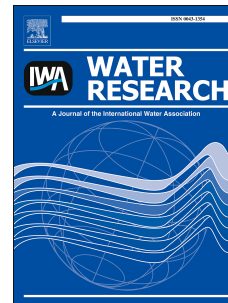


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Nitrogen recovery from wastewater using gas-permeable membranes: Impact of inorganic carbon content and natural organic matter

S. Daguerre-Martini, M.B. Vanotti, M. Rodriguez-Pastor, A. Rosal, R. Moral Herrero



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1 **Nitrogen recovery from wastewater using gas-permeable membranes: Impact of inorganic**
2 **carbon content and natural organic matter**

3

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25 **ABSTRACT**

26 Gas-permeable membranes coupled with low-rate aeration is useful to recover ammonia
27 (NH_4^+) from livestock effluents. In this study, the role of inorganic carbon (bicarbonate,
28 HCO_3^-) to enhance the N recovery process was evaluated using synthetic effluents with
29 various NH_4^+ to HCO_3^- molar ratios of 0.5, 1.0, 1.5 and 2.0. The study also evaluated the
30 effect of increased organic matter on the NH_4^+ recovery using humic acids (3000 to 6000
31 mg L^{-1}), and the N recovery from high-strength swine manure. The release of hydroxide
32 from the HCO_3^- with aeration increased the wastewater pH and promoted gaseous
33 ammonia formation and membrane uptake. At the same time, the recovery of gaseous
34 ammonia (NH_3) through the membrane acidified the wastewater. Therefore, an abundant
35 inorganic carbon supply in balance with the NH_4^+ is needed for a successful operation of the
36 technology. NH_4^+ removal efficiencies $> 96\%$ were obtained with NH_4^+ to HCO_3^- ratios ≤ 1 .
37 However, higher molar ratios inhibited the N recovery process resulting in lower efficiencies
38 ($< 65\%$). Fortunately, most swine manures contain ample supply of endogenous inorganic
39 carbon and the process can be used more economically recover the ammonia using the
40 natural inorganic carbon instead of expensive alkali chemicals. In 4 days, the recovered
41 NH_4^+ from swine manure contained $48,000 \text{ mg L}^{-1}$. Finally, it was found the process was not
42 inhibited by the increasing levels of organic matter in the wastewater evaluated.

43

44

45 **Keywords:** ammonia recovery, ammonia capture, gas-permeable membranes, livestock
46 wastewater, ammonia emissions control.

47

48 1. Introduction

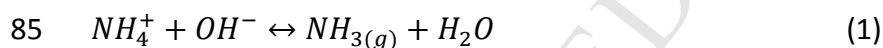
49 Ammoniacal nitrogen is one of the main contaminants of domestic and industrial
50 waste. The concentration of ammoniacal nitrogen varies from 10 to 200 mg L⁻¹ in urban
51 wastewater, from 5 to 1,000 mg L⁻¹ in industrial wastewater, such as those generated by the
52 production of chemical fertilizers, and from about 400 to 5,000 mg L⁻¹ in livestock effluents
53 (Lema and Suarez, 2017; USDA, 2008). Some of the environmental problems that have been
54 cited from ammoniacal nitrogen in wastewater and liquid wastes include the reduction of
55 the dissolved oxygen concentration, the toxic effects on fish, the reduction of disinfection
56 efficiencies, and metal corrosion (Lauterböck et al., 2012). Hence, its removal is necessary
57 in order to protect both natural resources and public health.

58 Traditionally, organic waste from livestock production has been a source of nutrients
59 which was added to agricultural soils. Intensive livestock farming in certain geographical
60 areas in Europe has made this type of waste a problem since it has caused the
61 contamination of aquifers and soils. Furthermore, in 2015, the EU-28 agricultural sector
62 emitted into the air a total of 3,751 kilotonnes of ammonia, and was responsible for 94 % of
63 total ammonia emissions across the region; they mainly occur as a result of volatilisation
64 from livestock excreta (EEA, 2017). While this happens, the global consumption of synthetic
65 fertilizers grows (Heffer and Prud'homme, 2013). Therefore, the capture and recovery of
66 ammonia from livestock farming and its transfer to areas suffering shortages is necessary, in
67 this way reducing the environmental impact while at the same time replacing commercial
68 fertilizers and opening new economic perspectives (Keyzer, 2010; Szogi et al., 2015; Vanotti
69 et al., 2017).

70 The different techniques to remove the nitrogen content can be classified into
71 biological, chemical and physical processes. The biological processes include nitrification-

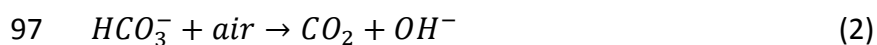
72 denitrification (Vanotti et al., 2009), anammox (Magri et al., 2012a) or microbial fuel cells
73 (Kuntke et al., 2012). The chemical and physical processes include struvite precipitation
74 (Nelson et al., 2003), ammonia stripping (Bonmatí and Flotats, 2003), reverse osmosis
75 (Masse et al., 2010), nanofiltration (Kertesz et al., 2010), ion exchange (Milan et al., 1997),
76 evaporation (Fuchs and Drogos, 2013) and, recently, the treatment using gas-permeable
77 membranes (Vanotti and Szogi, 2015; García-González and Vanotti, 2015).

78 Among numerous applications, the treatment with gas-permeable membranes has
79 been used to retrieve ammonium from liquid manures (García-González et al., 2015; García
80 and Vanotti, 2015). This process requires augmenting the pH of the solution to be treated so
81 as to favor the transformation of ammoniacal nitrogen (NH_4^+) into the un-ionized, gaseous
82 ammonia ($\text{NH}_{3(g)}$) (Eq.(1)) enabling it to cross a microporous hydrophobic membrane where
83 an acidic solution circulates (Figure 1). With a $\text{pH} < 2$, the acidic solution dissolves the NH_3 in
84 the form of ammonium.



86 The studies of García-González et al. (2015) and Vanotti and Szogi (2015) have
87 proposed using nitrification inhibitors and introducing low-rate aeration to obtain a higher
88 pH without the need of adding alkaline chemical elements, in this way reducing the
89 economic and environmental costs of ammonia treatment. During aeration of the manure,
90 carbonate alkalinity is consumed and OH^- is instantly released, increasing the pH and
91 reducing the bicarbonate in the wastewater environment according to Eq. (2) and
92 enhancing both the formation of NH_3 as defined in Eq. (1) and the NH_3 uptake via the gas-
93 permeable membrane (Vanotti et al., 2017). For the purpose of the enhancement of the
94 recovery of NH_3 N recovery using gas-permeable membranes, the term “low-rate aeration”

95 was defined as an aeration rate that is less than about 5% of the aeration rate used for
96 biological ammonia removal/nitrification (Vanotti et al., 2017).



98 However, according to Eq. (3), the recovery of $NH_{3(g)}$ through the gas-permeable
99 membrane causes an increase of acidity in the wastewater environment being treated as
100 the H^+ does not permeate the hydrophobic membrane. Therefore, it is necessary to
101 continually raise the pH levels in order to maintain the efficiency of the recovery (García-
102 Gonzalez and Vanotti, 2015).



104 The aeration effect is double, on one hand, the increase in pH and, on the other
105 hand, the increase in the concentration of free ammonia which allows active permeation of
106 NH_3 through the membrane (García-González et al. 2015). The implementation of this type
107 of physical-chemical treatment versus other types of nitrogen recovery systems has been
108 discussed in several essays, such as those of García-González et al. (2015), Zarebska et al.
109 (2015) and Dube et al. (2016). Zarebska et al. (2015) indicated that the energy
110 consumption of recovering the nitrogen is among the lowest ($0.18 \text{ kW}\cdot\text{h}\cdot\text{kg}^{-1}\text{NH}_3$), compared
111 in a review of six methods; it was also noted that the main economic drawback from gas-
112 permeable membrane systems was the addition of reactive alkaline chemical elements.
113 García-González et al. (2015) demonstrated the positive effect of low-rate aeration on the
114 use of gas-permeable membranes for the purpose of NH_4^+ recovery. With the aeration
115 approach applied to waste effluents from raw liquid swine manures, the NH_4^+ recovered
116 was 98% of the quantity initially present, the ammonia emission losses were less than 1.5%,
117 and the operational cost of ammonia recovery was reduced by 57% with respect to the
118 alternative approach using NaOH addition to increase pH (García-González et al., 2015).

119 The study of Dube et al. (2016) showed that the NH_4^+ recovery with the low-rate aeration
120 was between 5 and 6 times faster than the treatment without aeration, reducing treatment
121 costs by 70% in swine manure anaerobic digester effluent. Although the process was
122 proven to work in several experiments with livestock effluents, the mechanism is difficult to
123 understand when working with complex effluents with total alkalinities that may be
124 comprised of inorganic carbon (carbonate/bicarbonate) plus hydroxide and phosphate
125 compounds. For this reason, there is a need to reconstruct the process using simple
126 solutions to understand the role of the inorganic carbon in this N recovery process.

127 The objective of this research was to determine the role of inorganic carbon
128 (bicarbonate) on the effectiveness of ammonia removal using gas-permeable membranes
129 and low—rate aeration. A series of experiments were carried out using synthetic solutions
130 containing various carbonate to ammonia ratios on the efficiency of the process. Further,
131 the effect of organic matter content on ammonia capture was assessed using humic acids.
132 Lastly, the technology was applied to liquid swine manures from farm areas for fattening
133 pigs with various high-solids strengths to evaluate the behavior of the variables in the study
134 and their impact on the efficiency of ammonium removal and recovery.

135

136 **2. Materials and methods**

137 *2.1. Analytical Methods*

138 Total solids, volatile solids and ammoniacal nitrogen determinations were performed
139 according to APHA Standard Methods (1998). Total solids (TS) were determined after drying
140 to constant weight at 105°C (2540B method) and volatile solids (VS) were determined after
141 further ignition at 550°C for one hour (2540E method). The ammonium analysis was
142 performed with distillation (2100 Kjeltex Distillation Unit), capture of distillate in borate

143 buffer and subsequent titration with 0.10N H₂SO₄ (4500B and C methods). In experiment 2,
144 the ammonium analysis was done by colorimetry (4500-NH₃ G). Alkalinity was determined
145 with an automatic titrator (TitroLine easy, Schott Instruments) by measuring the amount of
146 0.01 M hydrochloric acid required to reach an end-point pH of 4.5 and was reported as mg
147 CaCO₃ L⁻¹ (total alkalinity, 2320 B method). Total carbon and inorganic carbon were
148 measured with a Total Organic Carbon analyzer (Shimadzu brand, TOC5000 model).
149 Density of the semi-solid manure was measured gravimetrically using buckets of known
150 volume, and density of the diluted manures was measured with a Bouyoucos hydrometer.

151 The concentrations of free ammonia, NH₃ (FA) were calculated using the equations
152 given by Anthonisen et al. (1976) based on wastewater temperature (°C), pH, and total NH₄-
153 N concentration (mg L⁻¹) values:

$$154 \quad \text{FA as NH}_3 \text{ (mg L}^{-1}\text{)} = (17/14) \times \{(\text{NH}_4\text{-N} \times 10^{\text{pH}}) / [(K_b/K_w) + 10^{\text{pH}}]\} \quad (4)$$

155 where K_b and K_w are ionization constants for NH₃ and H₂O and the ratio (K_b/K_w) = exp
156 [6344/(273 + T)].

157

158 2.2. Ammonia separation reactor

159 Batch experiments were performed using the ammonium separation reactor and
160 protocol of Dube et al. (2016) (Fig. 2). It consisted of wastewater vessels made of PET with
161 an effective volume of 2 L fitted with a submerged gas-permeable membrane connected
162 with a stripping solution reservoir that contained 200 mL acidic solution made with 0.5 M
163 H₂SO₄. The acidic solution was recirculated with a peristaltic pump (Watson Marlow brand,
164 120S model) at a rate of 5.8 L day⁻¹. This solution flowed inside the tubular membranes and
165 returned to the stripping solution reservoir, completing a closed loop. The gas-permeable
166 membrane used to capture NH₃ was tubular and made of expanded

167 polytetrafluoroethylene (ePTFE) (Phillips Scientific Inc., Rock Hill, SC). The length of the
168 tubular membrane was of 0.6 m and its characteristics are shown in Table 1. Aeration was
169 performed with aquarium pumps (Sera brand, air 110 plus model) and porous plate that
170 provided fine bubbles. The aeration rate was 0.24 L air per L of wastewater per minute
171 (García-González et al., 2015); it was about 4 times lower than aeration rates used by Magri
172 et al. (2012) that greatly inhibited nitrite production activity in experiments of partial
173 nitrification of swine wastewater (0.9 L-air L-liquid⁻¹min⁻¹). Even so, 10 mg L⁻¹ of N-
174 Allylthiourea (98%) were added as a nitrification inhibitor, following strategies presented in
175 other essays (Vanotti and Szogi, 2015).

176

177 2.3. *Experimental Design*

178 Four sets of experiments were carried out using the experimental device for NH₄⁺
179 capture shown in Fig. 2. Experiments 1, 3 and 4 were done in Alicante, Spain and
180 experiment 2 in South Carolina, USA. In the first experiment, the effect of NH₄⁺/HCO₃⁻ molar
181 ratios on N removal was evaluated. The pH evolution and NH₄⁺ elimination were
182 determined using synthetic wastewaters that were prepared with four different ratios of
183 NH₄⁺/HCO₃⁻ (four treatments) by varying the NH₄⁺ concentration and keeping the HCO₃⁻
184 concentration constant. Four complete experimental reactor modules were tested
185 simultaneously using the ammonia separator reactor described in section 2.2. The trials
186 were carried out in single reactors. Target NH₄⁺/HCO₃⁻ molar ratios were 0.5, 1.0, 1.5 and 2.
187 The synthetic wastewaters were prepared with the addition of NH₄NO₃ chemical to reach
188 concentrations of 1000, 2000, 3000 and 4000 mg NH₄⁺ L⁻¹ (56, 111, 167 and 222 mmol NH₄⁺
189 L⁻¹), and the same addition of 9660 mg L⁻¹ NaHCO₃ in all treatments (115 mmol L⁻¹ of
190 bicarbonate or 5750 mg L⁻¹ carbonate alkalinity).

191 The second experiment evaluated the effect of inorganic carbon on N recovery from
192 synthetic wastewaters by varying the amounts of HCO_3^- while keeping the NH_4^+
193 concentration constant. The experiment included three treatments based on results of the
194 first experiment regarding $\text{NH}_4^+/\text{HCO}_3^-$ ratios and N removal. The first treatment was an
195 ideal synthetic solution in terms of the balance of inorganic carbon and NH_4^+ : it contained
196 about 15% more HCO_3^- than the amount needed to remove all the NH_4^+ by the gas-
197 permeable membrane process ($\text{NH}_4^+/\text{HCO}_3^-$ molar ratio = 0.87). The second treatment was
198 a deficient synthetic solution also made of NH_4^+ and inorganic carbon but containing half
199 the HCO_3^- used in treatment 1 ($\text{NH}_4^+/\text{HCO}_3^-$ molar ratio = 1.74). The third treatment was a
200 control made only with NH_4^+ without the inorganic carbon. The synthetic wastewaters in
201 treatments 1, 2 and 3 were prepared with the addition of 6,900, 3450 and 0 mg L^{-1} NaHCO_3 ,
202 respectively (82, 41, and 0 mmol L^{-1} bicarbonate or 4100, 2050, and 0 mg L^{-1} carbonate
203 alkalinity), and the same amount of NH_4Cl (3,820 mg L^{-1}) in all cases that provided a
204 constant $\text{NH}_4\text{-N}$ concentration across treatments (1000 $\text{mg/L NH}_4\text{-N}$ or 71.4 $\text{mmol NH}_4^+ \text{L}^{-1}$).
205 The pH of the freshly made control solution (NH_4Cl without inorganic carbon) was lower (pH
206 = 5.2) than the initial pH of treatments 1 and 2 (pH = 7.8-7.9) and for this reason it was
207 adjusted from 5.2 to 7.8 with the addition of a small amount of NaOH (1.5 mmol NaOH L^{-1}).
208 The experiment used the set-up of Dube et al., (2016) with aeration rate of 0.12 L air per L
209 of wastewater per minute, 1.5 L effective reactor volume, 60 cm tubular membrane length
210 (same membrane described in section 2.2), 4 mL min acid circulation rate, and 250 mL 0.5 M
211 H_2SO_4 in the acid tank. The room temperature was constant ($20.9 \pm 1.0^\circ\text{C}$). The trials were
212 carried out in duplicate reactors. Results of treatment 1 were compared in regards to
213 alkalinity consumption and NH_4^+ removal with results obtained by other authors using a
214 variety of digested and raw manures.

215 The third experiment evaluated the effect that organic matter content in wastewater
216 could have on the flow of NH_3 through the membrane and the N recovery. Three synthetic
217 wastewaters were prepared containing different concentrations of humic acids (three
218 treatments): 3000, 4500 and 6000 mg L^{-1} (added humic acid sodium salt, Sigma Aldrich, ref
219 H16752). All treatments contained 1000 mg L^{-1} of NH_4^+ (778 $\text{mg NH}_4\text{-N L}^{-1}$) using NH_4NO_3
220 chemical and 9660 mg L^{-1} NaHCO_3 ($\text{NH}_4^+/\text{HCO}_3^-$ molar ratio = 0.5) that provided a non-
221 limited inorganic carbon supply. The trials were carried out in single reactors using the
222 ammonia separator reactor and conditions described in section 2.2.

223 The fourth experiment used real manure samples of high to very-high strength, from a
224 swine farm located in Santomera (Murcia, Spain) using the ammonia separator reactor
225 described in section 2.2. Representative (composite) samples were taken from vessels
226 containing a semisolid manure from the fattening production stage. Samples (10) were
227 collected at 3 points of the vessel from the top 1.50-m depth using 5-L sampling jars and
228 combined. The composite manure sample was transported to the laboratory. It was a
229 semisolid material (14.6% TS). For the N recovery experiments, the thick manure was
230 diluted with water 1:3 (liquid swine manure 1) and 1:5 (liquid swine manure 2) (Table 2).
231 Water used for dilution was farm well water simulating the effect of cleaning as a usual farm
232 practice. The farm water contained a high level of bicarbonate ($249 \text{ mg HCO}_3^- \text{ L}^{-1} = 204 \text{ mg}$
233 alkalinity L^{-1}). Other characteristics of the farm water were: $\text{pH} = 8.0 \pm 0.1$; $\text{EC (mS/cm)} = 0.80$
234 $\pm 6\%$; calcium = $68.9 \pm 13\%$; Ammonia N (mg L^{-1}) $\leq 0.05 \pm 14\%$; $\text{CO}_3^{2-} \leq 3 \pm 12\%$. The
235 strengths of swine manure have been classified based on TS concentration: low (0.4-0.8%),
236 medium (0.8-1.7%) and high (1.7-3.2%) (Garcia-Gonzalez and Vanotti, 2015). Accordingly,
237 the strength of liquid manure 1 having 3.65% TS was very-high and that of liquid manure 2
238 with 2.42% TS was high. The trials were carried out in duplicate reactors.

239

240 **3. Results and discussion**241 *3.1. Effect of the ratio $\text{NH}_4^+/\text{HCO}_3^-$ on NH_4^+ removal and recovery*

242 Figure 3 shows pH evolution in the four treatments in the first experiment using
243 wastewater with varied $\text{NH}_4^+/\text{HCO}_3^-$ molar ratios of 0.5, 1.0, 1.5 and 2. Measurements were
244 performed approximately every 20 minutes during the first hour of the experiment and
245 from that moment on, every 24 hours. In all the events, we observed an increase in the pH
246 of about 0.5-0.6 in the first hour. The pH increase at 24 hours varied among treatment: in
247 the two samples with lower $\text{NH}_4^+/\text{HCO}_3^-$ ratios (0.5 and 1.0), the pH increases were 0.91 to
248 1.15 reaching pH levels between 8.8 and 9.1 units; this contrasted with the lower pH
249 increases (about 0.6) in the other two samples with higher $\text{NH}_4^+/\text{HCO}_3^-$ ratios (1.5 and 2)
250 reaching pH levels at 24 hours of 8.3 to 8.5. Precisely, in all the cases and in this same 1-d
251 period, the highest rates of NH_4^+ removal were attained (Fig. 4a). The pH increases obtained
252 with synthetic solution and low rate aeration are consistent with pH increases of 1.1 (8.36 to
253 9.47) obtained by Vanotti et al. (2017) for anaerobically digested swine wastewater treated
254 with the same technique.

255 Nevertheless, from the first day onwards, the pH decreased in all the treatments,
256 except for the one with the lowest $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio of 0.5, where it rose, reaching a
257 final value at day 4 of around 9.5 units and a net pH increase of 1.5; at the same time, the
258 percentage of NH_4^+ removal grew to values of 98% (Table 3 and Fig. 4b). For the treatment
259 with $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio of 1, the decrease in the pH level from day 1 to 4 was small,
260 from 8.8 to 8.5 units, obtaining a net pH increase of 0.6 and a high NH_4^+ removal of 96%
261 similar to the first treatment. Regarding the treatments where higher $\text{NH}_4^+/\text{HCO}_3^-$ molar
262 ratio were used (1.5 and 2), the pH fall was sharp after 1 day (Fig. 3), with final pH values

263 averaging 4.5 units and percentages of NH_4^+ removal under 65% (Table 3). These results
264 indicate that the applied Na_2CO_3 , which provided a carbonate alkalinity concentration of
265 5750 mg L^{-1} in each of the experiments, was enough for handling NH_4^+ concentrations not to
266 exceed 2000 mg L^{-1} ($\leq 1556 \text{ mg NH}_4\text{-N L}^{-1}$). This suggested that, to obtain high removal
267 efficiencies by this process, the carbonate alkalinity concentration initially present in
268 wastewater should at least exceed 3.7 the initial $\text{NH}_4\text{-N}$ concentration. With lower
269 carbonate alkalinity to ammonia ratios (higher $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio), the carbonate was
270 used up quickly in the process of N recovery that generates acidity (eq. 3) and this caused a
271 decrease in the pH of the wastewater environment, pushing the equilibrium of Eq. 1
272 towards the left, inhibiting NH_4^+ removal by the gas-permeable membrane system.

273
274 As observed in Fig. 4 by analyzing the four treatments, the maximum concentration
275 of ammonium ion that was removed, approximately $106\text{-}115 \text{ mmol L}^{-1}$ of NH_4^+ ($1800\text{-}1950$
276 $\text{mg NH}_4^+ \text{ L}^{-1}$) just matches the concentration of bicarbonate initially added (115 mmol L^{-1}).
277 Therefore, approximately 1 mmol of NH_4^+ was removed by the process per 1 mmol of HCO_3^-
278 initially present in the solution. The percentages of NH_4^+ recovery as $(\text{NH}_4)_2\text{SO}_4$ (ratio of NH_4^+
279 recovered in the acidic solution to the NH_4^+ removed from wastewater) were high (>84%) in
280 all treatments. These results indicate that the bottleneck in the process was the availability
281 of gaseous NH_3 and this availability was positively affected by the relative abundance of
282 inorganic carbon. The difference between the NH_4^+ that was removed from wastewater
283 and the NH_4^+ that was recovered in the acidic solution is an unaccounted mass fraction
284 (Table 3). The unaccounted fraction was similar in percentage, approximately 10% of the
285 influent, irrespective of the $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio. It is concluded that there are two
286 distinct and interconnected mechanisms affecting the recovery of NH_4^+ using gas-permeable

287 membranes and low-rate aeration in the presence of inorganic carbon. One mechanism is
288 the release of OH^- from the natural carbonates that does not remove total alkalinity but
289 increases the wastewater pH (Eq. (2)), which in turn promotes NH_3 formation (Eq. (1)) and N
290 recovery by the membrane system. The other mechanism is the release of acidity and
291 consumption of alkalinity in the wastewater environment by the continuous passage of N
292 through the gas-permeable membrane (Eq. (3)). As shown in this experiment (treatments 3
293 and 4 in Figs. 3, 4 and Table 4), this acidification of the wastewater due to an imbalance in
294 the $\text{NH}_4^+/\text{HCO}_3^-$ ratio can completely halt the N recovery process by inhibiting the formation
295 of unionized ammonia (NH_3). Therefore, an abundant inorganic carbon supply in balance
296 with the NH_4^+ is needed for a successful operation of the process without addition of alkali
297 chemicals.

298

299 3.2. *Effect of inorganic carbon on NH_4^+ removal and recovery*

300 Based on the foregoing study, a synthetic wastewater with abundant inorganic
301 carbon content in balance with the NH_4^+ was designed and tested with the gas-permeable
302 membrane process with low-rate aeration. This ideal wastewater contained about 15%
303 more HCO_3^- than needed to remove all the NH_4^+ by the gas-permeable membrane process.
304 It was prepared with NaHCO_3 and NH_4Cl and contained 4100 mg/L alkalinity and 1000 mg/L
305 $\text{NH}_4\text{-N}$ (82 mmol $\text{HCO}_3^- \text{L}^{-1}$ and 71.4 mmol $\text{NH}_4^+ \text{L}^{-1}$ with an $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio = 0.87).
306 The ideal wastewater was compared with a carbon deficient synthetic wastewater
307 containing the same $\text{NH}_4\text{-N}$ content but half the HCO_3^- (41 mmol $\text{HCO}_3^- \text{L}^{-1}$ and 71.4 mmol
308 $\text{NH}_4^+ \text{L}^{-1}$ with an $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio = 1.74). A control treatment without inorganic
309 carbon was also included in the trials (0 mmol $\text{HCO}_3^- \text{L}^{-1}$ and 71.4 mmol $\text{NH}_4^+ \text{L}^{-1}$). Figure 5a
310 shows the observed changes in wastewater N concentration in the all three treatments and

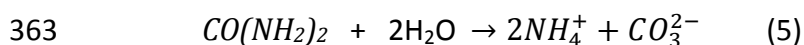
311 the simultaneous N concentration increase in the acid tank, while Fig. 5b shows the
312 cumulative N mass removed from the separation tank and the N mass recovered in the acid
313 tank. Over a period of 7 days, the treatment that used wastewater with abundant inorganic
314 carbon content in balance with the NH_4^+ content ($\text{NH}_4^+/\text{HCO}_3^-$ ratio = 0.87) removed 97% of
315 the NH_4 with 93% of it recovered in the acid tank (Table 4). The NH_4 -N concentration in
316 wastewater followed a negative exponential curve ($\text{NH}_4\text{-N} = 939 e^{-0.0271 \cdot \text{hours}}$, $R^2 = 0.999$) with
317 daily decreases of 52%. However, when inorganic carbon was deficient ($\text{NH}_4^+/\text{HCO}_3^-$ ratio =
318 1.74), the % N removals by the membrane systems were significantly less (57%). When the
319 carbonate was absent (control), the N removal by this system collapsed (6%). Figures 5c,d
320 show the evolution of pH and alkalinity of the three treatments over the same period. In
321 the treatment with $\text{NH}_4^+/\text{HCO}_3^-$ ratio of 0.87, the pH rose from 7.9 to 8.7 the first day and it
322 was maintained high till the end of treatment (pH = 8.9) at day 7 when only 3 % of the N
323 remained in the separation tank. The initial FA concentration in the wastewater calculated
324 using Eq. (4) was 39 mg N L⁻¹. The FA increased to 101 mg N L⁻¹ the first day as a result of
325 the higher pH, even though the NH_4^+ in wastewater was reduced 52% the first day.
326 Subsequently (days 4-7), FA decreased from 62 to 7 mg N L⁻¹ as N was being depleted. The
327 initial alkalinity (3913 mg L⁻¹) was significantly consumed (87%) during the N recovery
328 process leaving a residual alkalinity of 490 mg/L (Fig. 5d). With deficient inorganic carbon
329 relative to ammonia ($\text{NH}_4^+/\text{HCO}_3^-$ ratio = 1.74), the pH of wastewater (7.9) increased 0.6
330 units the first day and afterwards declined steadily to pH 5.5, a net pH decrease over initial
331 of 2.4 units. The initial alkalinity (2310 mg L⁻¹) was exhausted (98% reduction) by day 4 (Fig.
332 5d). At the same time, the wastewater pH declined to 6.9 (Fig. 5a) and the N recovery
333 process stopped leaving 43% of the NH_4^+ in the effluent (Fig. b,c). The FA concentrations in
334 the wastewater were 94 mg N L⁻¹ at day 1 with the higher pH, 2.0 mg N L⁻¹ at day 4 when the

335 recovery stopped, and < 0.2 afterwards. In the control without inorganic carbon, the small
336 initial alkalinity of 80 (due to NaOH addition) was eliminated the first day. The initial pH
337 (7.8) decreased to 6.1 the first day and to 5.07 at day 5; corresponding FA concentrations
338 were nil: 0.7 and 0.06 mg N/L. Therefore, it is concluded that the N uptake by the
339 membrane could be greatly affected when the inorganic carbonate level is deficient relative
340 to the NH_4^+ . This was evident in treatment 2 when alkalinity was consumed and the pH
341 decreased below about 7 that halted the N uptake by the gas-permeable membrane system.
342 It is also concluded from results obtained in this experiment that abundant inorganic carbon
343 in relation to the NH_4^+ is needed to sustain high N removal efficiencies by this gas-
344 permeable membrane and low-rate aeration process.

345 Table 5 shows the alkalinity consumption in the ideal synthetic wastewater
346 (treatment 1) compared with results obtained with manures of various origins by other
347 authors (Dube et al., 2016 and Garcia-Gonzalez et al., 2015). Using the synthetic
348 wastewater made with inorganic carbon and NH_4^+ , approximately 3.7 g of carbonate
349 alkalinity was consumed per g of $\text{NH}_4\text{-N}$ removed by the process. This consumption
350 approaches the theoretical ratio of 3.57 when 1 mmol of HCO_3^- is destroyed per mmol of
351 NH_4^+ removed. The comparison with other manures reveals that the ratio for alkalinity
352 consumption to $\text{NH}_4\text{-N}$ removal of 3.7 obtained in the synthetic wastewater with only
353 inorganic carbon and NH_4^+ was similar than the alkalinity consumption obtained with the
354 three manures (average 4.1) and that this ratio varied little (3.99-4.12) among manures of
355 varied characteristics.

356 The data in table 5 also reveal that all the manures contained an ample supply of
357 alkalinity (approximately 33% higher than minimal needs) to sustain the N recovery process
358 with gas-permeable membranes and low-rate aeration so as to be able to extract all the

359 NH_4^+ without the need of supplemental alkali chemicals. Liquid manure is a mixture of
360 urine, water, and feces. Livestock urine contains >55% of the excreted N, of which more
361 than 70% is in the form of urea (Sommer and Husted, 1995). Urea in combination with
362 water and urease enzyme produces NH_4^+ and carbonate, as described in Eq. (5)::



364 Therefore, a substantial part of the inorganic carbon in manure is produced during
365 decomposition of organic compounds that provide a balanced effluent for the membrane N
366 recovery process.

367

368 3.3. *The effect of organic matter (humic acids) on NH_4^+ recovery*

369 Figure 6A shows the evolution of the pH with time for the three concentrations of
370 humic acids evaluated (3000, 4500, and 6000 mg L^{-1}) with wastewater having an $\text{NH}_4^+/\text{HCO}_3^-$
371 molar ratio of 0.5. The pH increase due to the low-rate aeration was consistent among
372 treatments: it increased about 1 unit, most (0.8 units) in the first day, reaching a final pH of
373 around 9.2 units. The modified wastewater environment conditions were optimal for N
374 recovery by the gas-permeable membrane process. Figure 6B shows the corresponding
375 evolution of NH_4^+ concentration in the wastewater. In all three organic matter treatments,
376 the concentration of NH_4^+ in wastewater was consistently decreased, about > 80% at 1.5
377 days, and > 95% at the end of the run (3 days). The NH_4^+ recovery efficiencies were also
378 high (> 87%) and not affected by the organic matter treatments (Table 6). Therefore, the
379 presence of organic matter (humic acids) did not affect the ammonium removal rate and
380 efficiency. These results indicate that, while inorganic carbon in wastewater is critical, the
381 organic matter, in the concentrations evaluated, do not inhibit the process of N recovery
382 with gas-permeable membranes.

383 3.4. NH_4^+ recovery from swine manure

384 Figure 7A shows the evolution of pH during the experiment that treated two liquid
385 swine manures of very-high and high strength: swine manure 1 (TS 36,500 mg L⁻¹) and swine
386 manure 2 (TS 24,300 mg/L). They were 1:3 and 1:5 dilutions of the collected semisolid
387 manure (table 2). The experiment set-up and operating conditions were the same as
388 experiment 1. The pH increased as expected, approximately 0.5-0.7 units in one day. The
389 pH of manure 1 was about 0.2 units higher, probably due to the lower dilution and higher
390 strength. The higher pH environment obtained in the manure undoubtedly benefited the N
391 removal and recovery process. The manure NH_4^+ contained in the separation tanks
392 decreased at a steady state while the NH_4^+ in the concentrator tanks (acid tanks) increased
393 accordingly (Fig. 7B). The final level of NH_4^+ obtained in the acid tanks after 4 days of
394 treatment was 37,400 ± 4,200 mg $\text{NH}_4\text{-N L}^{-1}$ in the first treatment (manure 1) and 25,000 ±
395 2,800 mg $\text{NH}_4\text{-N L}^{-1}$ in the second treatment (manure 2). Table 7 shows the corresponding
396 NH_4^+ mass balances. During the short time frame of the experiment, the system removed
397 65% and 85% of the ammonia initially present in manure 1 and 2, respectively. The NH_4^+
398 recovery rate was improved with the higher strength manure: the recovery rate of
399 treatment 1 was about 1720 mg N day⁻¹ compared with 1340 mg N day⁻¹ in treatment 2
400 (Table 7). Corresponding ammonia fluxes were 8.90 and 7.11 mg N per cm² of membrane
401 per day. The results obtained with manures showed that the amounts of NH_4^+ recovered in
402 the acidic solution were higher than the amount removed from the liquid manure, providing
403 NH_4^+ recovery efficiencies of 107% and 115% (table 7). This is probably due to
404 mineralization of organic nitrogen during the 4-d treatment contributing additional NH_4^+ to
405 the recovered NH_4^+ pool. In any case, the results with fresh manures showed that the low-
406 rate aeration increased pH of the manure resulting in an active NH_4^+ uptake by the gas-

407 permeable membrane that gave quantitative recoveries of the NH_4^+ and that the overall N
408 recovery was thus optimized.

409

410 **4. Conclusions**

411 This research determined the role of inorganic carbon (bicarbonate alkalinity) on the
412 effectiveness of ammonia recovery using gas-permeable membranes and low-rate aeration.
413 There were two distinct and interconnected mechanisms in this new approach. One was
414 the release of OH^- from the natural carbonates that increased the wastewater pH and
415 promoted gaseous ammonia formation and membrane uptake. The other was the release
416 of acidity and consumption of alkalinity by the N recovery. This acidification of the
417 wastewater can completely halt the N recovery process. Therefore, an abundant inorganic
418 carbon supply in balance with the NH_4^+ is needed for a successful operation of the
419 technology. Fortunately, most swine manures contain ample supply of endogenous
420 inorganic carbon and the process can be used to more economically recover ammonia using
421 this endogenous, natural inorganic carbon instead of expensive alkali chemicals. Finally, we
422 found that the process was not inhibited by increasing levels of organic matter in the
423 wastewater.

424

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435

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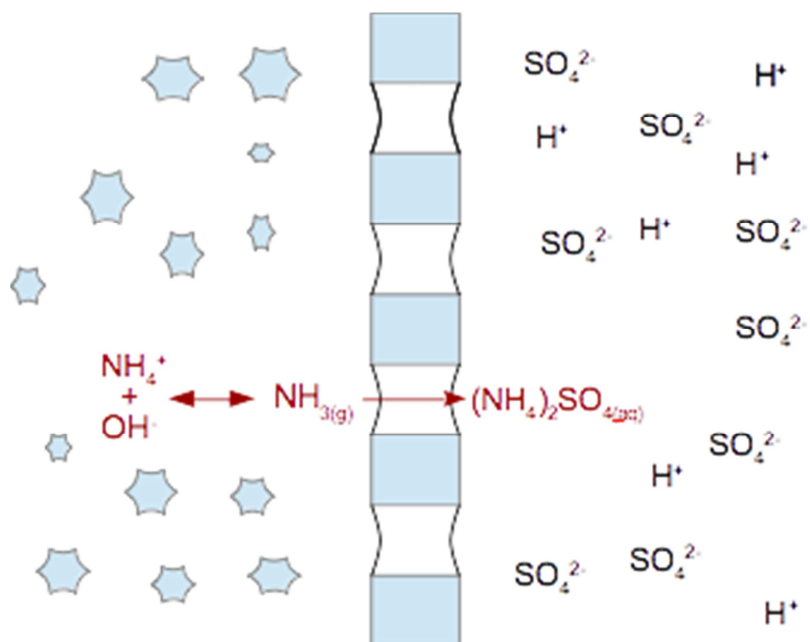


Figure 1. Gaseous ammonia [$\text{NH}_{3(g)}$] permeation through the gas-permeable membrane from the wastewater with dissolved and suspended solids into the stripping sulfuric acid solution.

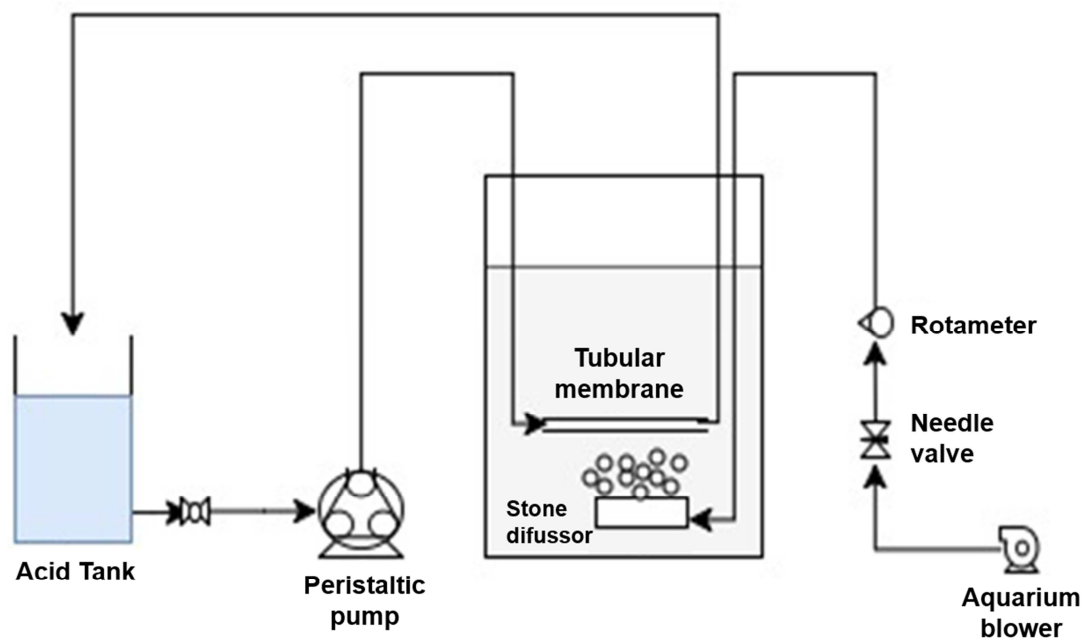


Figure 2. Experimental device for NH_4^+ capture from manure using gas-permeable membrane and low-level aeration to increase wastewater pH and NH_3 transfer using endogenous carbonates.

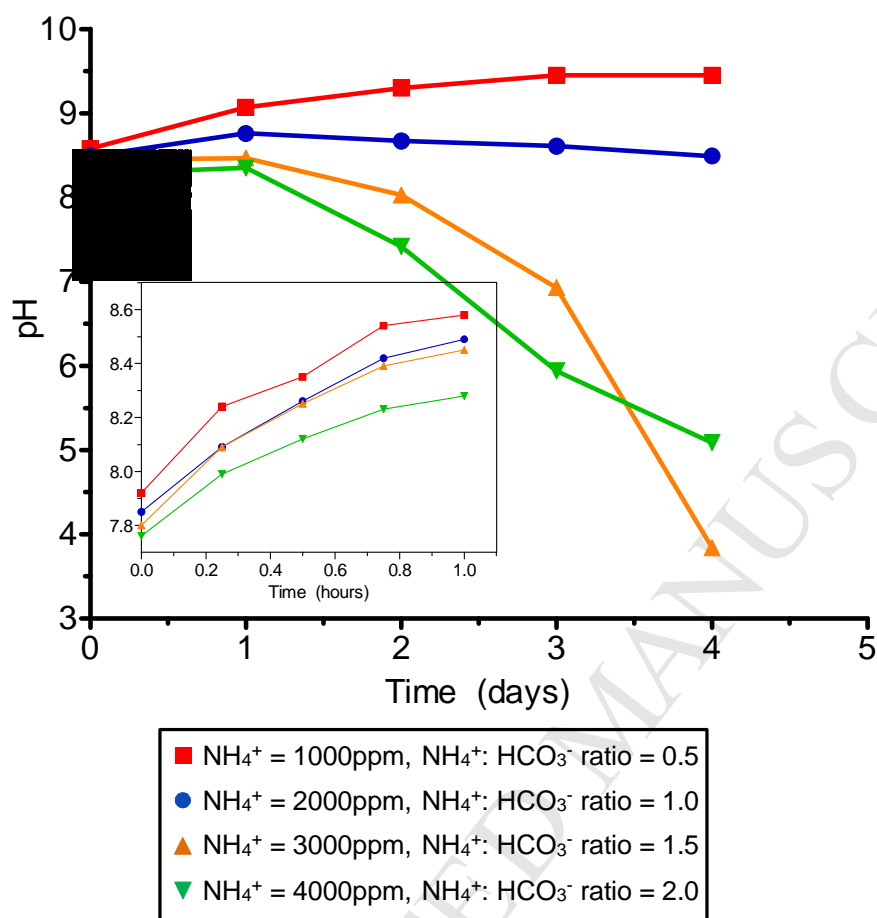


Figure 3. Effect of $\text{NH}_4^+/\text{HCO}_3^-$ ratio (0.5, 1.0, 1.5 and 2.0) on wastewater pH during capture of ammonia with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH_4^+ (56, 111, 167, and 222 mmol L^{-1}) and a constant level of HCO_3^- (115 mmol L^{-1}). Corresponding N removals shown in Fig. 4 and Table 3.

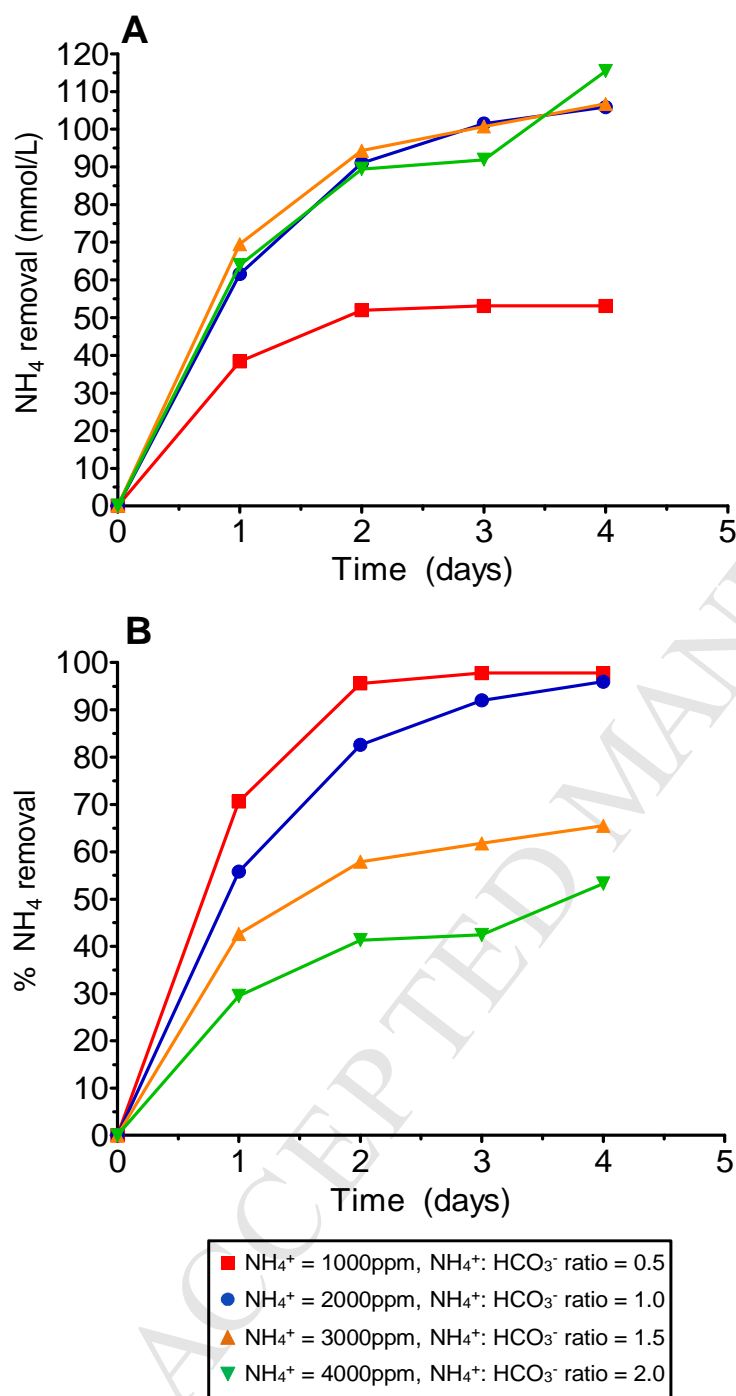


Figure 4. Effect of $\text{NH}_4^+/\text{HCO}_3^-$ ratio of wastewater (0.5, 1.0, 1.5 and 2.0) on the removal of NH_4^+ with gas-permeable membranes and low-rate aeration. Treatments included four levels of NH_4^+ (56, 111, 167, and 222 mmol L^{-1}) and a constant level of HCO_3^- (115 mmol L^{-1}). A: NH_4^+ removal from wastewater in mmol L^{-1} . B: percent NH_4^+ removal. Corresponding pH data are shown in Fig. 3.

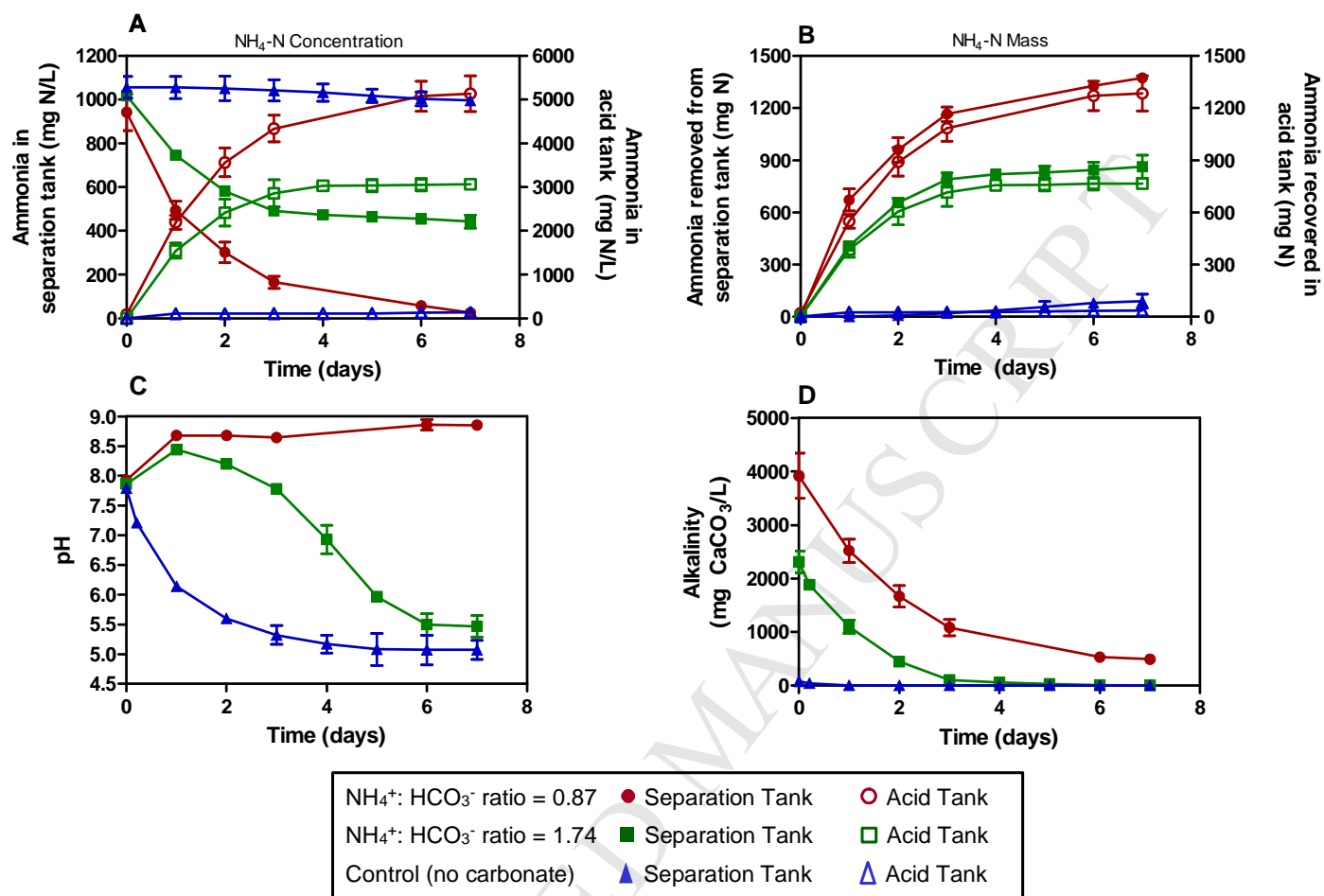


Figure 5. Removal of NH_4^+ with gas-permeable membranes and low-rate aeration as affected by inorganic carbon in wastewater. Treatments included three levels of inorganic carbon (82, 41 and 0 $\text{mmol HCO}_3^- \text{L}^{-1}$) and the same level of ammonia ($71.4 \text{ mmol NH}_4^+ \text{L}^{-1}$ or $1000 \text{ mg NH}_4\text{-N L}^{-1}$). A: N concentration in wastewater and recovery acid tank. B: mass N removal and recovery. C: wastewater pH. D: wastewater alkalinity. The error bars are standard deviation of duplicate reactors.

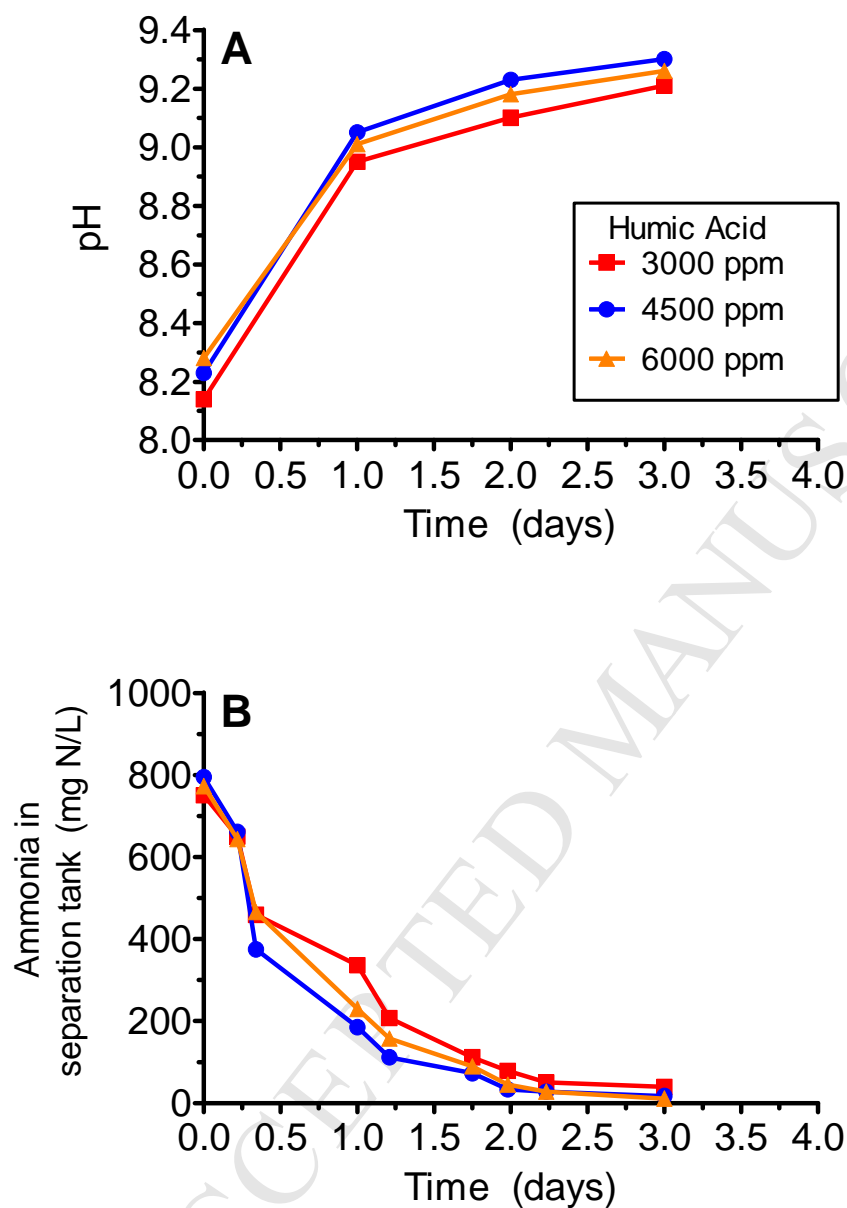


Figure 6. Evolution of pH (A) and NH_4^+ concentration (B) during recovery of ammonia from wastewater containing three levels of Humic Acids (3000, 4500 and 6000 mg L^{-1}) and a uniform $\text{NH}_4^+/\text{HCO}_3^-$ molar ratio of 0.5.

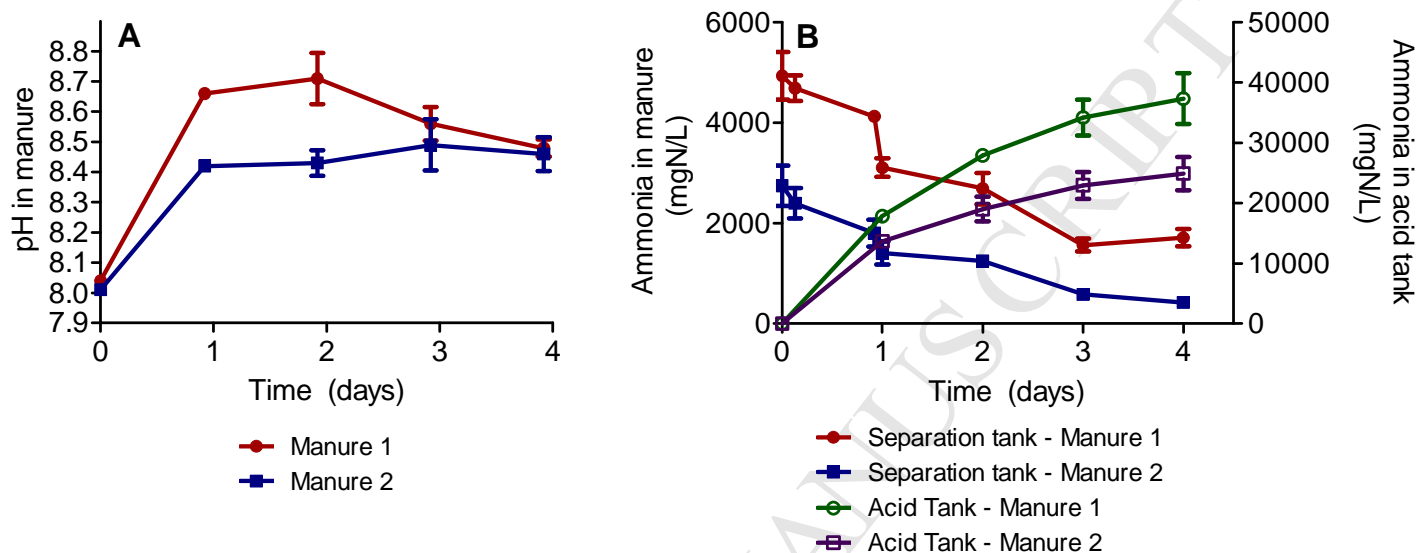


Figure 7. A: Effect of aeration on manure pH during recovery of ammonia using gas-permeable membranes. B: corresponding changes in NH_4^+ concentration in the manure and recovery acid tank. Manure 1 contained 36.5 g TS L^{-1} (very-high strength) and manure 2 contained 24.2 g TS L^{-1} (high strength). The error bars are standard deviation of duplicate reactors.

Table 1. Main characteristics of the tubular membrane used.

Length (cm)	60
Outer diameter (mm)	10.25
Width of the wall (mm)	0.75
Average pore size (μm)	2.5
Bubble point (kPa)	210
Polymer density (g/cm^3)	0.39

Table 2. Characteristics of the swine manures.

Parameters	Raw Manure (semi-solid)	1:3 dilution Manure 1	1:5 dilution Manure 2
pH	7.77	8.10	8.07
EC (mS/cm)	21.2	5.90	4.20
Total Solids (%)	14.60	3.65	2.43
Total Volatile Solids (%)	10.40	2.60	1.73
Ammonia Nitrogen (mg N/kg)	13,728	4939	2749
Density (g/L)	725	931	954

Table 3: Mass balances for the recovery of ammonia using gas-permeable membranes and low-rate aeration as affected by the $\text{NH}_4^+/\text{HCO}_3^-$ ratio in wastewater (experiment 1).

$\text{NH}_4^+/\text{HCO}_3^-$ molar ratio ^a	Carbonate alkalinity to $\text{NH}_4\text{-N}$ ratio	Influent NH_4^+ (mg N)	Effluent NH_4^+ (mg N)	Recovered NH_4^+ (mg N)	NH_4^+ removal efficiency ^b (%)	NH_4^+ recovery efficiency ^c (%)	Unaccounted NH_4^+ ^d (%)
0.5	7.4	1523	33	1288	98	86	13
1.0	3.7	3091	123	2744	96	92	7
1.5	2.5	4569	1579	2699	65	90	6
2.0	1.8	6071	2833	2705	53	84	9

^a Treatments included four levels of NH_4^+ : 56, 111, 167, and 222 mmol L^{-1} (1000, 2000, 3000, and 4000 $\text{mg NH}_4^+ \text{L}^{-1}$) and a constant level of HCO_3^- (115 mmol L^{-1}). Data are results of 4-day batches. Corresponding daily pH and N removal dynamics are shown in Figs. 3 and 4.

^b NH_4^+ removal efficiency = $(\text{NH}_4^+ \text{ removed from wastewater} / \text{initial } \text{NH}_4^+) \times 100$;
 $\text{NH}_4^+ \text{ removed from wastewater} = \text{initial } \text{NH}_4^+ \text{ in wastewater} - \text{remaining } \text{NH}_4^+ \text{ in wastewater}$

^c NH_4^+ recovery efficiency = $(\text{NH}_4^+ \text{ recovered in the acidic solution} / \text{NH}_4^+ \text{ removed from wastewater}) \times 100$

^d Unaccounted NH_4^+ = $(\text{initial } \text{NH}_4^+ \text{ in wastewater} - \text{remaining } \text{NH}_4^+ \text{ in wastewater} - \text{NH}_4^+ \text{ recovered in the acidic solution}) \times 100 / \text{initial } \text{NH}_4^+ \text{ in wastewater}$

Table 4: Mass balances for the recovery of ammonia using gas-permeable membranes and low-rate aeration as affected by inorganic carbon in wastewater (experiment 2).

$\text{NH}_4^+/\text{HCO}_3^-$ molar ratio ^a	Initial pH	Final pH	Influent NH_4^+ (mg N)	Effluent NH_4^+ (mg N)	Recovered NH_4^+ (mg N)	NH_4^+ removal efficiency ^b (%)	NH_4^+ recovery efficiency ^c (%)	Unaccounted NH_4^+ ^d (%)
0.87	7.9	8.9	1413	39	1284	97	93	6
1.74	7.8	5.5	1526	663	766	57	89	6
control	7.8	5.1	1584	1494	35	6	39	3

^a Treatments included three levels of inorganic carbon (82, 41 and 0 mmol $\text{HCO}_3^- \text{L}^{-1}$), all with the same level of ammonia (71.4 mmol $\text{NH}_4^+ \text{L}^{-1}$ or 1000 mg $\text{NH}_4\text{-N} \text{L}^{-1}$). Treatment time was 7 days. Daily pH, alkalinity and N removal dynamics are shown in Fig. 5.

^b NH_4^+ removal efficiency = $(\text{NH}_4^+ \text{ removed from wastewater} / \text{initial } \text{NH}_4^+) \times 100$;
 $\text{NH}_4^+ \text{ removed from wastewater} = \text{initial } \text{NH}_4^+ \text{ in wastewater} - \text{remaining } \text{NH}_4^+ \text{ in wastewater}$

^c NH_4^+ recovery efficiency = $(\text{NH}_4^+ \text{ recovered in the acidic solution} / \text{NH}_4^+ \text{ removed from wastewater}) \times 100$

^d Unaccounted NH_4^+ = $(\text{initial } \text{NH}_4^+ \text{ in wastewater} - \text{remaining } \text{NH}_4^+ \text{ in wastewater} - \text{NH}_4^+ \text{ recovered in the acidic solution}) \times 100 / \text{initial } \text{NH}_4^+ \text{ in wastewater}$

Table 5. Relationship between wastewater alkalinity and ammonia removal using gas-permeable membranes and low-rate aeration during N recovery step.

	Anaerobically Digested Swine Wastewater Farm 1 (Dube et al., 2016)	Anaerobically Digested Swine Wastewater Farm 2 (Dube et al., 2016)	Raw Swine Manure (Garcia-Gonzalez et al., 2015)	Synthetic wastewater made with NH_4^+ and CO_3^- (this study, Fig. 5, ratio = 0.87) ^a
Initial Alkalinity (mg $\text{CaCO}_3 \text{ L}^{-1}$)	11365	8121	13350	3913
Final Alkalinity (mg $\text{CaCO}_3 \text{ L}^{-1}$)	3034	2018	3590	493
Initial NH_4^+ (mg N L^{-1})	2089	1554	2390	942
Final NH_4^+ (mg N L^{-1})	64	23	20	26
Final pH	9.26	9.17	9.20	8.90
Initial Alkalinity:Initial NH_4^+ Ratio	5.44	5.23	5.59	4.15
Alkalinity Consumed ^b (mg $\text{CaCO}_3 \text{ L}^{-1}$)	8331	6103	9760	3420
NH_4^+ Removed ^c (mg N L^{-1})	2025	1531	2370	916
NH_4^+ recovery efficiency ^d (%)	98	96	99	93
Alkalinity Consumed: NH_4^+ Removed Ratio	4.11	3.99	4.12	3.73

^a Synthetic solution: treatment 1 in experiment 2 with $\text{NH}_4^+/\text{HCO}_3^-$ ratio = 0.87 (a mixture of 82 mmol L^{-1} HCO_3^- and 71.4 $\text{mmol NH}_4^+ \text{ L}^{-1}$).

^b Alkalinity consumed = Initial alkalinity – final alkalinity

^c NH_4^+ Removed from wastewater = Initial NH_4^+ - final NH_4^+

^d NH_4^+ recovery efficiency = (NH_4^+ recovered in the acid tank/ NH_4^+ removed from wastewater) x 100

Table 6: Mass balances for the removal and recovery of ammonia from wastewater using gas-permeable membranes and low-rate aeration as affected by the presence of organic matter (experiment 3).

Humic acid concentration (mg L ⁻¹)	NH₄⁺ Removal Efficiency^a (%)	NH₄⁺ Recovery Efficiency^b (%)	Unaccounted NH₄⁺ ^c (%)
3000	95	109	0
4500	98	87	11
6000	99	96	3

^a NH₄⁺ removal efficiency = (NH₄⁺ removed from wastewater/initial NH₄⁺) x 100;
NH₄⁺ removed from wastewater = initial NH₄⁺ in wastewater – remaining NH₄⁺ in wastewater.

Wastewater contained a uniform NH₄⁺/HCO₃⁻ molar ratio of 0.5. pH and N removal dynamics are shown in Fig. 6.

^b NH₄⁺ recovery efficiency = (NH₄⁺ recovered in the acidic solution/ NH₄⁺ removed from wastewater) x 100

^c Unaccounted NH₄⁺ = (initial NH₄⁺ in wastewater – remaining NH₄⁺ in wastewater - NH₄⁺ recovered in the acidic solution) x100/ initial NH₄⁺ in wastewater

Table 7. Mass balances of the recovery of ammonia from swine manure using gas-permeable membrane module with low-rate aeration (experiment 4)^a.

Treatments	Time	Initial NH ₄ ⁺ in Manure	Remaining NH ₄ ⁺ in Manure	NH ₄ ⁺ removed from manure (b)	NH ₄ ⁺ recovered in acidic solution	NH ₄ -N removal efficiency (c)	NH ₄ -N recovery efficiency (d)	Average NH ₄ ⁺ recovery rate (e)	Average NH ₄ ⁺ Flux (f)
	(days)			----- (mg N) -----		----- (%) -----		mg N/day	mg N /cm ² /day
Swine manure 1	4	9880	3430	6450	8841	65	107	1719	8.90
Swine manure 2	4	5500	840	4660	6908	85	115	1343	7.11

- a. Data are average of duplicate reactors. Characteristics of the manures are provided in table 2.
- b. NH_4^+ removed from manure = initial NH_4^+ in manure - remaining NH_4^+ in manure
- c. NH_4^+ removal efficiency = $(\text{NH}_4^+$ removed from manure / initial NH_4^+ in manure) x 100
- d. NH_4^+ recovery efficiency = $(\text{NH}_4^+$ recovered in the acidic solution / NH_4^+ removed from manure) x 100
- e. Average NH_4^+ recovery rate = mass $\text{NH}_4\text{-N}$ recovered in the acidic solution / treatment time
- f. Average NH_4^+ flux = average NH_4^+ recovery rate / membrane surface. Membrane surface = 193 cm²

Low-rate aeration enhanced ammonia recovery of the gas-permeable membrane process

Aeration reacted with the inorganic carbon and increased pH

Approximately 4.1 kg alkalinity was consumed per kg of N removed

NH_4^+ removal efficiencies > 96% were obtained with NH_4^+ to HCO_3^- molar ratios ≤ 1

In 4 days, the recovered NH_4^+ from swine manure contained 48,000 mg L^{-1}

