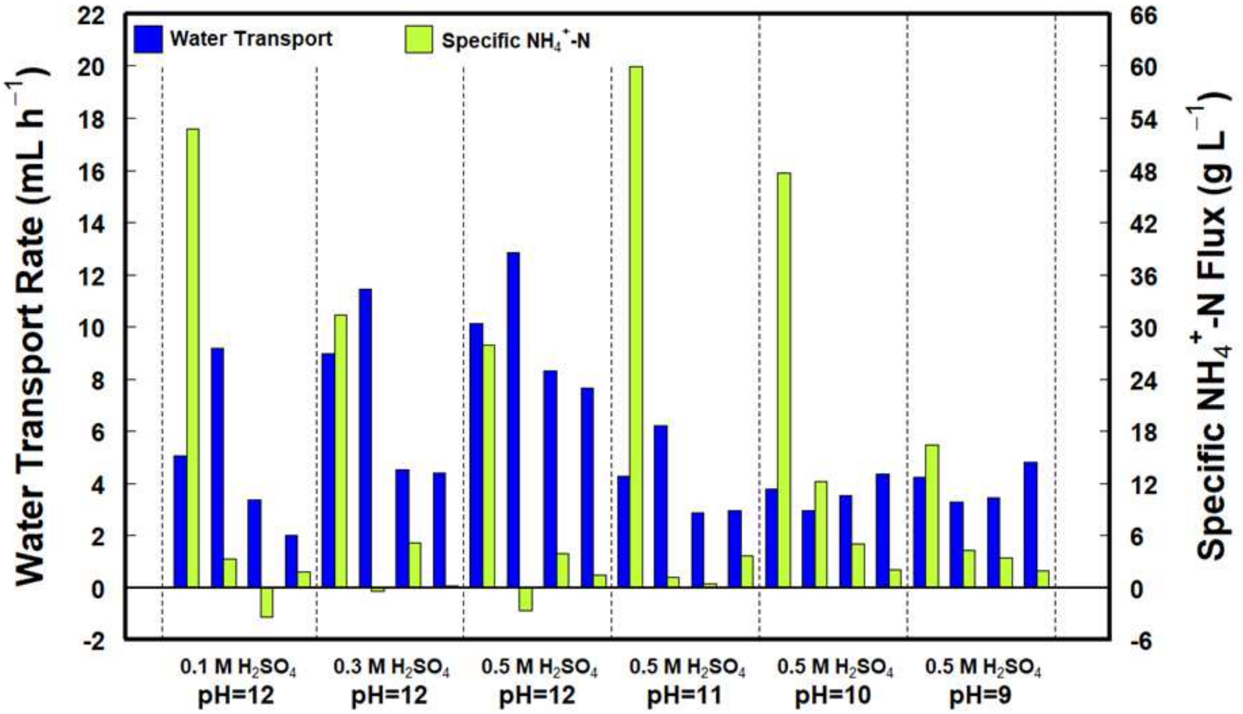

Figure 8. Water transport and specific NH_4^+ flux for MC operation modes

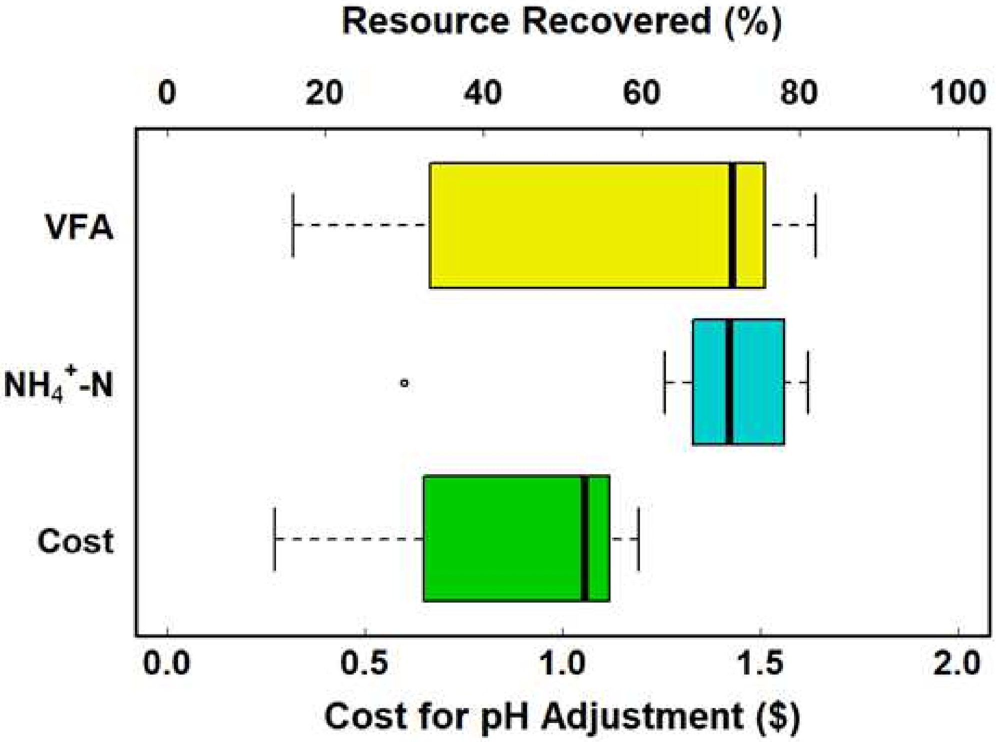

Figure 9. VFA and NH_4^+ recovered for every experiment iteration and cost based to generate either the NaOH or H_2SO_4 and adjust the feed pH

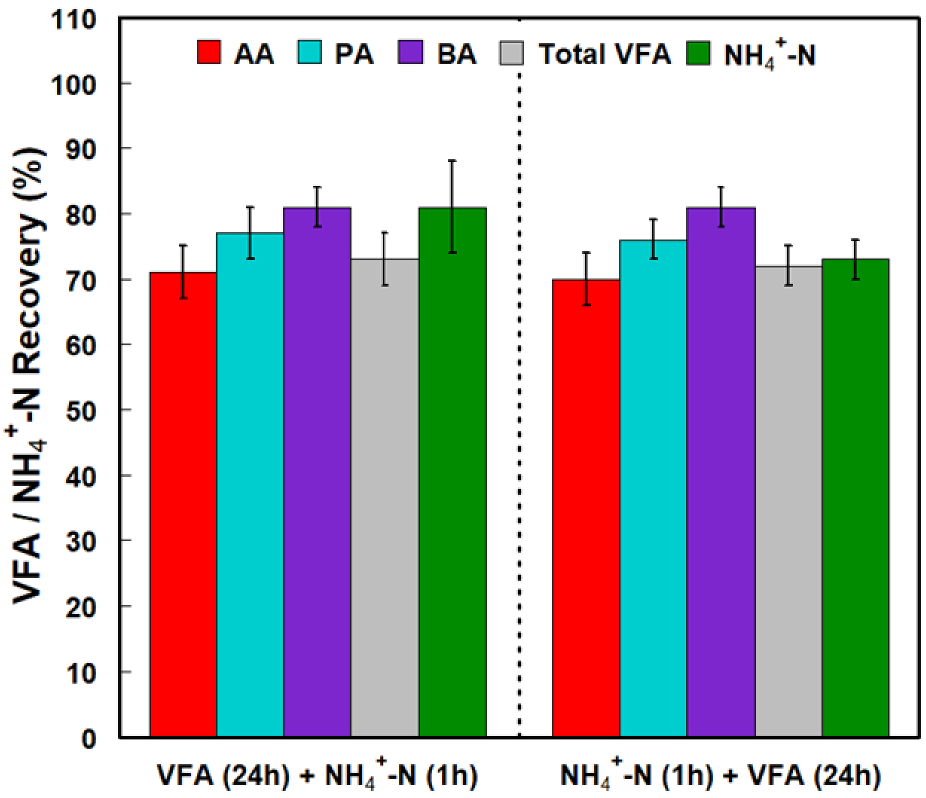

Figure 10. VFA and NH_4^+ recovered in two phases for both altering which compound was recovered first,