Effect of ammonia stripping and use of additives on separation of solids, phosphorus, copper and zinc from liquid fractions of animal slurries

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Abstract

To increase the sustainable reuse of animal manure as fertilizer, in many cases suitable treatment techniques are needed to modify the composition and obtain a balanced nutrient content. This study was conducted to evaluate the best strategies to remove solids, P, Cu and Zn, using two additives $Ca(OH)_2$ and $Al_2(SO_4)_3$, in combination with an ammonia stripping process. The assessment was carried out on five type of liquid fractions derived from the mechanically separation of: raw pig slurry, pig digested slurry, pig digested slurry after ammonia stripping, pig and cattle digested slurry, pig and cattle digested slurry after ammonia stripping. After the addition of the chemicals, the liquid fractions were mixed and then separated using a static filter. The contents of total solids P, Cu and Zn were determined. The additives effectively improved separation efficiencies which depended on the type of slurry and additive used. The P separation efficiencies ranged from 72% to 93% using $Al_2(SO_4)_3$, and from 20 to 74% using $Ca(OH)_2$. The use of $Al_2(SO_4)_3$ always had a more consistent effect on the removal efficiencies than $Ca(OH)_2$. The ammonia stripping process, reducing the alkalinity of the digested liquid fractions, facilitated a higher concentration of elements in the separated fraction. With the addition of $Al_2(SO_4)_3$ to digestate after stripping the concentration of P, Cu and Zn in the solid fraction generally increased when compared to the same liquid fraction without stripping. The addition of $Ca(OH)_2$ might be effective in removing P before the stripping process with the additional benefit to raise pH and improve the ammonia removal efficiency. These findings indicate that solid-liquid separation of animal manure slurries, assisted by chemical additives and coupled with ammonia stripping, can be a viable option for improving the sustainable use of animal manure as a fertiliser.

Keywords: solid-liquid separation, calcium hydroxide, aluminium sulfate, heavy metals, manure, nitrogen removal

1. Introduction

As much as 40 million tonnes of phosphorus (P) as phosphate (P_2O_5) is used worldwide mainly for agriculture; this consumption will increase P demand by 1.5% annually (Harris et al., 2008). The production of P fertilisers from phosphate rock is energy intensive and leads to significant emissions of carbon, radioactive by-products and heavy metals (Cordell et al., 2009; Tervahauta et al., 2014). Furthermore, rock phosphate is not a renewable resource and can be exhausted in 100–250 years at the present rate of use (Grigatti et al., 2015; Tervahauta et al., 2014). Therefore, unnecessary P use must be limited and an alternative found to mining phosphate rock. Because of the imbalance in the amounts of N and P in animal manure relative to crop needs, P is often applied in excess of crop requirements, increasing the P concentration in soils and consequently the potential for P movement to water resources. Thus, removing P from manure can reduce the risk of environmental pollution from this element when manure is applied to the land. Similarly, changing the relative amounts of P in the solid and liquid fractions of manure can facilitate its use as a renewable source of P fertiliser in agriculture.

Besides the need to recover P from livestock manure to avoid over-application (especially in intensive livestock production areas), another concern about the correct utilisation of livestock manure is related to their content in heavy metals, especially copper (Cu) and zinc (Zn) (Sommer et al., 2013). Heavy metals are present in low concentrations in livestock diets and can be added to certain feeds for improving health and wellbeing or as growth promoters (Nicholson et al., 2003; Sommer et al., 2013). Nevertheless, only a small percentage of ingested heavy metals are absorbed by animals (10-20% of Cu and Zn); the remainder is excreted in the faeces or urine, as is 60-85% of the P ingested (Suzuki et al., 2010). Over time, land-applied elements not used by plants can accumulate and cause soil and water pollution (Almasri and Kaluarachchi, 2004). Approximately 40% of total annual input of Zn and Cu to agricultural land is derived from livestock manures (Marcato et al., 2008; Nicholson et al., 2003; Suzuki et al., 2010) and the continuous application of manure can lead to an increase of the concentration of Cu and Zn in soils and in the food chain (Provolo et al., 2018).

61   One possibility for recovering P and removing heavy metals from animal manure is solid-liquid

62   separation. This physical treatment technique produces a solid fraction having a high dry

63   matter (DM) content that is rich in nutrients, as well as a liquid fraction; the fractions can be

64   managed separately. The solid fraction, which has a relatively small volume, contains high

65   concentrations of carbon (C) and nutrients, particularly N and P. Even though solid-liquid

66   separation alone can be considered a suitable method to remove N and P from animal slurry

67   (Møller et al., 2007a), high removal efficiencies can be achieved only with the use of chemical

68   additives, flocculants and/or coagulants (Fernandes et al., 2011; Vanotti et al., 2017).

69   Concerning chemical precipitation, several types of additives have been studied to coagulate

70   manure, to flocculate it or to remove orthophosphate (PO_4^{3-}). Experimental and actual

71   applications have used iron (Fe), aluminium (Al) and calcium (Ca) salts, several types of

72   polyacrylamides and clay as coagulants/flocculants (Christensen et el., 2009; Hjorth &

73   Christensen, 2008; Møller et al. 2007b; Vanotti et al., 2002).

74   While there are several reported P removal efficiencies from livestock manure using

75   mechanical separation with or without additives, the effect of these treatments on Cu and Zn

76   removal is not adequately addressed, especially with regard to digestate from anaerobically

77   digested animal manure. Moreover, there is little information on P, Cu and Zn removal

78   efficiencies from animal slurries after N removal process based on ammonia stripping. With

79   this treatment ammonia is transferred from the waste stream into air, then absorbed from the

80   air into a strong acid solution (generally sulphuric acid) generating an ammonium salt (Bonmatí

81   and Flotats, 2003). This treatment is generally performed in a double column process: the first

82   column is dedicated to ammonia stripping from the liquid fraction while the second column is

83   dedicated to the recovery of nitrogen as ammonium salt (Bolzonella et al., 2018). The process

84   in this configuration requires a pre-treatment for solid-liquid separation and a further treatment

85   for suspended solid removal to avoid clogging of the stripping column (Bolzonella et al., 2018).

86   Alternatively, the ammonia stripping can be performed with a simplified technique based on

87   slow release of ammonia in a mixed container (Provolo et al., 2017). With this solution, there

88   are less limitation for solid contents and a mechanical solid-liquid separation (for example a

89   screw-press) is the only pre-treatment required.

90   The ammonia stripping process modify the characteristics of the slurry: besides the reduction

91   of ammonia, one of the more relevant effect is the reduction of alkalinity. The formation and

92   precipitation of salts and stripping of CO_2 and ammonia may explain this reduction (Bonmatí

93   and Flotats, 2003). The ammonia stripping process might affect P, Cu, Zn separation

94   efficiencies with additives due to the side reactions of the additives with alkalinity to form

95   precipitates (Mohammed and Shanshool, 2009).

96   In order to define the best strategies to remove P, Cu and Zn in combination with ammonia

97   stripping process, a pig and two co-digested liquid fractions after mechanical separation, with

98   and without ammonia stripping treatment, were treated for solid-liquid separation with different

99   doses of $Al_2(SO_4)_3$ and $Ca(OH)_2$. The overall goal of the research was to evaluate the efficiency

100   of phosphorus recovery and heavy metals removal process, and to determine if such a

101   treatment can be combined with a simplified stripping process for N recovery.

102

2. Materials and methods

2.1. Liquid fractions and ammonia stripping

105   Laboratory scale solid-liquid separation experiments were conducted on liquid fraction of

106   animal slurries (LF) using two additives $Ca(OH)_2$, hereafter shortened to CaH, and $Al_2(SO_4)_3$,

107   hereafter shortened to AlS) to study the effect of different doses of the additives on removals

108   of total solids (TS), P, Cu and Zn. Three types of LFs obtained using a screw-press equipment

109   were used, two of which were tested both with and without being subjected to an ammonia

110   stripping process:

111   -   LF of pig slurry (PS), collected from a fattening pig farm;

112   -   LF of anaerobically co-digested pig slurry and corn silage (PD) and the same LF

113   after a stripping process for ammonia removal (PDS); and

114   -   LF of anaerobically digested pigs and cattle slurry (C+P)D and the same LF after a

115   stripping process for ammonia removal ((C+P)DS).

116   All LFs were collected from farms located in the province of Bergamo (Italy).

117   The laboratory scale stripping process was carried out in 50 L reactors, each having a hydraulic

118   residence time of 12 days. During the process the reactor temperature was maintained at 40°C

119   and LFs were mixed at 50 rpm. The airflow over the liquid surface was set at two headspaces

120   per minute. In the first 2 days, 33% of the airflow was provided from the bottom of the reactor

121   through air stones and the rest was introduced into the headspace. Subsequently, 100% of the

122   aeration was introduced into the headspace. The stripping process achieved an N removal

123   efficiency of approximately 80% (Provolo et al., 2017).

124   *2.2. Determination of optimal chemical doses*

125   Preliminary tests were conducted using 500 mL samples of each LF to determine the correct

126   doses of CaH and AlS for precipitation and separation treatments. An optimal dose (D) of each

127   chemical was identified by observing the pH and electrical conductivity (EC) responses to

128   increasing doses of each additive. Doses of each chemical were increased in increments of

129   0.25 g/L of Ca^{2+} (or Al^{3+}).

130   As reported by other studies (Szogi et al., 2015) there is no direct relation between P

131   concentration in animal manure slurries and the CaH dose necessary for its precipitation. In

132   addition, P precipitation using CaH occurs only after the precipitation of CO_3^{-2}. CaH induces

133   significant CO_3^{-2} precipitation as confirmed by the decreasing EC, a decrease that continues

134   until the CO_3^{-2} concentration becomes limiting and prevents the solubility limit of this salt from

135   being exceeded. The optimal dose of CaH for CO_3^{-2} precipitation was determined at the

136   minimum EC. In excess of the optimal dose, all inorganic C is consumed and the excess

137    $Ca(OH)_2$ introduced in the solution, which increases the Ca^{2+} content and thus the EC (Renou

138   et al., 2008).

139   Regarding AlS, in addition to observing pH and EC, the foaming and the size of flocs were

140   evaluated. To determine the size of flocs, after the AlS was added, samples were mixed at 200

141 rpm for 20 s and then at 30 rpm for 2 min. Then the predominant dimension of the flocs was

142 evaluated visually using an arbitrary scale from 1 (all liquid) to 5 (mostly flakes ~5 mm). The

143 level of the foam produced was also measured. The reference dose selected corresponded to

144 the Al^{3+} concentration beyond which the floc dimension did not change and the foam level

145 remained relatively constant.

2.3. Solid-liquid separation tests

147 Jar tests with mechanical stirring were used to examine the effect of CaH and AlS on solid-

148 liquid separation of the LFs. Each separation test was conducted using each additive at three

149 different doses: (1) null dosage, (2) the optimal dose determined from the preliminary tests for

150 each LF (described in Section 2.2) and (3) 25% lower dosage than optimal. CaH was

151 introduced into the sample as "lime milk" at concentration of 200 g/L. A 1 M solution of AlS was

152 prepared for each experiment and added at the desired concentration using a micropipette.

153 In each test, 500 mL of LF and the required dose of either CaH or AlS were added

154 simultaneously to a 1 L glass beaker; then the mixing began. The first rapid mixing phase (5

155 min at 250 rpm for CaH, and 30 sec at 250 rpm for AlS) was followed by a slow mixing phase

156 at 30 rpm for 20 min for CaH and 20 rpm for 20 min for AlS. Then, the suspensions were

157 allowed to settle for 30 minutes (Renou et al., 2008; Szabó et al., 2008). At the end of settling,

158 each solution was separated using a 0.25-mm mesh static filter and allowing 30 min of

159 drainage time. The two different fractions obtained, filtrate and retained solids, were weighed.

160 All tests were conducted in duplicate.

2.4. Analytical methods

162 Each LF was characterized using standard procedures (Rice et al. 2012) for total Kjeldahl

163 nitrogen (TKN), EC, total ammonia nitrogen (TAN), pH, and dry matter as total solids (TS) and

164 volatile solids (VS). The total contents of P, Cu and Zn in the LFs were evaluated using

165 inductively coupled plasma mass spectrometry after acid mineralisation (EPA 1998; Rice et al.

166 2012). All analyses were conducted in duplicate.

2.5. Calculations and statistical analyses

To evaluate the separation results, two indexes were calculated (Sommer et al., 2013). The separation efficiency, $E_{t(x)}$, was determined to express the distribution of TS, N, P, Cu and Zn. between the solid fraction (retained by the static filter) and liquid fraction (passing through the filter). This calculation (Eq. 1) uses the ratio between the mass of a specific entity in the solid fraction and the mass of the same entity in the input slurry (i.e., the combined liquid and solid fractions) (Cocolo et al. 2016).

$$E_t(x) = \frac{m_{x(solid)}}{m_{x(solid)} + m_{x(liquid)}} \qquad (1)$$

where $m_{x(solid)}$ and $m_{x(liquid)}$ are the mass of the component x respectively in the solid and liquid fractions of the separated LFs.

The simple separation efficiency defined by Eq. (1) gives no indication of how the concentration of entity *x* may change (increase) in the solid fraction. Therefore, the reduced separation index, $E'_{t(x)}$, was also calculated (Cocolo et al. 2016):

$$E'_t(x) = \frac{E_{t(x)} - \frac{m_{solid}}{m_{slurry}}}{1 - \frac{m_{solid}}{m_{slurry}}} \qquad (2)$$

where m_{solid} and m_{slurry} are the total masses of solid fraction and separated slurry, respectively, and $E_{t(x)}$ is defined by Eq. (1). Eq. 2 fulfils all requirements for an efficiency definition because it yields a 0 value when no separation takes place and 1 when complete separation is achieved (Møller et al., 2000). In particular, $E'_{t(x)}$ ranges from -1 to +1, such that positive values indicate an increase in concentration of entity *x* in the solid fraction compared with the raw slurry and negative values indicate an increase in concentration of entity *x* in the liquid fraction.

Statistical analyses were conducted using SPSS v25 software (IBM Corp., Armonk, NY, USA). A descriptive statistical analysis was performed on all of the data, and the results were expressed as means and standard deviations. The data were also subjected to analysis of variance (ANOVA) using a full factorial model (fixed factors were additive dose, additive type

189   and LF type). The homogeneity of the variances was checked using Levene's test. The

190   significant treatments were compared using Tukey's HSD multiple range test ($p < 0.05$).

3. Results and discussion

191

3.1. LF characteristics

192

193   The physico-chemical characteristics of the five LFs are summarized in Table 1. The P

194   concentrations in LFs were comparable to those reported by Finzi et al. (2015) and Møller et

195   al. (2007b). The Cu and Zn contents are similar to those reported by Nicholson et al. (2003),

196   but are higher than those reported by Suzuki et al. (2010). It has to be considered, however,

197   that slurries analysed by these authors were not liquid fractions. The increase in concentrations

198   of heavy metals and other elements in LFs after the stripping process can be explained as the

199   consequence of water evaporation that occurs during stripping (at 40°C). The same

200   explanation applies to solids: the stripping process increased the TS concentration by 16%

201   and 19% for pig and cattle and pig digestate, respectively. Notably, the VS content (expressed

202   as percentage of TS) decreased; probably in the digested LFs there were still biodegradable

203   components that were degraded during the stripping process. As expected, the main effect of

204   the stripping process was a reduction of TAN concentration and TKN concentration. Alkalinity

205   also decreased after ammonia stripping. In fact, stripping affected the content of carbon dioxide

206   and ammonia nitrogen, both of which are strictly connected with alkalinity concentration. It is

207   important to highlight the fact that the stripping process used a retention time of 12 days with

208   the effect of removing carbon dioxide still present in the LFs derived from digestate. Therefore,

209   the effect was to lower alkalinity and increase pH values, despite the ammonia volatilisation

210   should reduce pH (Bonmatí and Flotats, 2003; Provolo et al., 2017).

3.2. Determination of chemical dose

211

212   Fig. 1 reports a selection of results from the preliminary tests for determining chemical doses.

213   As shown in Figs. 1a and 1b for (C+P)D, an optimal dose of 7.58 g/L of Ca^+ was identified,

214   corresponding to an EC of 7.4 mS/cm and a pH of 11.5.

215   Concerning Al^{3+}, the optimal dose of 1.25 g Al^{3+}/L corresponded to pH 6.68 and, EC

216   18.06 mS/cm, a foam level of 400 mL and floc dimension slightly larger than 2.5 mm (Figs. 1b,

217   1c and 1d). The optimal doses identified for each LF are reported in Table 2. Notably, the

218   optimal dose of CaH was lower for both types of stripped digestate than for raw digestate. This

219   was due to the decreased alkalinity concentration resulting from the stripping process, which

220   in turn decreased the amount of CaH required to precipitate carbonate.

221   3.3. Influence of additives on physico-chemical characteristics and
222   separation of solids, P, Cu and Zn from LFs

223   3.3.1 Separation efficiency

224   The separation efficiencies $E_{t\,(x)}$ obtained for TS, P, Cu and Zn are reported in Fig. 2. The

225   addition of AlS generally improved the separation efficiencies for all parameters for all the LFs

226   tested. The separation efficiencies for TS varied according to LF type, ranging between

227   approximately 5% at the null dose to approximately 92% at the optimal dose. For (C+P)D, the

228   maximum TS separation efficiency (79%) was achieved with the optimal dose of AlS and was

229   significantly better than the efficiency without chemicals (58–60%). After the stripping process,

230   the TS separation efficiency for the same LF without chemicals was very low (29–40%). These

231   differences could be due to the physical-chemical changes in the LFs caused by the stripping

232   treatment. In fact, the reduction of alkalinity, the release of Carbon and the reduction of EC

233   after stripping may reduce the aggregation of solid particles and limit the separation efficiency

234   without the use of additives.

235   Using AlS, the highest TS separation efficiency (92%) was achieved for PSD. In contrast, the

236   opposite response was observed when using CaH, and the maximum separation efficiency

237   (63%) was achieved at the sub-optimal dose applied to PD. Using CaH, the lowest TS

238   separation efficiency among all LFs occurred with PS, both at null dose (< 10% TS separation)

239   and when additives were used.

240   The variation of $E_{t(x)}$ obtained for TS can be partly explained also by the difference in TS content

241   of the different LFs. It is well known, in fact, that high contents of TS are related to high Et

242   values (Fangueiro et al., 2012; Sommer et al., 2013). The TS contents of PD and PDS are 1.5-

243   2 times higher than the other LFs and this partly explain the higher Et values, although for PDS

244   they can be obtained only with AlS.

245   The highest P separation efficiencies (Fig. 2b) from all LFs were obtained with AlS and the

246   addition of both chemicals achieved in general higher P separation efficiencies, as expected.

247   The P separation efficiencies achieved for PDS and (C+P)DS using both additives were higher

248   than those obtained for the non-stripped digestates with the exception of PDS with CaH,

249   probably due to the lower dose of additive used. The maximum P separation efficiency

250   obtained were 93% with PDS using a sub-optimal dose and 71% with (C+P)DS at the optimal

251   dose respectively for AlS and CaH.

252   The application of Ca compounds for P removal may initially precipitate a number of Ca

253   phosphate minerals (Szogi et al., 2015). By adding calcium hydroxide $Ca(OH)_2$ to increase the

254   solution pH, soluble P can be precipitated as amorphous calcium phosphate. In addition, the

255   hydroxide not only reacts with the existing bicarbonate (HCO_3^-) to form carbonate (CO_3^{-2}), but

256   also reacts with NH_4^+ to form NH_3, and with phosphate to form phosphate-containing

257   precipitates (Szogi et al., 2015). Due to these multiple reactions the required dosage of CaH

258   determined on EC might be not lead to the best $E_{t(x)}$ for P. Furthermore, the higher content of

259   solids in PDS might have influenced the effect of CaH considering that the dose used for this

260   LF was one third of the one used for PD (Table 2).

261   The P separation efficiencies in PS were not particularly high (72% using AlS and 39% using

262   CaH); however, the results using AlS were comparable with those obtained Ndegwa et al.

263   (2001). In their research, the addition of aluminium sulfate to swine manure prior to quiescent

264   natural sedimentation achieved P separation efficiencies of 78% and 65% at dosages of 1.5

265   and 2.0 g/L, respectively. In contrast, the P separation obtained using CaH in the present study

266   was lower than that observed by Szogi et al. (2009). In fact, in that study, the $Ca(OH)_2$

267   concentration range (0.17–0.89 g/L) used to treat swine wastewater raw or pre-treated in a

268   nitrification process was lower than in this study; yet the doses achieved P removal efficiencies

269   ranging from 20% to 100%.

270   Both AIS and CaH produced a greater increase in P separation efficiencies in relation to the

271   null dose for PS than for other LFs. This observation is also true for Cu and Zn. In fact, for this

272   LF, Cu separation efficiency increased from 1% without chemical to 44% and 79% for CaH

273   and AIS, respectively (Figure 2 c and d).

274   Similarly, without the application of chemicals the Cu separation efficiency for (C+P)D and

275   (C+P)DS was 54–59% and 31–39%, respectively.

276   The maximum Cu separation efficiency was achieved for stripped digestates using the optimal

277   dose of AIS. Furthermore, for this LF the difference between the Cu separation efficiencies

278   with and without application of chemical was also higher than for other LFs (22%–93% for PDS

279   and 31%–81% for (C+P)DS). Using CaH, the lowest Cu separation efficiency was achieved

280   with PS.

281   The general behaviour of Zn separation was comparable with that of Cu, but the Zn separation

282   efficiencies obtained for all LFs using both chemicals were higher than those observed for Cu.

283   As reported by Marcato et al. (2009), Zn is much more sensitive to pH than Cu, so it is possible

284   that the chemical characteristics of different LFs influenced Zn separation differently. Notably,

285   the Zn content was higher than the Cu content in all LFs (Table 1).

286   The results of the statistical analysis, reported in table 3, demonstrate that the use of the AIS

287   instead of CaH always improve the separation efficiency and thus it can be considered more

288   efficient in removing TS, P, Cu and Zn from LFs. Furthermore, the use of suboptimal doses

289   has not resulted in a significant reduction of the separation index.

290   The separation efficiencies for TS and P are similar for all LFs with the exception of PS, that

291   has lower values. The difference for the other parameters are less straightforward and the

292   difference for Cu and Zn are significant only comparing PD and PDS. The lowest separation

293   index is obtained also for these elements by PS.

294   The reduction of the dose of CaH with the stripped LFs did not reduce the separation

295   efficiencies. This result cannot be related to the pH as it is similar to the others LFs, but might

296   be explained by a lower buffer capacity and the reduced EC of the stripped LFs. The reduction

297   of buffer capacity after stripping is expected as two of its main component (inorganic carbon

298   and total ammoniacal N) are removed during the process. In line with the findings of Szogi at

299   al. (2009), who developed a multi-stage process to reduce inorganic buffering in slurry before

300   the addition of CaH, the ammonia stripping process in the present study decreased NH_3

301   alkalinity in all slurry types, thus lowering the required chemical dosage.

302   As shown in Fig. 3, increasing doses of both CaH and AlS influenced the pH and EC of the

303   LFs. In general, for all LFs, solid-liquid separation without the use of chemicals produced a

304   liquid fraction having a pH slightly higher than that of the raw LF.

305   With the use of AlS, the EC increased as the dosage increased and (as expected) pH

306   decreased. At the maximum dose, pH decreased to less than 5.5. In contrast, using CaH, the

307   pH of the liquid fraction increased (Renou et al., 2008), and pH exceeded 12 at the maximum

308   dose. The use of AlS as expected reduced the pH in all the LFs (Fig. 3 B). However, the effect

309   on PS is more relevant than with digestates due to their higher buffer capacity.

310   It can be noticed that the EC values obtained with the Optimal and Sub-optimal dose are very

311   similar, explaining the limited differences obtained in the separation efficiencies.

312   **3.3.2 Reduced separation index**

313   Values of the reduced separation index $E'_{t\,(x)}$ at the optimal dose (Fig. 4) attest that the solid

314   fraction increased in concentration more when AlS was used than when CaH was used. The

315   solid-fraction P concentration increased markedly (17–67%) when AlS was used on raw or

316   stripped LFs. A lower reduced index was observed only when AlS was added to (C+P)D.

13

317   Generally, the application of AlS showed a greater increase in P reduced separation index (up

318   to 0.67), that were higher than those observed with CaH with the exception of (C+P)D.

319   The reduced separation index for Cu and Zn, showed that the concentrations of these elements

320   increased in the solid fraction of pig LF and in digestates after the stripping process (Fig. 4).

321   This variation is mainly observed using AlS than CaH, for which the E'(x) was lower (0.08-2.8).

322   Also, with CaH the increase in concentration was larger after the stripping process, confirming

323   the role of alkalinity in the separation process.

324   The use of CaH with PDS decreased the reduced separation indexes for both Cu and Zn. In

325   contrast, for both Cu and Zn the reduced separation indexes were significantly larger when

326   AlS was added to PS ($E_{t'(x)}$ = 0.6–0.7) and to the stripped digestates ($E_{t'(x)}$ = 0.7–0.8). compared

327   to when CaH was used. The higher $E_{t'(x)}$ values for PS than for PD might be partly explained

328   by its relatively lower pH (6.7) compared to the digestate (> 8). However, this explanation

329   cannot be applied to the stripped digestates as their pH values are similar to those of the un-

330   stripped digestates. Rather, the stripping process might increase the concentrations in the

331   soluble fraction of these heavy metals.

332   The results of ANOVA for the reduced separation index, reported in table 4, confirms that the

333   two additives have a different behaviour and that AlS can concentrates the substances in the

334   solid fraction. Moreover, the sub-optimal doses show for this index significantly lower values.

335   This indicates that also if the separation efficiency is the same, the optimal dose can produce

336   a solid fraction easier to dewater and therefore with higher concentration.

337   The effect of AlS in increasing the reduced separation index of stripped digestates is very clear

338   from Figure 4 and confirmed by the analysis in table 4, although the effect for Cu and Zn for

339   PDS is not significant as the overall mean is affected also by the values for CaH.

340   **3.3.3 Practical indications**

341 The results obtained in this study can give indications on the use of additives when there is the

342 need for an improved separation efficiency of TS, P, Cu and Zn on the LFs obtained by

343 mechanical separation.

344 In any case, the use of AlS should be preferred if high separation efficiency and high

345 concentrations in the solid fractions are required. However, also CaH can be effective in

346 improving the separation efficiency and might be a suitable additive especially if an increase

347 of pH can be beneficial for subsequent use. For example, in the case of an ammonia stripping

348 treatment, a separation of LFs with addition of CaH might obtain a P removal of about 60%

349 and an increase of the pH to values of 9.5-12, depending on the type of LF used. This

350 modification can be beneficial to the stripping treatment due to the higher concentration of NH_3

351 in the liquid.

352 On the contrary, the use of AlS might be more effective after a stripping process in order to

353 remove P, but also Cu and Zn before land use of LFs. In this case, the addition of AlS can also

354 help in reducing the pH of the final product and can result in high separation efficiencies with

355 good increase in the concentrations in the solid fraction.

356 In addition, the LFs after the stripping process requires a lower dose of chemicals to reach a

357 given removal rate. In any case, the high doses of chemical additives required to achieve high

358 separation efficiencies should be carefully evaluated due to the high cost and potential

359 environmental impact of the chemicals. Nevertheless, complete removal of P or other elements

360 such as Cu and Zn from animal manure slurry is not generally the objective of solid-liquid

361 separation; rather, the objective is to only reduce the contents of these elements to match crop

362 requirements. This objective can be achieved using less chemical than the dose needed for

363 maximum removal of the elements.

364 4. Conclusions

365 Livestock manure represent an important source of some nutrients, which can be recovered

366 and reused. The study attests the suitability of solid-liquid separation for recovering a solid

367 fraction rich in P from different types of LFs. The results confirm that additives such as CaH

368 and AlS can increase the removal efficiency of TS, P, Cu and Zn in the solid-liquid separation

369 process. In particular, the use of AlS gives removal rates that are higher than those obtained

370 with CaH.

371 The maximum efficiencies achievable using chemicals to remove TS, P, Cu and Zn from

372 animal manure depend on the type of slurry and the additive used. In general, the lowest

373 separation efficiencies have been obtained with PS while the higher removal rates have been

374 achieved with digested LFs after ammonia stripping and addition of AlS.

375 Thus, solid-liquid separation complemented with the addition of chemicals and coupled with

376 ammonia stripping can produce a liquid fraction from animal manure that can be directly used

377 in the field, as well as a solid fraction that is rich in P. While the addition of AlS gives better

378 separation efficiencies and increase of concentrations in the solid fraction, the use of CaH

379 before an ammonia stripping process might obtain an interesting removal efficiencies, with the

380 further benefit to increase the pH and therefore improve the ammonia volatilisation process

381 and the recovering ammonium sulfate.

382 Sub-optimal and optimal doses of CaH and AlS based on EC and floc formation, respectively,

383 do not give significantly different results in the separation efficiency for TS, P, Cu and Zn, even

384 though the higher dose does increase the concentration of these elements in the solid fraction.

385 Therefore, using the sub-optimal dose of either additive can achieve equally acceptable results

386 at lower cost compared to those achieved using the optimal dose, if the concentration of

387 elements in the solid fraction is not an issue.

388 The solid-liquid separation of animal manure slurries using additives might increase the

389 concentration of heavy metals in the resulting solid fraction. Therefore, the subsequent use of

390 the solid fraction in agriculture should be carefully evaluated and controlled to avoid over-

391 application of heavy metal elements and their possible negative effects on environmental

392 quality and human health.

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495

496 **Figure captions**

497

498 **Figure 1**
499 Example results from jar tests to determine optimal doses (D) of $Ca(OH)_2$ (CaH) and $Al_2(SO_4)_3$. (AlS) for "cattle and
500 pig digestate": a) pH and EC responses to CaH; b) pH and EC responses to AlS; c) Level of solid/liquid interface
501 (HC) and foam fraction (HF) in response to AlS; d) Floc dimension in response to AlS. The lowest value of EC
502 (denoted by the red circle) was used to identify D for CaH. The reference dose of AlS selected corresponded to the
503 Al^{3+} concentration beyond which the floc dimension did not change and the foam level remained relatively constant.
504

505 **Figure 2**
506 Separation efficiencies (Et) achieved using and $Al2(SO_4)_3$ (left) and $Ca(OH)_2$ (right) as additives to different LF
507 types: a) total solids (TS); b) phosphorus (P); c) copper (Cu); d) zinc (Zn). N: null dose; SO: sub-optimal dose; O:
508 optimal dose. PS: pig LF; PD: pig digestate; PDS: pig digestate stripped; (C+P)D: cattle and pig digestate; (C+P)DS:
509 cattle and pig digestate stripped.
510

511 **Figure 3**
512 Variation of pH (left) and EC (right) in different LFs as a function of a) $Ca(OH)_2$ dose and b) $Al_2(SO_4)_3$ dose. Data
513 reported are means and the error bars represent standard deviation. PS: pig LF; PD: pig digestate; PDS: pig
514 digestate stripped; (C+P)D: cattle and pig digestate; (C+P)DS: cattle and pig digestate stripped.
515

516 **Figure 4**
517 Reduced separation indexes resulting from $Ca(OH)_2$ (CaH) and $Al_2(SO_4)_3$ (AlS) for a): total solids (TS); b)
518 phosphorus (P); c) copper (Cu); and d) zinc (Zn). PS: pig LF; PD: pig digestate; PDS: pig digestate stripped; (C+P)D:
519 cattle and pig digestate; (C+P)DS: cattle and pig digestate stripped.
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