

1 **Nitrogen removal from digested slurries using a simplified ammonia**
2 **stripping technique**

3 Giorgio Provolo, Francesca Perazzolo*, Gabriele Mattachini, Alberto Finzi, Ezio Naldi,

4 Elisabetta Riva

5 Department of Agricultural and Environmental Sciences, Università degli Studi di Milano,

6 Via Celoria 2, 20133 Milano, Italy

7 *Corresponding author. Tel.: +390250316858. E-mail address: francesca.perazzolo@unimi.it

8 Co-authors e-mail addresses:

9 giorgio.provolo@unimi.it; gabriele.mattachini@unimi.it; a.finzi@fastwebnet.it;

10 ezio.naldi@unimi.it; elisabetta.riva@unimi.it

11 Abbreviation footnote¹

12

¹ Abbreviations:

LFSD: Liquid fraction of separated digestate

USD: Unseparated digestate

13 **Abstract**

14 This study assessed a novel technique for removing nitrogen from digested organic waste
15 based on a slow release of ammonia that was promoted by continuous mixing of the digestate
16 and delivering a continuous air stream across the surface of the liquid. Three 10-day
17 experiments were conducted using two 50-L reactors. In the first two, nitrogen removal
18 efficiencies were evaluated from identical digestates maintained at different temperatures (30
19 °C and 40 °C). At the start of the first experiment, the digestates were adjusted to pH 9 using
20 sodium hydroxide, while in the second experiment pH was not adjusted. The highest
21 ammonia removal efficiency (87%) was obtained at 40 °C with pH adjustment. However at
22 40 °C without pH adjustment, removal efficiencies of 69% for ammonia and 47% for total
23 nitrogen were obtained. In the third experiment two different digestates were tested at 50 °C
24 without pH adjustment. Although the initial chemical characteristics of the digestates were
25 different in this experiment, the ammonia removal efficiencies were very similar
26 (approximately 85%). Despite ammonia removal, the pH increased in all experiments, most
27 likely due to carbon dioxide stripping that was promoted by temperature and mixing. The
28 technique proved to be suitable for removing nitrogen following anaerobic digestion of
29 livestock manure because effective removal was obtained at natural pH (≈ 8) and 40 °C,
30 common operating conditions at typical biogas plants that process manure. Furthermore, the
31 electrical energy requirement to operate the process is limited (estimated to be 3.8 kWh m^{-3}
32 digestate). Further improvements may increase the efficiency and reduce the processing time
33 of this treatment technique. Even without these advances slow-rate air stripping of ammonia
34 is a viable option for reducing the environmental impact associated with animal manure
35 management.

36 **Keywords**

37 Ammonia removal; nitrogen reduction; biogas anaerobic digestion; manure management; CO₂
38 stripping

39
40 **1. Introduction**

41 Anaerobic digestion of animal manure for biogas production can improve both the
42 characteristics of the manure and the sustainable recycling of nutrients, while simultaneously
43 recovering energy. Frequently, biogas installations do not own the necessary area for the land
44 application of the high-nitrogen digestate at acceptable rates, and this limitation is more
45 severe in nitrate-sensitive regions and in regions where a nitrogen surplus already exists.
46 Thus, digestate must be treated further to reduce the nitrogen content and comply with agro-
47 environmental guidelines and rules for land application. Nitrogen can be removed from
48 digestate biologically through processes such as nitrification and denitrification, but these
49 processes do not facilitate recovery of the nitrogen. Furthermore, the high ammonia,
50 phosphate and solids contents of digestates make biological processing difficult (Lei et al.,
51 2007). Even in areas where there is no nitrogen surplus, the management of digestate may
52 benefit a nitrogen recovery process to produce a mineral fertiliser that is easy to transport and
53 utilize on crops. For this reason physico-chemical nitrogen removal processes such as struvite
54 formation, membrane filtration or NH₃ stripping are more attractive than biological
55 processes.

56
57 In particular, NH₃ stripping has been successfully used to remove nitrogen from different
58 wastewaters, e.g. pig slurry, landfill leachate and wastewaters from the production of mineral
59 fertilizers (Gustin and Marinsek-Logar, 2011; Laurenzi et al., 2012). The efficiency of air
60 stripping depends on four main factors: pH, temperature, ratio of air to liquid volume, and
61 liquid characteristics. Combined stripper/absorber plants operate by heating the influent (to

62 80 °C) fed to the plant and adding lime or NaOH to increase pH to 10.5–11 and promote NH₃
63 volatilization. When lime is used, a precipitation tank is normally provided prior to stripping
64 in which phosphates, salts and carbonates can precipitate. Generally in industrial plants, the
65 recommended volumetric gas-to-liquid flow ratio is 600–700:1 (Zarebska et al., 2014) and
66 95% efficiency of ammonia removal is expected. Unfortunately, temperature and pH
67 modification both require extra effort and often entail added cost. In addition, pH control can
68 require the use of dangerous chemicals that introduce health and safety concerns. Thus,
69 although the design of NH₃ stripping technology is well advanced, there exist limitations in
70 its practical application at farm facilities. In this context digested animal manure slurries (i.e.,
71 digestates) present important advantages over untreated slurries for NH₃ stripping; the
72 necessary heat to stimulate the stripping process is readily available from the biogas that is
73 generated during digestion, and higher pH resulting from digestion favours un-ionized NH₃
74 (Gustin and Marinsek-Logar, 2011; Jiang et al., 2014; Serna-Maza et al., 2014). In fact, in the
75 anaerobic conditions of a biogas reactor, the mineral fraction of total nitrogen (as total
76 Kjeldahl nitrogen, TKN) increases owing to conversion of organic nitrogen (Jiang et al.,
77 2014), but remains in the liquid as ammoniacal nitrogen (i.e., NH₄⁺ and NH₃). Furthermore,
78 many biogas plants treat the digestate using solid-liquid separation to obtain a solid fraction
79 rich in phosphorus and organic nitrogen, and a low-solids liquid fraction where most of the
80 ammoniacal nitrogen remains. The separated liquid, from a stripping prospective, has even
81 better characteristics than the raw digestate due to the lower solids content. Studies have
82 demonstrated that slurry and digestate characterised by higher solids content exhibit a lower
83 nitrogen removal efficiency than those with low-solids content, probably due to binding of
84 ammonium ions by organic matter in high-solids inputs (Bonmatí and Flotats, 2003; Zarebska
85 et al., 2014).

86

87 The potential applicability of the stripping process to digestate has been widely reported
88 (Bonmatí and Flotats, 2003; Gustin and Marinsek-Logar, 2011; Jiang et al., 2010; Jiang et al.,
89 2014; Laurení et al., 2012; Lei et al., 2007; Limoli et al., 2016; Morales et al., 2013; Quan et
90 al., 2010; Zeng et al., 2006). However, most of these studies achieved good removal
91 efficiencies in a short time by combining a high air-to-liquid feed ratio (from 5:1 to 850:1)
92 with pH corrections and/or high temperature (up to 80 °C). Bonmatí and Flotats (2003)
93 obtained complete NH₃ removal from digested pig slurry at 80 °C without pH modifications;
94 however, the difficulty and expense of operating at this temperature was recognized as an
95 obstacle to the practical application of this approach. Gustin and Marinsek-Logar (2011)
96 investigated the effect of pH, temperature and airflow on the continuous stripping of NH₃
97 from the effluent of an anaerobic wastewater treatment plant (treating pig slurry and other
98 organic materials) and showed that pH had the most relevant effect on NH₃ stripping. At the
99 beginning of the stripping process pH may increase. García-González et al. (2015) and Zhu et
100 al. (2001) showed that when manure was mixed and aerated, pH would increase due to CO₂
101 stripping, and good nitrogen removal efficiencies could be obtained without using chemicals.
102 Particularly interesting was the study of Lei et al. (2007), which showed that the pH of an
103 anaerobic digestate can be increased from 7.5 to 9.1 by CO₂ stripping in only one day at 15
104 °C.

105

106 These studies suggest the possibility of developing a slow-release stripping process that is
107 easy to implement and manage at farm facilities and overcomes the limitations typical of this
108 technology, which are mainly related to the large demand for thermal energy and the need for
109 additives. In fact, although the principle of the stripping process is well known, its application
110 to digested slurry has not yet been fully successful due mainly to (a) the need to remove
111 solids prior to the stripping columns, (b) the large energy (thermal and electrical) demand and

112 (c) the requirement for chemicals. Therefore, there is the need to develop new solutions based
113 on simplified technologies that are able to achieve adequate nitrogen removal and have only
114 limited pre-treatment and energy requirements. Recent studies (Garcia-González and Vanotti,
115 2015; Garcia-González et al., 2015; Starmans and Timmerman, 2013; Vanotti et al., 2017)
116 have examined some alternative systems that might meet these design criteria; however, none
117 of the techniques evaluated were able to satisfy all constraints, especially the one related to
118 the high solids content of the slurry processed.

119
120 The study here presented investigated the performance of a stripping process based on a new
121 concept of installation in which slow-rate NH_3 volatilization was promoted in a closed reactor
122 containing continuously mixed digestate. The volatilised ammonia was removed by an air
123 stream through the headspace of the reactor. The objectives of the study were to assess the
124 effect on nitrogen removal efficiency of temperature, pH correction and type of digestate.

125

126 **2. Material and methods**

127 ***2.1. Experimental apparatus***

128 The pilot plant used in the study (Fig. 1) consisted of two Poly(methyl methacrylate)
129 containers (reactors), each with a volume of 50 L (40-cm diameter and 40-cm height) and a
130 tight-fitting polyvinylchloride lid with ports for sampling and inserting probes. Each container
131 had an (ambient) air inlet regulated by a flow meter ($2\text{--}30 \text{ L min}^{-1}$, Key Instruments, Trevose,
132 PA, USA) and an outlet for the NH_3 -charged air. The air flow was generated by a membrane
133 pump (EVO30 series, ELECTRO A.D., Barcelona, Spain) and was set at 10 L min^{-1} to ensure
134 one air exchange of the headspace every minute and enhance the slow release of NH_3 . This
135 flowrate correspond to an air velocity over the liquid surface of 0.1 m s^{-1} in agreement with
136 the results of Ye et al. (2008).

137 The reactors were equipped with a mechanical stirrer that consisted of two horizontal blades
138 mounted on a vertical shaft and oriented to mix the liquid in a downward direction. The mixer
139 was driven by an electrical motor with a gearbox and a shaft rotation of 50 rpm. The
140 temperature of reactors was regulated using a 13 W m^{-1} self-regulating heating tape (part no.
141 665-7485, RS Components, Corby, UK) installed externally around the circumference of the
142 reactors and controlled by a thermostat (Ecotron T, Jumo, Fulda, Germany) connected to a
143 temperature probe (Pt1000, Italcoppie, Cremona, Italy) immersed in the reactor liquid. Probes
144 to measure pH (PHE-1335, Omega Engineering, www.omega.com) and Redox potential
145 (ORE-1311, Omega Engineering, www.omega.com) were continuously monitored using a
146 computer and LabView Software (National Instruments, Austin, USA). The probes were
147 positioned approximately 10 cm beneath the surface of the reactor contents and connected to
148 pH and redox circuits (EXP-R35-062 and EXP-R35-058, respectively, Atlas Scientific LLC,
149 New York, USA).

150

151 ***2.2. Experimental methodology and nitrogen loss assessment***

152 Three experiments (A, B and C) were conducted using the equipment described in Section
153 2.1. Experiment A was designed to evaluate the nitrogen removal efficiency at a defined pH
154 and two different temperatures (30 °C and 40°C). Therefore, the digestate pH was increased
155 to pH 9 by adding an appropriate amount of sodium hydroxide (NaOH). Experiment B was
156 similar to A but the pH was not modified; this facilitated assessing the possibility of using
157 this process without additives. Experiments A and B were performed in duplicate to obtain a
158 repetition of results.

159 The third experiment (C) was conducted to evaluate the process using different types of
160 digestate (experiments C1 and C2). As in experiment B the pH of the digestates was not
161 modified. The temperature was set at 50°C.

162

163 The experimental conditions are summarised in Table 1. All experiments had 10-d durations,
164 a time chosen because it is a reasonable hydraulic residence time for a full-scale installation.

165 At the start of each experiment, each reactor was filled with approximately 40 L of digestate
166 from a batch of 100 L that had been thoroughly mixed manually.

167

168 Experiments A and B used the liquid fraction of separated digestate (LFSD) that was
169 collected following mechanical (screw press) separation from a 1-MW biogas plant
170 processing animal manure (pig and cattle slurry, cattle farmyard manure and poultry manure)
171 and a limited amount (5%) of maize silage. Experiment C examined unseparated digestates
172 (USD), one (USD-C1) from the same source as for experiments A and B, and another (USD-
173 C2) from a 360-kW biogas plant that processed cattle slurries and a small amount of maize
174 silage (2%).

175

176 Digestate samples were analysed at the beginning and the end of each experiment for TKN,
177 total ammoniacal nitrogen (TAN), pH, dry matter content (total solids, TS) and volatile solids
178 content (VS), which were determined using standard procedures (APHA, 2012). Daily, a
179 sample of digestate from each reactor was collected and analysed for TAN and pH to identify
180 the transformation of digestate over time. Additionally, during experiment B the
181 concentrations of NH_3 , CO_2 , N_2O and CH_4 were measured using a trace gas analyser (P-TGA
182 1302 Photoacoustic gas-monitor, Innova AirTech Instruments, Ballerup, Denmark).

183

184 During the experiments some water evaporation occurred; therefore, the volume in each
185 reactor was noted daily and used to obtain a mass balance of the nitrogen losses. To compare
186 the nitrogen losses that occurred in the different experiments, the TAN contents were indexed

187 relative to the initial TAN content of each digestate that was measured at the beginning of the
188 experiment. Thus an NH₃ removal index from 0 (no removal) to 1 (complete removal) was
189 developed as an indicator of the efficiency of the process. Because a moderate mineralization
190 of organic nitrogen might have occurred during an experiment, the calculated TAN removal
191 efficiencies were conservative and might underestimate the actual efficiencies achieved in
192 some cases.

193

194 **3. Results and discussion**

195 *3.1. Digestate transformation during the process*

196 Table 2 presents the initial and final chemical characteristics of the digestates. Although the
197 digestates used in experiments A and B were drawn from the same source, their
198 characteristics were slightly different because the samples were retrieved at different times. In
199 particular, digestate in experiment B had a higher concentration of TKN than that in
200 experiment A, but both had very similar TAN contents (1.84–2.14 g kg⁻¹). Because digestate
201 USD-C1 had not been subjected to mechanical separation, it was characterised by higher
202 solids (3.14%) and nitrogen contents (TKN 4.5 g kg⁻¹) than digestates used in experiments A
203 and B, although all were sourced from the same biogas plant. Digestate USD-C2 had the
204 highest TS content (3.82%) and the lowest TAN content (1.58 g kg⁻¹) because this digestate
205 was mainly derived from cattle slurry and had not been subjected to liquid-solid separation.
206 The pH of digestate in experiment A was adjusted to 9 using NaOH; the pH of digestates at
207 the start of experiments B, C1 and C2 were 8.35, 8.13 and 7.81, respectively.

208

209 At the end of the experiments the main treatment effect was a reduction of TAN
210 concentration, and consequently of TKN concentration. During the NH₃ stripping process in
211 experiments A and B, reactors did not experience conversion of organic nitrogen. García-

212 González and Vanotti (2015) also found that organic nitrogen remained stable in swine
213 slurries for which pH had been in the range 8.5–9. In contrast, during experiment C at 50 °C,
214 digestates USD-C1 and USD-C2 had 66% and 73%, respectively, of their initial organic
215 nitrogen converted to inorganic forms.

216

217 These results highlight that after anaerobic digestion, further organic matter degradation can
218 occur under several conditions. In this study, the degradation was probably stimulated by
219 mixing of the digestates, by reactor temperatures higher than 40 °C and by pH lower than 9
220 (Sommer et al., 2013).

221

222 ***3.2. Nitrogen removal efficiencies***

223 Nitrogen removal from the reactors was reflected by trends of the NH₃ removal index as shown
224 in Fig. 2. As expected, NH₃ emission from digestates adjusted to pH 9 (experiment A) was
225 different than from digestates having lower, natural pH because the artificially elevated pH
226 moved the chemical equilibrium towards ammonia gas. At both temperatures, the NH₃
227 volatilization rate was very high initially but decreased noticeably after the first 3–4 days.
228 Probably, the reduced concentration of NH₃ in the liquid after the first few days of emissions
229 reduced the driving force, and thus the rate, of further emissions. At the end of experiment A,
230 NH₃ reductions of 64% and 87% were obtained at 30 °C and 40 °C, respectively.

231

232 Nitrogen removal in experiments on digestates without pH corrections (experiment B) showed
233 similar patterns as in experiment A, but lower efficiencies. At 30 °C, the NH₃ stripping process
234 was slower than at the higher temperatures; after 10 days only 41% of the initial ammoniacal N
235 was lost from digestate B at 30 °C. At this temperature, ammoniacal N in the reactor
236 occasionally increased, albeit slightly, probably due to the mineralization of organic N together

237 with the restricted NH₃ emissions. At higher temperatures, nitrogen removal was more apparent
238 than at lower temperatures. Without pH correction at 40 °C the initial TAN of digestate B was
239 reduced by 69%. In comparison to the nitrogen removal efficiency achieved in experiment A
240 (using pH-adjusted digestate), the removal efficiency achieved with digestate B (same as
241 digestate A, but without pH correction) was lower by 35% at 30 °C and by 21% at 40 °C. These
242 results were comparable with those of García-González and Vanotti (2015) who observed that
243 81% and 57% of TAN was removed from swine manure with and without pH adjustment,
244 respectively.

245

246 Results shown in Fig. 2 from experiment C illustrate that at 50 °C, NH₄-N removal efficiencies
247 up to 84 % can be achieved from raw (i.e., unseparated) digestate. This efficiency was very
248 close to that achieved at 40°C during experiment A in which only the liquid fraction of
249 separated digestate was used, proving that good nitrogen removal efficiencies can be obtained
250 even from digestates with high solids contents. Although the chemical characteristics of
251 digestates USD-C1 and USD-C2 were different, the nitrogen removal efficiencies were very
252 similar at 50 °C. Garcia-Gonzalez and Vanotti (2015) found similar removal efficiencies (>
253 89%) from three manures characterised by a low (1.07 g kg⁻¹), medium (1.68 g kg⁻¹) and high
254 TAN content (2.3 g kg⁻¹). These results suggest that probably nitrogen removal efficiencies can
255 be relatively stable from digestates of different origin if processed under the same conditions
256 (temperature, airflow, mixing, pH).

257

258 The trends in NH₃ removal rates during the experiments can be explained also by the effect of
259 pH modifications (Fig. 3). In experiment A, the initial digestate pH was artificially adjusted to
260 9, but thereafter only slightly increased during the experiment and fluctuated little (between pH
261 9 and 9.2). The pH patterns of experiment A were comparable to those observed by García-

262 González et al. (2015), who found that pH increases in swine manure following initial pH
263 adjustment were slight (to 9.4 from 9 initially). In experiment B (using digestate without pH
264 correction), digestate pH steadily increased until the end of the experiment. The highest pH
265 (8.99) was observed at 30 °C, but at both 30 °C and 40 °C, the pH trends were similar. Because
266 NH₃ volatilization should decrease pH, the observed pH trends might be unexpected; as
267 discussed previously, NH₃ volatilization decreased over time. However, it is well known that
268 digested slurry contains considerable CO₂ that can be easily released in conditions such as those
269 of the experiment (i.e., heating and mixing). Thus, the changes in pH can be interpreted as the
270 net result of two opposing phenomena: CO₂ stripping that increases pH and NH₃ stripping that
271 reduces pH. A single unit of pH increment after just an hour of mixing was observed by García-
272 González et al. (2015) and by Lei et al. (2007) who showed that the pH of anaerobic digestion
273 effluent could increase from 7.4 to 9.3 because of CO₂ stripping. Thus, the lower pH measured
274 in the reactors kept at 50 °C during experiment C was more expected considering that NH₃
275 removal was more substantial at this temperature than at the lower reactor temperatures in
276 experiments A and B.

277

278 These results confirmed that temperature is one of the most influential parameters, together with
279 pH, on the efficiency of NH₃ removal from digestate (Jiang et al., 2014). Besides moving the
280 equilibrium of ammoniacal nitrogen toward the gaseous form, increasing temperature enhances
281 the molecular diffusion in both liquid and gas films, thus increasing the rate of mass transfer.
282 Değemenci et al. (2012) found that the mass transfer coefficient for a synthetic ammonia
283 solution increased 7.25-fold when temperature increased from 20 °C to 50 °C.

284

285 ***3.3. Gas concentration measurements***

286 Figure 4 shows the gas concentrations measured in the reactor headspace during experiment
287 B. After 3–4 days, when the maximum pH was recorded, the maximum NH₃ concentrations
288 also were observed (545 ppm at 40 °C and 297 ppm at 30°C). The CO₂ concentrations
289 decreased during the experiment from very high values of almost 7.5 g m⁻³ initially to values
290 lower than 2 g m⁻³ at the end of the 10-d experiment. Thus, although the main cause of pH
291 increases initially was clearly due to CO₂ stripping (Zhu et al., 2001), another process that
292 might have contributed to the pH increase was NH₃ production caused by the mineralization
293 of organic matter (Sommer et al., 2013). Methane concentrations in the headspace were high
294 (261 ppm at 40 °C and 120 ppm and 30 °C) during the first day (Fig. 4) and thereafter
295 decreased; this may have occurred because continuous mixing facilitated the gas bubble
296 release of residual biogas. The very low N₂O concentrations that were measured confirm that
297 the nitrification process was not established during the NH₃ stripping process.

298

299 While NH₃ and CH₄ concentrations showed a strong dependency on temperature, the other
300 gases were not so sensitive to temperature. For CO₂ and CH₄ the main factor determining the
301 observed patterns seemed to be the mixing of the digestate, which provoked the release of
302 remaining CH₄ and CO₂ still dissolved in the digestate and inside gas bubbles within the
303 digestate. During anaerobic digestion a large amount of CO₂ is produced, so the anaerobic
304 effluent (i.e., digestate) has a high concentration of dissolved inorganic carbon (Moller,
305 2015). During storage of digestate, gas bubbles of CO₂ and CH₄ form in the bulk liquid and
306 are easily released by mixing, which leads to a high volatilization of these compounds
307 (Blanes-Vidal et al., 2012). The initial peak in CO₂ release after starting the mixing is related
308 to the low solubility of CO₂ (Henry constant at 25 °C = 0.034 mol l⁻¹ atm⁻¹). In comparison to
309 CO₂, NH₃ has a much higher solubility (Henry constant at 25 °C = 60.381 mol l⁻¹ atm⁻¹)
310 (Blanes-Vidal and Nadimi, 2011) and this is the reason why NH₃ concentration did not

311 increase (and subsequently decrease) as rapidly as CO₂ and CH₄. Instead, NH₃ tended to stay
312 in solution as NH₄⁺ (Sommer et al., 2007) and did not become one of the major components
313 of gas bubbles (Blanes-Vidal and Nadimi, 2012). The gradual increase in NH₃ release also
314 can be attributed to the increase in the pH of the digestate surface layer, caused by the co-
315 release of CO₂ (Ni et al., 2009).

316

317 Although not a part of this study, the rate of mixing probably can be partly optimised.

318 Nevertheless, an important function of mixing is its effect on the digestate surface. Crust
319 formation or development of any film acting as a barrier on the digestate surface should be
320 avoided to enhance gas release, especially of those components characterised by a low
321 solubility (Sommer et al., 2013). Although the mixing strategy used in this study successfully
322 prevented crust formation, further evaluation could improve the efficiency with which this
323 was accomplished.

324

325 ***3.4. Practical application of the process***

326 These experiments demonstrated the potential of a slow-release NH₃ stripping technology,
327 based on a relatively long retention time and on limited pH adjustment, for the treatment of
328 anaerobically digested livestock slurry. As discussed in Section 3.2, ammonia reductions of 80–
329 90% were achieved. As shown in experiments, the relatively high dry matter content of
330 unseparated digestate at the beginning of treatment did not seem to adversely affect the NH₃
331 removal efficiency. Such high ammonia removal efficiencies are encouraging because this
332 technique is rather simple and does not require dedicated pre-processing of the digested slurry.
333 In fact, considering that solid-liquid separation is already a common treatment step in many
334 biogas plants, this novel modification of a trusted nitrogen removal process can be implemented
335 easily in existing biogas installations.

336

337 As expected, better NH₃ removal was achieved at increased pH. However, as pH is not the only
338 determinant of NH₃ volatilization, choices can be made among the influential operating
339 parameters to achieve a desired NH₃ removal efficiency. For example, in these experiments the
340 NH₃ removal efficiencies achieved in 10 days of retention time at 30 °C with digestate pH
341 adjusted to 9 were the same as those achieved at 40 °C without pH adjustment (Fig. 2).
342 Moreover, the same NH₃ removal efficiencies can be obtained by modifying the retention time.
343 For example, achieving a target NH₃ removal efficiency of 60% was possible under almost all
344 the experimental conditions tested in this study (with the exception treating digestate at 30 °C
345 without pH adjustment) simply by varying the retention time.

346

347 These experimental results can be put in the context of a full scale installation. For example, a
348 full scale facility could consist of modules, each capable of treating 10 m³ d⁻¹ digestate after
349 separation. This size of module is adequate to maintain the same conditions as those of the pilot
350 scale reactors while maintaining a reasonable height of the installation. The characteristics of
351 the module, reported in Table 3, have been determined keeping the same proportion between
352 the height and the diameter of the tank. The calculated air flow rate will maintain an air
353 exchange of one headspace per minute (as in the pilot scale reactors). The stripping process has
354 to be followed by a scrubber to wash the ammonia-charged air with acid (generally sulphuric
355 acid) and recover nitrogen in the form of ammonia sulphate.

356

357 The total energy requirement of the low-rate volatilization system is related to the aeration,
358 the pumps and the mixer. A centrifugal fan assuring the required air flowrate with a pressure
359 drop of 500 Pa has a power rating of 0.84 kW. The mixing energy requirement (5.76 kWh 100
360 m⁻³ d⁻¹; Lemmer et al., 2013) has been assumed to be similar to that for full scale biogas

361 plants. In addition, a power of 0.5 kW has been considered for ancillary equipment (control
362 systems, pumps, and lights). The total energy requirement is thus 3.8 kWh m⁻³ of digestate
363 treated (Table 3). For the NH₃ removal efficiencies demonstrated in this research, the energy
364 demand would be 2.1 kWh kg⁻¹ of N removed (based on 1.8 kg m⁻³ of N removed at 40 °C).
365 The reactor temperature of 40 °C used in this study was consistent with that of a typical
366 mesophilic anaerobic digester. Thus, because these installations produce more heat than is
367 required for sustained operation, the surplus energy could be used (at no extra energy cost) to
368 maintain digestate in an NH₃ stripping reactor at the required temperature. Consequently, the
369 energy cost of this low-rate NH₃ stripping system would be considerably lower than that for
370 industrial NH₃ stripping systems. In such plants energy consumption depends mainly on
371 system design (use of packed columns or tray columns) and heat recovery (Zarebska et al.,
372 2014). Electricity consumption in the range 0.2–94 kWh m⁻³ feed has been reported (Morales
373 et al., 2013; Zarebska et al., 2014) with the lower consumption associated with lower process
374 temperature (e.g., 35 °C). Other proposed nitrogen removal systems, such as that presented by
375 Starman and Timmerman (2013), have a higher calculated energy cost (5 kWh m⁻³) than that
376 of the low-rate stripping system investigated in the present study.

377

378 Thus, considering an average electricity price for industries in the European Union of 0.125
379 €kWh⁻¹ (Eurostat, 2016), the operational costs for the novel slow-rate N removal process
380 examined in this study are 0.5 € m⁻³ of digestate. Including maintenance and investment cost
381 (i.e., interest charges) the overall cost of the slow-rate stripping technique is 3.5 € m⁻³ of
382 digestate processed, which is lower than the cost of other stripping technologies or other
383 nitrogen removal processes (Lyngsø et al., 2011).

384

385 Furthermore the low-rate stripping process here presented requires no pre-treatment for
386 increasing pH and phosphorus removal, thus there are no costs related to the purchase of
387 chemicals such as NaOH or lime. The only costs for chemicals are related to the purchase of
388 acids used for the scrubber. Generally sulphuric acid is used and its cost is about 0.08–0.10 €
389 L⁻¹. Consequently the average chemical cost per kilogram of nitrogen removed is estimated to
390 be in the range 0.5–0.7 €. However, these costs can be offset by income from the sale of the
391 ammonium sulphate that is produced (about 0.5 € m⁻³ of ammonia sulphate at 6–8% N)
392 (Ledda et al., 2013). Thus, the cost of the sulphuric acid can be at least be partially
393 compensated by income from the ammonia sulphate produced.

394

395 Therefore, from a practical perspective the results of this study confirm the feasibility of using
396 slow-rate NH₃ stripping following anaerobic digestion of livestock slurry, which naturally
397 produces a digestate that has higher TAN content and pH than the untreated slurry. Moreover,
398 because anaerobic digestion stimulates the mineralization of organic nitrogen, the process
399 provides nitrogen in ample quantities that can be volatilized, enhancing the possibility of
400 obtaining good nitrogen removal efficiency without the need for additives to raise pH.

401

402 **4. Conclusions**

403 This study evaluated the effectiveness of a novel modification of the NH₃ stripping process for
404 removing nitrogen from anaerobically digested livestock slurry. The results of the study justify
405 a number of conclusions. (1) Slow rate air stripping of digested livestock slurry is an effective
406 technique by which to remove nitrogen as ammonia from this substrate; nitrogen removal
407 efficiencies of 80–90% with the pilot scale trials were achieved. (2) Air stripping with pH
408 adjustment to 9 or high temperature (50 °C) promotes a greater reduction of NH₃ from digested
409 animal slurry than does lower pH and lower temperature. (3) Different combinations of three

410 important operating variables (digestate pH, temperature and retention time) can yield similar
411 nitrogen removal efficiencies. (4) Effective NH_3 reduction can be achieved at pH 8 and 40 °C,
412 which are common operating conditions at typical biogas plants. (5) When utilized at a biogas
413 plant operated at mesophilic temperatures, the stripping process can avail of surplus heat from
414 the biogas plant to maintain digestate at the required temperature for NH_3 removal; thus, the
415 added energy requirements for the slow-release stripping process are limited. (6) The nitrogen
416 removal efficiency of the novel slow-release NH_3 stripping system is close to that of faster
417 treatments that require higher pH and temperature conditions and have much higher energy
418 costs.

419

420 To confirm the applicability of the air stripping technique for a wider range of conditions than
421 those studied, further research is necessary. The process should be tested on different digested
422 livestock slurries to define the system performance when the waste material has
423 characteristics different from those in this study. A second investigation should optimize the
424 process in terms of airflow and mixing requirements to minimise energy requirements. Lastly,
425 because CO_2 stripping can be a very good method by which to increase pH without using
426 additives, research should evaluate if it would be advantageous to raise the reactor pH rapidly
427 by optimizing the aeration system to accelerate the volatilization of CO_2 .

428

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433

434 **References**

435 APHA, 2012. Standard Methods for the Examination of Water and Wastewater, 20th ed.
436 American Public Health Association, American Water Works Association and Water
437 Environment Federation, Washington, DC.

438 Blanes-Vidal, V., Nadimi, E.S., 2011. The dynamics of ammonia release from animal
439 wastewater as influenced by the release of dissolved carbon dioxide and gas bubbles. *Atmos.*
440 *Environ.* 45, 5110–5118.

441 Blanes-Vidal, V., Guàrdia, M., Dai, X.R., Nadimi, E.S., 2012. Emissions of NH₃, CO₂ and
442 H₂S during swine wastewater management: Characterization of transient emissions after air-
443 liquid interface disturbances. *Atmos. Environ.* 54, 408–418.

444 Bonmatí, A., Flotats, X., 2003. Air stripping of ammonia from pig slurry: Characterization and
445 feasibility as pre- or post- treatment to mesophilic anaerobic digestion. *Waste Manage.* 23, 261–
446 272.

447 Değemenci, N., Nuri Ata, O., Yildiz, E., 2012. Ammonia removal by air stripping in a semi-
448 batch jet loop reactor. *J. Ind. Eng. Chem.* 18, 399–404.

449 Eurostat, 2016. Energy Price Statistics.
450 http://ec.europa.eu/eurostat/statisticsexplained/index.php/Energy_price_statistics. (Data
451 extracted in July 2016. Site accessed 5/08/2016).

452 García-González, M.C., Vanotti, M.B., 2015. Recovery of ammonia from swine manure using
453 gas permeable membranes: effect of waste strength and pH. *Waste Manage.* 38, 455–461.

454 García -González, M.C., Vanotti, M.B., Szogi, A.A., 2015. Recovery of ammonia from swine
455 manure using gas-permeable membranes: effect of aeration. *J. Environ. Manage.* 152, 19–26.

456 Gustin, S., Marinsek-Logar, R., 2011. Effect of pH, temperature and air flow rate on continuous
457 ammonia stripping of anaerobic digestion effluent. *Process. Saf. Environ. Prot.* 89, 61–66.

458 Jiang, A., Zhang, T., Zhao, Q., Li, X., Chen, S., Frear, C.S., 2014. Evaluation of an integrated
459 ammonia stripping, recovery, and biogas scrubbing system for use with anaerobically digested
460 dairy manure. *Biosyst. Eng.* 119, 117–126.

461 Jiang, A., Zhang, T., Zhao, Q., Frear, C., Chen, S., 2010. Integrated ammonia recovery
462 technology in conjunction with dairy anaerobic digestion in, *Climate Friendly Farming:
463 Improving the Carbon Footprint of Agriculture in the Pacific Northwest.*
464 http://csanr.wsu.edu/pages/Climate_Friendly_Farming_Final_Report/ (accessed 30/03/2017).

465 Laurení, M., Paltsi, J., Llovera, M., Bonmatí, A., 2012. Influence of pig slurry characteristics on
466 ammonia stripping efficiencies and quality of the recovered ammonium-sulfate solution. *J.*
467 *Chem. Technol. Biotechnol.* 88, 1654–1662.

468 Ledda, C., Schievano, A., Salati, S., Adani, F., 2013. Nitrogen and water recovery from animal
469 slurries by a new integrated ultrafiltration, reverse osmosis and cold stripping process: a case
470 study. *Water Res.* 47, 6157–6166.

471 Lei, X., Sugiura, N., Feng, C., Maekawa, T., 2007. Pretreatment of anaerobic digestion effluent
472 with ammonia stripping and biogas purification. *J. Hazard. Mater.* 145, 391–397.

473 Lemmer A., Naegele, H.J., Sondermann, J. 2013. How efficient are agitators in biogas
474 digesters? Determination of the efficiency of submersible motor mixers and incline agitators by
475 measuring nutrient distribution in full-scale agricultural biogas digesters. *Energies* 6, 6255–
476 6273.

477 Limoli, A., Langone, M., Andreottola, G., 2016. Ammonia removal from raw manure digestate
478 by means of a turbulent mixing stripping process. *J. Environ. Manage.* 176, 1-10.

479 Lyngsø, F.H., Flotats, X., Bonmati, A., Schelde, K.M., Palatsi, J., Magri, A., Juznik, Z., 2011.
480 Assessment of economic feasibility and environmental performance of manure processing
481 technologies. Technical Report No. IV to the European Commission Directorate General
482 Environment. 130 pp.

483 Moller, K., 2015. Effect of anaerobic digestion on soil and nitrogen turnover, N emissions, and
484 soil biological activity: A review. *J. Agron. Sust. Dev.* 35, 1021–1041.

485 Morales, N., Boehler, M.A., Buettner, S., Liebi, C., Siegrist, H., 2013. Recovery of N and P
486 from urine by struvite precipitation followed by combined stripping with digester sludge liquid
487 at full scale. *Water* 5, 1262–1278.

488 Ni, J.Q., Heber, A.J., Sutton, A.L., Kelly, D.T., 2009. Mechanisms of gas releases from swine
489 wastes. *Trans. ASABE* 52, 2013–2025.

490 Quan, X., Ye, C., Xiong, Y., Xiang, J., Wang, F., 2010. Simultaneous removal of ammonia, P
491 and COD from anaerobically digested piggery wastewater using an integrated process of
492 chemical precipitation and air stripping. *J. Hazard Mater.* 178, 326–332.

493 Serna-Maza, A., Heaven, S., Banks, C.J., 2014. Ammonia removal in food waste anaerobic
494 digestion using a side-stream stripping process. *Bioresour. Technol.* 152, 307–315.

495 Sommer, S.G., Petersen, S.O., Sorensen, P., Poulsen, H.D., Moller, H.B., 2007. Methane and
496 carbon dioxide emissions and nitrogen turnover in stored liquid manure. *Nutr. Cycl.*
497 *Agroecosyst.* 78, 27–36.

498 Sommer, S. G., Christensen, M. L., Schmidt, T., Jensen, L. S. (Eds.), 2013. *Animal Manure*
499 *Recycling: Treatment and Management.* John Wiley & Sons Ltd. Chichester, UK, pp. 82–87.

500 Starmans, D.A.J., Timmerman, M., 2013. Apparatus for the ammonium recovery from liquid
501 animal manure. *Appl. Eng. Agric.* 26, 761–767.

502 Vanotti, M. B., Dube, P. J., Szogi, A. A. and García-González, M. C., 2017. Recovery of
503 ammonia and phosphate minerals from swine wastewater using gas-permeable membranes,
504 *Water Res.* 112, 137-146.

505 Ye, Z., Zhang, G., Li, B., Strøm, J.S., Dahl, P.J., 2008. Ammonia emissions affected by
506 airflow in a model pig house: Effects of ventilation rate, floor slat opening, and headspace
507 height in a manure storage pit. *Trans. ASABE*, 51, 2113–2122.

508 Zarebska A., Romero Nieto, D., Christensen, K. V., Fjerbæk Søtoft, L., Norddal, B., 2014.
509 Ammonium fertilizers production from manure: a critical review. *Crit. Rev. Environ. Sci.*
510 *Technol.* 45, 1469–1521.
511 Zeng, L., Mangan, C., Li, X., 2006. Ammonia recovery from anaerobically digested cattle
512 manure by steam stripping, *Water Sci. Technol.* 54, 137–145.
513 Zhu, J., Luo, A., Ndegwa, P.M., 2001. The effect of limited aeration on swine manure
514 phosphorus removal. *J. Environ. Sci. Health B36*, 209–218.
515

516 **Table 1** Experimental conditions of the study.

Experiment	Initial pH	Reactor 1 Temperature (°C)	Reactor 1 Digestate	Reactor 2 Temperature (°C)	Reactor 2 Digestate
A	Corrected to pH 9	30	LFSD	40	LFSD
B	Not corrected	30	LFSD	40	LFSD
C	Not corrected	50	USD (C1)	50	USD (C2)

517

518 LFSD: liquid fraction of separated digestate from the same biogas plant

519 USD: unseparated digestate from two different biogas plants (C1 and C2)

520

521 **Table 2** Digestate characteristics at the beginning and end of the experiments.

Experiment	A*				B*				C			
	30		40		30		40		50 - C1		50 - C2	
T (°C)	Start	End	Start	End	Start	End	Start	End	Start	End	Start	End
TS (%)	2.81 (0.19)	2.61 (0.22)	2.81 (0.19)	2.69 (0.09)	2.96 (0.26)	2.71 (0.35)	2.96 (0.26)	2.90 (0.07)	3.14	2.92	3.82	3.81
VS (%)	1.78 (0.19)	1.5 (0.24)	1.78 (0.19)	1.49 (0.3)	1.84 (0.18)	1.61 (0.21)	1.84 (0.18)	1.66 (0.04)	2.1	1.9	2.45	2.54
TAN (g kg⁻¹)	1.84 (0.13)	0.66 (0.06)	1.84 (0.13)	0.24 (0.06)	2.14 (0.29)	1.25 (0.13)	2.14 (0.29)	0.67 (0.16)	2.38	0.45	1.58	0.25
TKN (g kg⁻¹)	2.49 (0.1)	1.61 (0.03)	2.49 (0.1)	1.06 (0.28)	3.15 (0.19)	2.22 (0.12)	3.15 (0.19)	1.67 (0.06)	4.5	1.16	2.3	0.45
pH	9.05 (0.02)	9.07 (0.02)	9.05 (0.02)	9.07 (0.05)	8.35 (0.23)	8.99 (0.01)	8.35 (0.23)	9.04 (0.25)	8.13	8.63	7.81	8.5
TAN/TKN (%)	63 (4)	41 (3)	63 (4)	24.5 (12)	68 (6)	56 (3)	68 (6)	40 (8)	53	39	69	56

522 *Experiments A and B were replicated, thus results are the average of two sets of measurements. The standard deviation is shown in brackets.

523 Experiment C was not replicated.

524

525 **Table 3** Estimated characteristics of a module to treat $10 \text{ m}^3 \text{ d}^{-1}$ of manure and the associated energy
 526 requirement of the slow-rate ammonia stripping process

Dimensions	Height	m	5
	Diameter	m	5.0
	Total volume	m^3	120
	Headspace	m^3	20
	HRT	days	10
	Air flowrate	$\text{m}^3 \text{ h}^{-1}$	1,200.00
Energy requirement for 10 days			
	Blower	kWh m^{-3} treated	2.02
	Mixer	kWh m^{-3} treated	0.576
	Ancillary	kWh m^{-3} treated	1.2
	Total	kWh m^{-3} treated	3.80
	kg N removed		1.8
	kWh kg N^{-1} removed		2.11

527