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Published in:
Waste and Biomass Valorization

Link to article, DOI:
[10.1007/s12649-015-9466-0](https://doi.org/10.1007/s12649-015-9466-0)

Publication date:
2016

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Oliveira, V., Ottosen, L. M., Labrincha, J., & Dias-Ferreira, C. (2016). Valorisation of Phosphorus Extracted from Dairy Cattle Slurry and Municipal Solid Wastes Digestates as a Fertilizer. *Waste and Biomass Valorization*, 7(4), 861–869. <https://doi.org/10.1007/s12649-015-9466-0>

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Valorisation of Phosphorus Extracted from Dairy Cattle Slurry and Municipal Solid Wastes Digestates as a Fertilizer

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Abstract

Phosphorus is a vital cell component and an essential and irreplaceable element. Yet at the current rate of exploitation, the phosphate's reserves will be fast depleted. Dairy cattle slurry and digestates from anaerobic digestion of municipal solid wastes (MSW) are organic wastes containing phosphorus which can potentially be used as a secondary source of this nutrient. The present study investigated the effect of pH in phosphorus release from these wastes using acid and base extraction followed by phosphorus recovery via precipitation, targeting the production of a fertilizer. Results showed that when using HNO₃, 100% of P content was extracted from dairy cattle slurry (2.0 < pH < 3.3) and 90% from MSW digestates (1.2 < pH < 1.5). The maximum extraction was obtained after 2.5 hours for dairy cattle slurry and 48 hours for MSW digestates. The extraction efficiencies using NaOH were only 22% for dairy cattle slurry (12.9 < pH < 13.4) and 9% for MWS digestates (13.0 < pH < 13.4). Phosphorus precipitation from extracted solutions was carried out at a molar ratio of 1:1:1 for Mg:N:P and at pH around 8.0. Analysis of the harvested precipitates by XRD and SEM-EDS ruled out the formation of struvite, but validated the formation of amorphous calcium phosphates, a potential fertilizer that can help to close the cycle of this nutrient. During the process, heavy metals might become enriched in the precipitates. In the perspective of producing a fertilizer this is an undesirable process, and one that should be taken into account when considering phosphorus recovery from wastes.

Keywords

Phosphorus recovery; Struvite; Calcium phosphate, dairy cattle; Anaerobic digestion; Municipal Solid Waste

1. Introduction

Currently there is a growing demand for phosphorus at global level because it is an essential and irreplaceable nutrient in food production [1] [2]. This resource is obtained mainly from phosphate deposits, which are controlled mostly by Morocco, United States of America and China, while Europe is dependent on phosphorus imports to meet its needs [3]. According to some estimates, the existing reserves of phosphate will reach their peak by 2030 and will be exhausted in the next 50-100 years [2].

39 In this context, the development of new strategies for phosphorus recovery from secondary sources becomes
40 highly relevant. Phosphorus is present in various agricultural wastes, especially animal manure. Manure was
41 traditionally applied to agricultural fields to close the cycle of nutrients. At present such recycling practices are
42 limited due to manure transportation costs [4], more stringent health safety requirements and, most especially,
43 the pressure to grow enough food to feed the ever growing human population. Due to these reasons intensive
44 agriculture uses mostly synthetic and conventional phosphate fertilizers, such as triple super phosphate (TSP),
45 single super phosphate (SSP), di-ammonium phosphate (DAP) or mono-ammonium phosphate (MAP).

46 In the last decade several investigations have been carried out targeting phosphorus extraction, mainly from
47 municipal wastewaters [5] and derived waste streams, such as sewage sludges or their incineration ashes [6–8].
48 Acid extraction of phosphorus from sewage sludge ashes has been reported by Ottosen et al [9] and both acid
49 and alkaline leaching from the same material have been referred by Petzet et al [10]. Stark et al [11] studied the
50 influence of acid or base extraction of phosphorus from sludge ash, dried sludge and sludge residue from
51 supercritical water oxidation. Other residues have also been investigated as a secondary source of phosphorus
52 [12], and examples include MSW fly ash [13], animal manures [14–16], and swine wastewater [17, 18]. Acid
53 extraction was tested for poultry litter and swine manure [14] using the patented “quick wash process” with citric
54 acid, acetic acid and hydrochloric acid.

55 However, recent reports on phosphorus flows indicated that municipal solid wastes and their incineration
56 residues contain as much phosphorus as sewage sludge on an annual basis [19–21], highlighting that these wastes
57 are an under-valorised source of phosphorus. In Portugal, separate collection of biowaste is not a common
58 practice [22] and MSW is mechanically sorted after collection to separate the organic fraction (OFMSW).
59 OFMSW undergoes anaerobic digestion, in which energy is recovered in the form of biogas [23]. The semi-solid
60 organic material left over at the end of the anaerobic digestion process, and referred herein as MSW digestate, is
61 a waste from this process, being potentially a good source for secondary phosphorus that so far has not been
62 explored.

63 The phosphorus recovery from waste streams to be used as a fertilizer or as a raw material for the fertilizer
64 industry can be done by chemical precipitation [12]. The precipitation technologies used to recover phosphorus
65 are mainly based on the addition of metal salts of magnesium (Mg) or calcium (Ca) [24, 25]. The most common
66 precipitate for phosphorus recovery from waste streams with Mg is magnesium ammonium phosphate
67 ($\text{MgNH}_4(\text{PO}_4)\cdot 6\text{H}_2\text{O}$), also known as struvite. Brushite, octacalcium phosphate, hydroxyapatite, whitlockite,
68 monetite or amorphous calcium phosphate are other precipitated compounds formed by Ca and P [12]. These
69 precipitation processes require increasing the pH in the presence of Mg or Ca. The raise in pH and the relative
70 amounts of the species present will have a huge influence on the crystalline and amorphous phases formed
71 during inorganic phosphate precipitation [25].

72 In this work we target for the first time the extraction and recovery of phosphorus from the organic fraction of
73 municipal solid wastes after anaerobic digestion. In addition, we also test the extraction from another waste:
74 cattle yard slurry. We aim to investigate the influence of pH on phosphorus release overtime and identify the
75 conditions that optimise extraction. Another objective is to promote the precipitation of phosphorus from

76 solution in the form of a phosphorus-rich precipitate which might be used in place of synthetic fertilizers or as a
77 raw material for the fertilizer industry.

78

79 **2. Materials and methods**

80 **2.1 Dairy cattle slurry and MSW digestates**

81 The MSW digestates were collected in April 2015 from a facility for the treatment and valorisation of municipal
82 solid wastes (Portugal), specifically from the anaerobic digester, fed with mechanically-separated OFMSW. The
83 sample was collected after the centrifugation process.

84 The dairy cattle slurry sample was collected in April 2015 from a local farm (Coimbra, Portugal). The sample
85 was collected from the ditch connecting the animal housing to the slurry storage pit and comprises scraped cattle
86 excreta and some wash down. The sample was collected at 3 different spots in the ditch and mixed thoroughly in
87 a plastic bucket.

88 Immediately after collection the samples were refrigerated until use (less than 48h). For both samples the
89 following parameters were determined: water content, ash content, organic matter, pH, electric conductivity,
90 total P, Ca, Mg, K and heavy metals (Cu, Zn, Cd and Pb). Prior to being used the samples were dried in a forced
91 draft oven at a temperature of 105°C, ground, sieved (1 mm) and stored in closed glass containers at room
92 temperature.

93

94 **2.2 Characterization of waste samples**

95 The water content of waste samples was determined by weighing out approximately 50 g of sample into pre-
96 weighed porcelain dishes, drying at 105°C in a forced draft oven for 24 hours and weighting after cooling to
97 room temperature (in triplicate). The ash content was determined by placing the previously dried sample in a
98 muffle at a temperature of 550°C for 2 hours and weighting after cooling (in triplicate). pH and electric
99 conductivity of fresh and dry samples were measured (in triplicate) using pH and conductivity electrodes by
100 taking 2 g of sample and 10 mL of distilled water and shaking for 1 hour. The organic matter content (in
101 percentage) was considered equivalent to the volatile solids and calculated as: $(\text{mass of dried sample} - \text{mass of}$
102 $\text{ash sample}) / (\text{mass of initial sample}) * 100$.

103 The concentration of total P, Ca, Mg, K, Cu, Zn, Cd and Pb in the waste samples was measured after a pre-
104 treatment described in Peters et al [26] (in duplicate): 0.5 g of dried sample were placed into a digestion tube
105 and 5 ml of concentrated nitric acid (65%) was added (in duplicate). The tubes were heated in a block digester
106 (SCP Science) at 120°C until solution turned pale yellow or clear. Then the samples were filtered through 0.45
107 μm filter (SCP Science) into 50 mL volumetric flasks and the solutions analysed for heavy metal content by
108 atomic absorption spectrometry (Perkin Elmer AAnalyst 300) and for total phosphorus using the
109 vanadomolybdophosphoric acid colorimetric method [26] at a wavelength of 470 nm (spectrophotometer
110 HITACHI: U-2000). All concentrations are given on a dry weight basis and represent mean values.

111

112 2.3 Selection of the phosphorus extractants

113 Initially both organic acids and mineral acids were considered as possible extractants. Sulfuric acid is cheaper,
114 but it causes the formation of gypsum in high quantities [9]. The formation of gypsum is not of interest, because
115 when handling the remaining material an increased volume needs to be disposed of. Since struvite precipitation
116 occurs in the presence of nitrogen (ammonium), nitric acid was selected to acidify the solution, thus avoiding the
117 introduction into the system of yet another anion (e.g. Cl⁻) that might eventually interfere with the precipitation
118 process. Selection of citric acid was based on previously reported experiments for other wastes [14].

119

120 2.4 Phosphorus-Extraction Experiments

121 Extractions experiments were made (in duplicate) using 40.0 g of dry sample and 1000 ml of extractant (HNO₃
122 or NaOH at different concentrations) at a liquid to solid ratio (L/S) of 25 for 48 hours. The experimental
123 conditions are shown in Table 1. One preliminary experiment with citric acid and extractions with distilled water
124 were also carried out, for comparison purposes.

125 **Table 1** Experimental conditions for the extraction step

Experiment	Extractant	Sample	Final pH	Liquid to Solid ratio	Duration (h)
A1	Nitric Acid 0.075M	Dairy cattle slurry	3.3	25	48
A2	Nitric Acid 0.05M	Dairy cattle slurry	4.7		
A3	Distilled Water	Dairy cattle slurry	6.7		
A4	Sodium Hydroxide 1M	Dairy cattle slurry	12.9		
B1	Nitric acid 0.20M	MSW digestates	1.5	25	48
B2	Nitric acid 0.09M	MSW digestates	4.1		
B3	Nitric Acid 0.05M	MSW digestates	6.9		
B4	Distilled Water	MSW digestates	7.5		
B5	Sodium Hydroxide 1M	MSW digestates	13.0		
C1	Citric Acid 0.5M	Dairy cattle slurry	4.3	2.5	24

126

127 To assess the phosphorus release over time samples were collected at 0, 2.5, 24 and 48 hours and centrifuged at
128 10000 rpm for 20 minutes. The supernatant was then filtered (0.45µm filter, SCP Science) and analysed for
129 soluble phosphorus by ICP-OES. At the end of experiments the concentrations of Ca, Mg, K, Cu, Zn, Cd and Pb
130 in solution were measured using atomic absorption spectrometry and the ammonium concentration (NH₄) was
131 measured by the Nessler method, as described in [27].

132 Phosphorus-extraction efficiencies were defined as the ratio of soluble phosphorus at end of this extraction step
133 to the initial total phosphorus.

134

135 **2.5 Phosphorus precipitation**

136 Precipitation experiments were conducted with 100 mL of extraction solutions resulting from experiments A1
137 and A2 (dairy cattle slurry) and B1 and B2 (MSW digestates), after filtering through Whatman 0.45 µm
138 membrane filters. Each experiment was made at the conditions leading to struvite formation, that is pH=8.0 and a
139 molar ratio Mg:N:P of 1:1:1. The solutions were stirred and the pH value was quickly adjusted with 5M NaOH,
140 followed by addition of ammonium chloride (NH₄Cl) as nitrogen source. Afterwards, the mixture was slowly
141 stirred (magnetic stirrer) for 1 hour. At the end the precipitate formed was separated by filtration and the
142 phosphorus remaining in solution was measured using the vanado-molybdophosphoric acid colorimetric method
143 [26]. The harvested precipitates were dried at 35°C for 72 hours and then analysed by X-ray Diffraction (XRD)
144 and Scanning Electron Microscopy coupled with Energy Dispersion Spectroscopy (SEM-EDS). The XRD
145 analysis of the precipitates was carried out on a Rigaku Geigerflex (JP) with a Cu anode operating at 45kV and
146 40 mA. The patterns were collected in the 10 – 80°2theta range (0.02 °2theta s⁻¹ step-scan, and 3°/min). SEM
147 was carried out using a Hitachi S4100 equipped with EDS - Rontec.

148 Removal efficiency of phosphorus in the precipitation process was defined as the ratio of soluble phosphorus
149 remaining in solution at end of the precipitation step to the initial soluble phosphorus, calculated as $([\text{Soluble P}]_{\text{initial}} - [\text{Soluble P}]_{\text{final}}) / [\text{Soluble P}]_{\text{initial}}$.

151

152 **3. Results and discussion**

153 **3.1 Physical and chemical characterization of dairy cattle slurry and MSW digestates**

154 Characteristics of the dairy cattle slurry and MSW digestates are shown in table 2. The MSW digestates was
155 centrifuged prior to sample collection and has a lower water content than dairy cattle slurry. The pH of MSW
156 digestates is slightly higher than dairy cattle slurry, but nevertheless close to neutrality. The concentration of
157 phosphorus in MSW digestates is 0.8% (dry weight) and in the dairy cattle slurry 0.4% (dry weight). These
158 levels are low compared with ash residues from the incineration of sewage sludge, where concentrations of 8-
159 10% have been reported [9], because as organic materials are destroyed during the combustion phosphorus
160 becomes enriched in the ash. Even so, the levels of phosphorus obtained in this work are similar to the values
161 reported for dairy cattle manure by Karunanithi et al [12] (4.1 to 18.3 mg g⁻¹) and by Jin et al [28] (5.70 mg g⁻¹).

162 Given that in the EU on person produces on average 481 kg of MSW a year [29], of which roughly 45% is
163 organic waste with 70% water content, and that during anaerobic digestion there is a reduction of roughly 70% in
164 the dry mass of waste, we can estimate that per each person 0.36 kg of phosphorus will appear in MSW
165 digestates per year. This is equivalent to a small city of 100 000 inhabitants potentially recovering 36 tonnes of
166 phosphorus per year, or a larger city with 3.4 million inhabitants (e.g. Madrid, Berlin) potentially recovering over
167 one thousand tonnes of phosphorus per year.

168 In addition to phosphorus, other elements are also present. Calcium was by far the macroelement in higher
169 concentrations in both wastes, likely because this element is an important constituent of the dairy cow's diet as
170 well the human's diet (cheese, milk, cream, butter, etc.).

171 The content in heavy metals is higher in MSW digestates than in dairy cattle slurry, with lead (Pb) concentrations
 172 being more than 10 times higher in MSW digestates. This is possibly due to the presence of metal contaminants
 173 in MSW as the organic wastes are collected together with other wastes (and separation occurs only at a later
 174 stage, during mechanical sorting). The heavy metals present in the dairy cattle slurry come from the feed or from
 175 farm equipment used to scrap the excreta into the ditch. Both dairy cattle slurry and MSW digestates are well
 176 within the heavy metals limiting values for sludge application in agricultural soils reported in the Portuguese
 177 legislation [30], indicated in Table 2.

178 **Table 2** Characteristics of the two waste samples (mean \pm standard deviation) and limiting values for sludge application to
 179 agricultural soils according to the Portuguese legislation

Parameter	Dairy cattle slurry	MSW digestates	Limiting Values [30]
Physical and chemical characteristics			
Fresh sample			
pH (H ₂ O)	8.2 – 8.3	8.9 – 9.0	-
Conductivity (mS cm ⁻¹)	3.64 \pm 0.02	3.38 \pm 0.04	-
Water Content (%)	85.11 \pm 0.08	63.40 \pm 0.51	-
Ash Content (%)	4.49 \pm 0.07	18.55 \pm 0.88	-
Organic Matter (%)	10.40 \pm 0.14	18.05 \pm 0.41	-
Dry sample			
pH (H ₂ O)	6.6	7.8	-
Conductivity (mS cm ⁻¹)	8.60 \pm 0.18	5.22 \pm 0.04	-
Macro elements			
Total P (mg g ⁻¹ dw)	4.04 \pm 0.08	8.11 \pm 0.25	-
Ca (mg g ⁻¹ dw)	142.82 \pm 3.85	103.68 \pm 3.64	-
Mg (mg g ⁻¹ dw)	4.04 \pm 0.13	12.59 \pm 0.39	-
K (mg g ⁻¹ dw)	13.70 \pm 3.28	9.38 \pm 0.19	-
Heavy metals			
Cu (mg kg ⁻¹ dw)	42.41 \pm 0.95	156.04 \pm 3.77	1000
Zn (mg kg ⁻¹ dw)	177.71 \pm 5.51	452.44 \pm 15.59	2500
Pb (mg kg ⁻¹ dw)	16.69 \pm 1.89	195.86 \pm 8.55	750
Cd (mg kg ⁻¹ dw)	1.64 \pm 0.07	2.17 \pm 0.33	20

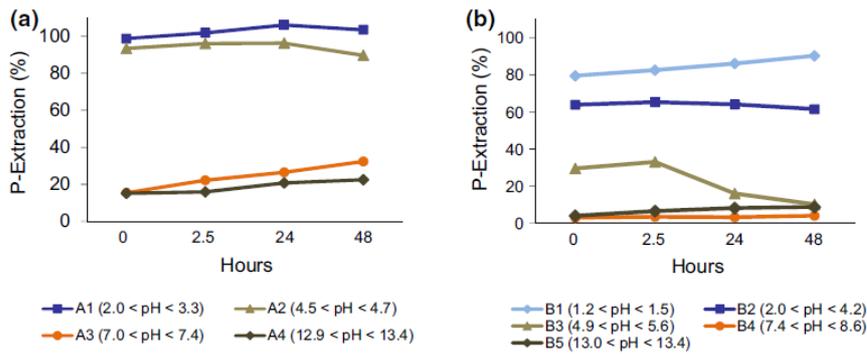
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181 3.2 Phosphorus extraction from dairy cattle slurry and MSW digestates

182 Nitric acid (HNO₃) and sodium hydroxide (NaOH) were used to investigate the effect of pH in phosphorus
 183 extraction from dairy cattle slurry and MSW digestates.

184 The extraction from these wastes into solution over time is presented in Fig. 1. For both wastes extractions were
 185 higher when HNO₃ was used than when NaOH or water, expressly indicating that base extraction was not
 186 effective and the release of phosphorus from both wastes was better at lower pH values.

187



188 **Fig. 1** Extraction of phosphorus from wastes by acid and base treatment: (a) Dairy cattle slurry; (b) MSW digestates

189
190

191 In the case of dairy cattle slurry the phosphorus extracted with acid reached between 90-100% of total
192 phosphorus (A1 and A2), with the differences between the two experiments being relatively small. This means it
193 is not necessary to lower the pH from the original value (around 7) to 2 to get good extractions, and the process
194 can be conducted with similar success at pH 4.5 (reducing the need for the acid reagent). 50% of phosphorus was
195 extracted in the preliminary experiment with citric acid (C1), while for nitric acid extraction reached 96% (at pH
196 approximately 4.5, for both experiments). Given the lower extraction, citric acid was not considered further in
197 this work.

198 The best phosphorus extraction from MSW digestates was about 90% (B1, pH between 1.2 and 1.5). Opposite of
199 dairy cattle slurry, to achieve extraction percentages close to 100% in MSW digestates it was necessary to
200 decrease pH to below 2 (experiment B1). The higher difficulty in extracting phosphorus from MSW digestates is
201 likely due to the form of phosphorus present. During the anaerobic digestion process, the phosphorus is
202 incorporated into the cellular structure of the microorganisms, making extraction from this waste more difficult,
203 whereas in dairy cattle slurry 60 to 90% of phosphorus is in inorganic form [12] and so it is more readily
204 available. The use of nitric acid and low pH values (<2) has also lead to phosphorus extractions close to 100% in
205 previously reported experiments with a different waste: sewage sludge ash [9].

206 The phosphorus extracted with NaOH was very low and did not exceed 22% for dairy cattle slurry and 9% for
207 MSW digestates. The results obtained in this study are lower compared with the investigation made by Stark et al
208 [11] were the phosphate release from dried sludge at 1M NaOH (corresponding to pH 14) was above 50%. Xu et
209 al [6] also tested phosphorus extraction with NaOH in sewage sludge ash and obtained percentage extractions
210 similar to the ones presented here (< than 30%). At around pH 7 (experiments A3 and B4, with distilled water)
211 the phosphorus extraction was also low, being only slightly higher than with NaOH.

212 According to results above we assume that acid extraction of phosphorus could be applied to other organic
213 wastes. However, the origin of the waste should be considered because in case the waste has underwent
214 biological treatment prior to the acid extraction then phosphorus might be more difficult to extract and
215 consequently lower pH might be required.

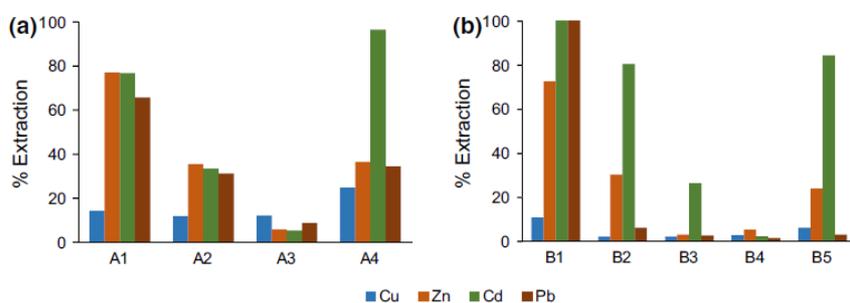
216 Biswas et al [7] and Cohen [8] stated that the extraction efficiency of phosphorus increase with the extraction
217 time. As illustrated in Fig. 1, phosphorus extraction in dairy cattle slurry was almost immediate when the sample

218 come into contact with acid, and the amount of solubilised phosphorus did not increase significantly overtime.
 219 Xu et al [6] investigated the effect of extraction time from sewage sludge ash, achieving more than 95% of
 220 extraction after 120 minutes of reaction. These results are in accordance with the ones presented here and the
 221 acid soluble nature of the waste materials can be responsible for the rapid phosphorus extraction.

222

223 3.3 Influence of pH on Heavy Metals Extraction

224 During extraction experiments, in addition to the phosphorus also heavy metals get solubilized. The percentages
 225 of Cu, Zn, Cd and Pb in solution at the end of extraction step (expressed against the total amount of each metal
 226 present at the beginning) are shown in Fig. 2. As with phosphorus, the extraction of heavy metals was also higher
 227 in dairy cattle slurry than in MSW digestates.



228

229 **Fig. 2** Heavy metals in solution after the extraction step, as a percent of the initial mass of each metal in the waste: (a) Dairy
 230 cattle slurry; (b) MSW digestates

231

232 Cd extraction was highest compared with other heavy metals. For the MSW digestates all Cd in waste got
 233 solubilized in B1 experiment. This is likely explained because of the relatively high solubility of cadmium salts
 234 compared to those of Zn, Cu and Pb, and other wastes present similar results [9, 31].

235 Around pH 7 (A3 and B4) the solubility of all the metals decreased considerably, while increasing at lower and
 236 higher pH values, and this is related to the variation of metal speciation with pH, in which charged metal
 237 hydroxides are formed at higher pH and metals ions at lower pH. Due to the polar nature of the water molecule
 238 these charged ions and compounds formed at low and high pH are more easily extracted than neutral species.

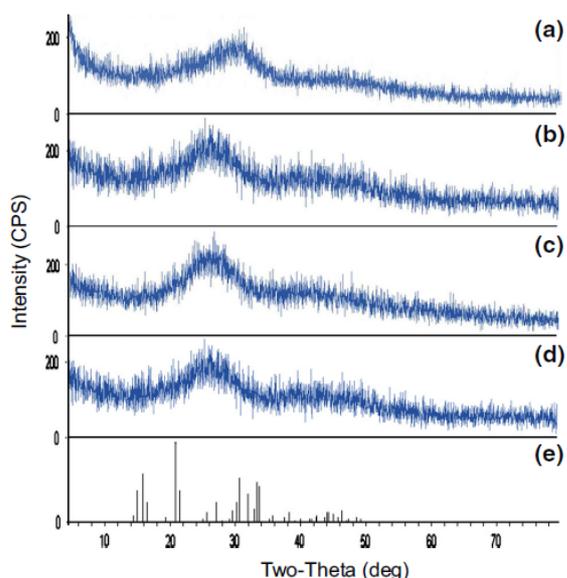
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240 3.4 Recovery of phosphorus as a precipitate

241 The second step of the recovery process was the precipitation of phosphorus, which was carried out from the
 242 solutions obtained at the end of experiments A1 and A2 (dairy cattle slurry) and B1 and B2 (MSW digestates).
 243 The selection was based on the two best phosphorus extraction results obtained for each waste.

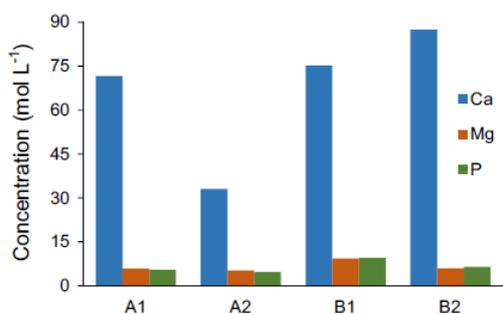
244 The reduction of phosphorus in solution after the precipitation experiments was $94.0 \pm 0.3\%$ in A1 and $97.8 \pm 0.1\%$
 245 in A2 (dairy cattle slurry). In the MSW digestates precipitation experiments the percentage of phosphorus

246 removed was $95.8 \pm 0.8\%$ in experiment B1 and $99.2 \pm 0.01\%$ in experiment B2. Jin [28] obtained about 80%
 247 phosphate removal efficiency for a dairy cattle slurry sample in which phosphorus was extracted by microwave-
 248 based thermochemical pre-treatment with H_2SO_4 and HCl. Burns & Moody [15] reported a reduction of 91% of
 249 phosphorus in solution when using swine slurry during laboratory and field tests. Ours results overcome these
 250 values. The results of XRD carried out on the precipitate are shown in Fig. 3 a) to d), indicating that in the
 251 harvested precipitates there were no crystalline phases present.



252
 253 **Fig. 3** X-ray diffractograms of the phosphorus' precipitates obtained after the acid extraction step in experiments (a) A1; (b)
 254 A2; (c) B1; (d) B2; and (e) struvite standard

255
 256 Le Corre [32] reported that the struvite crystal growth can be affected significantly by the presence of calcium in
 257 solution and that above a molar ratio of Ca:Mg of 1:1 the formation of amorphous calcium phosphate occurs.
 258 The concentration of calcium and magnesium compounds in extraction solutions A1 - A2 and B1 - B2 are shown
 259 in Fig. 4. The Ca:Mg ratio was 12:1 in experiment A1, 6:1 in A2, 8:1 in B1 and 15:1 in B2, thus indicating a
 260 large excess of calcium when compared to magnesium.

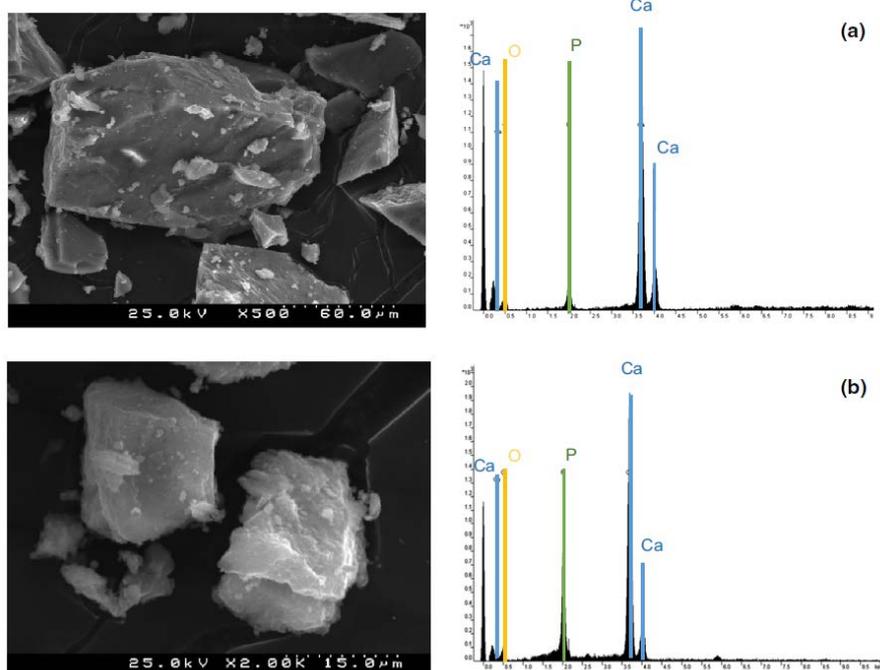


261
 262 **Fig. 4** Concentration of Ca, Mg and P found in the solutions extracted under acidic conditions (A1 and A2 – Dairy cattle
 263 slurry; B1 and B2 - MSW digestates), prior to the precipitations step

264 SEM pictures of the precipitates coupled with energy dispersive spectrometry (Fig. 5) showed the presence of
265 distinctive peaks for Ca and P without any peak for Mg, which means that phosphorus in solution reacted with
266 Ca to form calcium phosphates, in place of struvite.

267 Similarly to struvite, calcium phosphate, can be used as phosphate fertilizer in agriculture [14] [12] or as raw
268 material for fertilizer industry. However, the use of recovered phosphorus as fertilizer, be it struvite or calcium
269 phosphates requires some precautions related to the presence of contaminants such as heavy metals. In case the
270 harvested precipitates can not be applied directly on agricultural land, the phosphorus product might still be used
271 as secondary resource and substitute the virgin phosphate ore in the conventional mineral fertilizer production
272 [13], provided metal levels are acceptable for industry.

273



274
275 **Fig. 5** SEM pictures and their respective EDS of the material obtained after the precipitation step in experiments using: (a)
276 Dairy cattle slurry and (b) MSW digestates

277

278 4. Conclusions

279 In this work two different wastes were evaluated for the recovery of phosphorus: MSW digestates, arising from
280 the anaerobic digestion of municipal solid wastes and dairy cattle slurry. The concentration of phosphorus in the
281 MSW digestates was 0.8% (dry weight) and in the dairy cattle slurry 0.4% (dry weight). These levels are low
282 compared with values reported for ash residues (8-10%) because as organic materials are destroyed during the
283 combustion process phosphorus becomes enriched in the ash. Nevertheless, given the large amounts of MSW
284 digestates and dairy cattle slurry wastes arising annually it is worthwhile considering these wastes for
285 phosphorus recovery. When trying to extract phosphorus from the wastes using nitric acid (HNO_3) and sodium
286 hydroxide (NaOH), 100% of the phosphorus contained in dairy cattle slurry could be extracted into solution after
287 only 2.5 hours at a pH of 4.5. For MSW digestates the maximum extraction was 90% at pH below 2, indicating
288 that even though phosphorus concentration is higher in this residue, phosphorus is not so easily extracted and the

289 extraction process needs to be carried out at a pH below 2. For both wastes extractions were higher with HNO₃
290 than with NaOH or water, expressly indicating that base extraction was not as effective to release the
291 phosphorus.

292 After solubilizing the phosphorus present in the wastes the initial purpose was to recover it in the form of struvite
293 for use as a fertilizer or as raw material in the fertilizer industry. Removals of phosphorus from solution were
294 very high (approx. 95%), indicating that phosphorus was effectively precipitated from solution. But even though
295 precipitation was carried out at conditions prone to struvite formation regarding pH and molar ratios of Mg:N:P,
296 the presence of large amounts of calcium originated the formation of amorphous calcium phosphate, also a
297 possible fertilizer. Analysis of the original wastes indicated the presence of the heavy metals Cu, Zn, Cd and Pb.
298 Metal levels were up to 10 times higher in MSW digestates than in dairy cattle slurry. Similarly to phosphorus,
299 these metals were also solubilised during the extracting phase. In the perspective of producing a fertilizer by
300 precipitating phosphorus, the co-precipitation of metals is undesirable and this should be taken into account
301 when considering phosphorus-recovery from wastes.

302

303 **Acknowledgements**

304 The authors would like to thank Robert C. Pullar for help in obtaining SEM images. C. Dias-Ferreira gratefully
305 acknowledges the FCT – Fundação para a Ciência e a Tecnologia for the financial support
306 (SFRH/BPD/100717/2014).

307

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