

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

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11 Abbreviation footnote<sup>1</sup>

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<sup>1</sup> 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 ( $\approx 8$ ) 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  $3.8 \text{ kWh m}^{-3}$   
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; CO<sub>2</sub>  
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 NH<sub>3</sub> stripping are more attractive than biological  
55 processes.

56

57 In particular, NH<sub>3</sub> 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 NH<sub>3</sub>  
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 NH<sub>3</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub>  
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., NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>). 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 NH<sub>3</sub> 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 NH<sub>3</sub>  
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 NH<sub>3</sub> 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 CO<sub>2</sub>  
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 CO<sub>2</sub> 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  $\text{NH}_3$  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  $\text{NH}_3$ -charged air. The air flow was generated by a membrane  
133 pump (EVO30 series, ELECTRO A.D., Barcelona, Spain) and was set at  $10 \text{ L min}^{-1}$  to ensure  
134 one air exchange of the headspace every minute and enhance the slow release of  $\text{NH}_3$ . This  
135 flowrate correspond to an air velocity over the liquid surface of  $0.1 \text{ m s}^{-1}$  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  $13 \text{ W m}^{-1}$  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  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  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 NH<sub>3</sub> 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<sup>-1</sup>). 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<sup>-1</sup>) 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<sup>-1</sup>) 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 NH<sub>3</sub> 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 NH<sub>3</sub> removal index as shown  
224 in Fig. 2. As expected, NH<sub>3</sub> 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 NH<sub>3</sub>  
227 volatilization rate was very high initially but decreased noticeably after the first 3–4 days.  
228 Probably, the reduced concentration of NH<sub>3</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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, NH<sub>4</sub>-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<sup>-1</sup>), medium (1.68 g kg<sup>-1</sup>) and high  
254 TAN content (2.3 g kg<sup>-1</sup>). 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 NH<sub>3</sub> 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 NH<sub>3</sub> volatilization should decrease pH, the observed pH trends might be unexpected; as  
267 discussed previously, NH<sub>3</sub> volatilization decreased over time. However, it is well known that  
268 digested slurry contains considerable CO<sub>2</sub> 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: CO<sub>2</sub> stripping that increases pH and NH<sub>3</sub> 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 CO<sub>2</sub> stripping. Thus, the lower pH measured  
274 in the reactors kept at 50 °C during experiment C was more expected considering that NH<sub>3</sub>  
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 NH<sub>3</sub> 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 NH<sub>3</sub> concentrations  
288 also were observed (545 ppm at 40 °C and 297 ppm at 30°C). The CO<sub>2</sub> concentrations  
289 decreased during the experiment from very high values of almost 7.5 g m<sup>-3</sup> initially to values  
290 lower than 2 g m<sup>-3</sup> at the end of the 10-d experiment. Thus, although the main cause of pH  
291 increases initially was clearly due to CO<sub>2</sub> stripping (Zhu et al., 2001), another process that  
292 might have contributed to the pH increase was NH<sub>3</sub> 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 N<sub>2</sub>O concentrations that were measured confirm that  
297 the nitrification process was not established during the NH<sub>3</sub> stripping process.

298

299 While NH<sub>3</sub> and CH<sub>4</sub> concentrations showed a strong dependency on temperature, the other  
300 gases were not so sensitive to temperature. For CO<sub>2</sub> and CH<sub>4</sub> the main factor determining the  
301 observed patterns seemed to be the mixing of the digestate, which provoked the release of  
302 remaining CH<sub>4</sub> and CO<sub>2</sub> still dissolved in the digestate and inside gas bubbles within the  
303 digestate. During anaerobic digestion a large amount of CO<sub>2</sub> 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 CO<sub>2</sub> and CH<sub>4</sub> 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 CO<sub>2</sub> release after starting the mixing is related  
308 to the low solubility of CO<sub>2</sub> (Henry constant at 25 °C = 0.034 mol l<sup>-1</sup> atm<sup>-1</sup>). In comparison to  
309 CO<sub>2</sub>, NH<sub>3</sub> has a much higher solubility (Henry constant at 25 °C = 60.381 mol l<sup>-1</sup> atm<sup>-1</sup>)  
310 (Blanes-Vidal and Nadimi, 2011) and this is the reason why NH<sub>3</sub> concentration did not

311 increase (and subsequently decrease) as rapidly as CO<sub>2</sub> and CH<sub>4</sub>. Instead, NH<sub>3</sub> tended to stay  
312 in solution as NH<sub>4</sub><sup>+</sup> (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 NH<sub>3</sub> release also  
314 can be attributed to the increase in the pH of the digestate surface layer, caused by the co-  
315 release of CO<sub>2</sub> (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 NH<sub>3</sub> 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 NH<sub>3</sub>  
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 NH<sub>3</sub> removal was achieved at increased pH. However, as pH is not the only  
338 determinant of NH<sub>3</sub> volatilization, choices can be made among the influential operating  
339 parameters to achieve a desired NH<sub>3</sub> removal efficiency. For example, in these experiments the  
340 NH<sub>3</sub> 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 NH<sub>3</sub> removal efficiencies can be obtained by modifying the retention time.  
343 For example, achieving a target NH<sub>3</sub> 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 m<sup>3</sup> d<sup>-1</sup> 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<sup>-3</sup> d<sup>-1</sup>; 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<sup>-3</sup> of digestate  
363 treated (Table 3). For the NH<sub>3</sub> removal efficiencies demonstrated in this research, the energy  
364 demand would be 2.1 kWh kg<sup>-1</sup> of N removed (based on 1.8 kg m<sup>-3</sup> 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 NH<sub>3</sub> stripping reactor at the required temperature. Consequently, the  
369 energy cost of this low-rate NH<sub>3</sub> stripping system would be considerably lower than that for  
370 industrial NH<sub>3</sub> 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<sup>-3</sup> 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 Starmans and Timmerman (2013), have a higher calculated energy cost (5 kWh m<sup>-3</sup>) 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<sup>-1</sup> (Eurostat, 2016), the operational costs for the novel slow-rate N removal process  
380 examined in this study are 0.5 € m<sup>-3</sup> 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<sup>-3</sup> 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<sup>-1</sup>. 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<sup>-3</sup> 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub> 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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{CO}_2$  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  $\text{CO}_2$ .

428

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433

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515

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

<b>Experiment</b>	<b>Initial pH</b>	<b>Reactor 1 Temperature (°C)</b>	<b>Reactor 1 Digestate</b>	<b>Reactor 2 Temperature (°C)</b>	<b>Reactor 2 Digestate</b>
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
<b>TS (%)</b>	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
<b>VS (%)</b>	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
<b>TAN (g kg<sup>-1</sup>)</b>	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
<b>TKN (g kg<sup>-1</sup>)</b>	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
<b>pH</b>	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
<b>TAN/TKN (%)</b>	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	$\text{m}^3$	120
	Headspace	$\text{m}^3$	20
	HRT	days	10
	Air flowrate	$\text{m}^3 \text{ h}^{-1}$	1,200.00
Energy requirement for 10 days			
	Blower	$\text{kWh m}^{-3}$ treated	2.02
	Mixer	$\text{kWh m}^{-3}$ treated	0.576
	Ancillary	$\text{kWh m}^{-3}$ treated	1.2
	Total	$\text{kWh m}^{-3}$ treated	3.80
	kg N removed		1.8
	$\text{kWh kg N}^{-1}$ removed		2.11

527