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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  $\text{HNO}_3$ , 100% of P content was extracted from dairy cattle slurry ( $2.0 < \text{pH} < 3.3$ ) and 90% from MSW digestates ( $1.2 < \text{pH} < 1.5$ ). 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 ( $12.9 < \text{pH} < 13.4$ ) and 9% for MWS digestates ( $13.0 < \text{pH} < 13.4$ ). 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  $\mu\text{m}$  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<sup>-</sup>) 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 (HNO<sub>3</sub>  
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 (NH<sub>4</sub>) 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 (NH<sub>4</sub>Cl) 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<sup>-1</sup> 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<sup>-1</sup>) and by Jin et al [28] (5.70 mg g<sup>-1</sup>).

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 <sub>2</sub> O)	8.2 – 8.3	8.9 – 9.0	-
Conductivity (mS cm <sup>-1</sup> )	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 <sub>2</sub> O)	6.6	7.8	-
Conductivity (mS cm <sup>-1</sup> )	8.60 $\pm$ 0.18	5.22 $\pm$ 0.04	-
Macro elements			
Total P (mg g <sup>-1</sup> dw)	4.04 $\pm$ 0.08	8.11 $\pm$ 0.25	-
Ca (mg g <sup>-1</sup> dw)	142.82 $\pm$ 3.85	103.68 $\pm$ 3.64	-
Mg (mg g <sup>-1</sup> dw)	4.04 $\pm$ 0.13	12.59 $\pm$ 0.39	-
K (mg g <sup>-1</sup> dw)	13.70 $\pm$ 3.28	9.38 $\pm$ 0.19	-
Heavy metals			
Cu (mg kg <sup>-1</sup> dw)	42.41 $\pm$ 0.95	156.04 $\pm$ 3.77	1000
Zn (mg kg <sup>-1</sup> dw)	177.71 $\pm$ 5.51	452.44 $\pm$ 15.59	2500
Pb (mg kg <sup>-1</sup> dw)	16.69 $\pm$ 1.89	195.86 $\pm$ 8.55	750
Cd (mg kg <sup>-1</sup> dw)	1.64 $\pm$ 0.07	2.17 $\pm$ 0.33	20

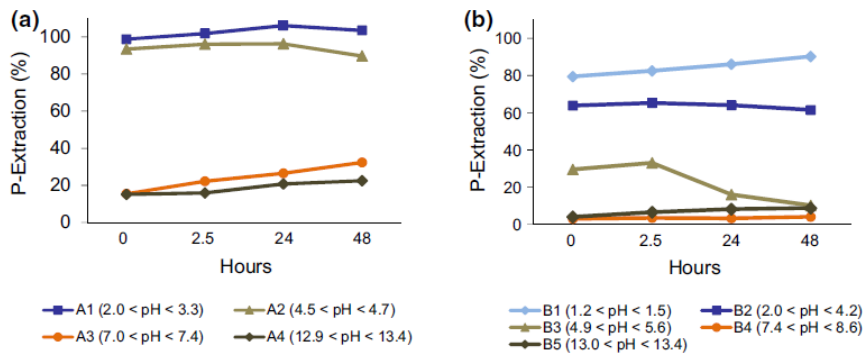
180

### 181 3.2 Phosphorus extraction from dairy cattle slurry and MSW digestates

182 Nitric acid (HNO<sub>3</sub>) 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 HNO<sub>3</sub> 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  
189 **Fig. 1** Extraction of phosphorus from wastes by acid and base treatment: (a) Dairy cattle slurry; (b) MSW digestates  
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

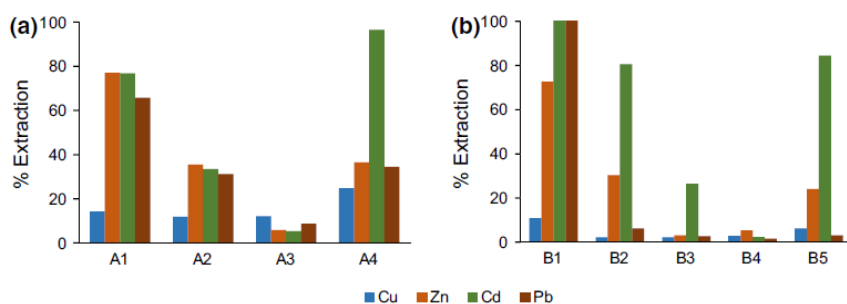


218 come into contact with acid, and the amount of solubilised phosphorus did not increase significantly overtime.  
219 Xu et al [6] investigated the effect of extraction time from sewage sludge ash, achieving more than 95% of  
220 extraction after 120 minutes of reaction. These results are in accordance 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.

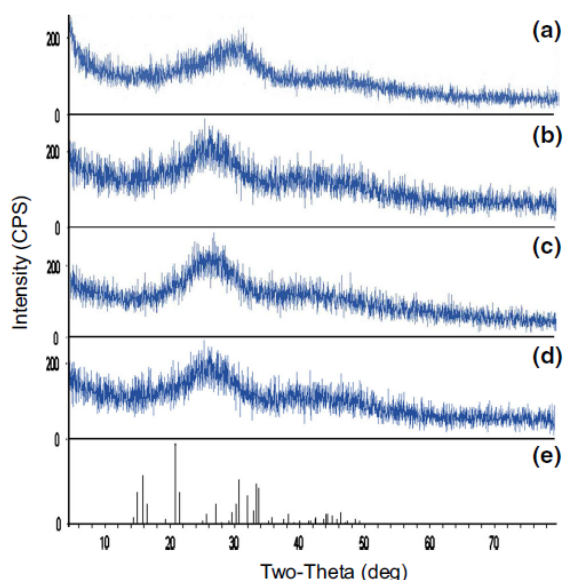
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### 240 3.4 Recovery of phosphorus as a precipitate

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.

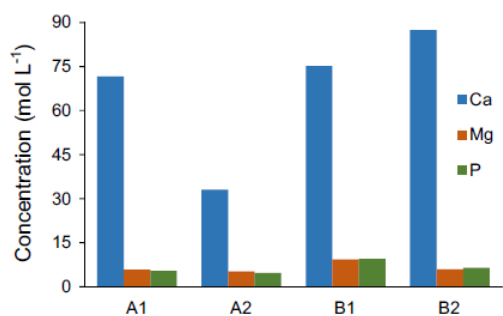
244 The reduction of phosphorus in solution after the precipitation experiments was  $94.0 \pm 0.3\%$  in A1 and  $97.8 \pm 0.1\%$   
245 in A2 (dairy cattle slurry). In the MSW digestates precipitation experiments the percentage of phosphorus

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.

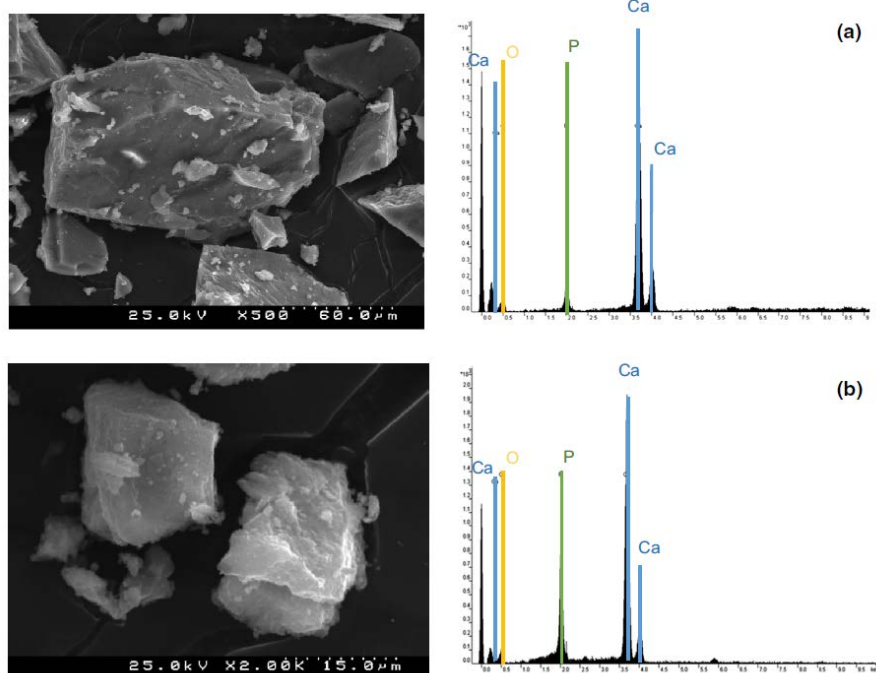


261  
 262 **Fig. 4** Concentration of Ca, Mg and P found in the solutions extracted under acidic conditions (A1 and A2 – Dairy cattle  
 263 slurry; B1 and B2 - MSW digestates), prior to the precipitations step

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 ( $\text{HNO}_3$ ) and sodium  
286 hydroxide ( $\text{NaOH}$ ), 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 HNO<sub>3</sub>  
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

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### 308 **References**

- 309 1. Cornel, P., Schaum, C.: Phosphorus recovery from wastewater: Needs, technologies and costs. *Water*  
310 *Sci. Technol.* 59, 1069–1076 (2009).
- 311 2. Cordell, D., Drangert, J.O., White, S.: The story of phosphorus: Global food security and food for  
312 thought. *Glob. Environ. Chang.* 19, 292–305 (2009).
- 313 3. Cordell, D., Rosemarin, A., Schröder, J.J., Smit, A.L.: Towards global phosphorus security: A systems  
314 framework for phosphorus recovery and reuse options. *Chemosphere.* 84, 747–758 (2011).
- 315 4. Keplinger, K.O., Hauck, L.M.: The economics of manure utilization: Model and application. *J. Agric.*  
316 *Resour. Econ.* 31, 414–440 (2006).
- 317 5. Ye, Z., Shen, Y., Ye, X., Zhang, Z., Chen, S., Shi, J.: Phosphorus recovery from wastewater by struvite  
318 crystallization: Property of aggregates. *J. Environ. Sci. (China).* 26, 991–1000 (2014).
- 319 6. Xu, H., He, P., Gu, W., Wang, G., Shao, L.: Recovery of phosphorus as struvite from sewage sludge ash.  
320 *J. Environ. Sci. (China).* 24, 1533–1538 (2012).
- 321 7. Biswas, B.K., Inoue, K., Harada, H., Ohto, K., Kawakita, H.: Leaching of phosphorus from incinerated  
322 sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. *Environ. Sci.*  
323 21, 1753–1760 (2009).

- 324 8. Cohen, Y.: Phosphorus dissolution from ash of incinerated sewage sludge and animal carcasses using  
325 sulphuric acid. *Environ. Technol.* 30, 1215–1226 (2009).
- 326 9. Ottosen, L.M., Kirkelund, G.M., Jensen, P.E.: Extracting phosphorous from incinerated sewage sludge  
327 ash rich in iron or aluminum. *Chemosphere.* 91, 963–969 (2013).
- 328 10. Petzet, S., Peplinski, B., Cornel, P.: On wet chemical phosphorus recovery from sewage sludge ash by  
329 acidic or alkaline leaching and an optimized combination of both. *Water Res.* 46, 3769–3780 (2012).
- 330 11. K. Stark, E. Plaza, B.H.: Phosphorus release from ash, dried sludge and sludge residue from supercritical  
331 water oxidation by acid or base. *Chemosphere.* 62, 827 – 832 (2006).
- 332 12. Karunanithi, R., Szogi, A.A., Bolan, N., Naidu, R., Loganathan, P., Hunt, P.G., Vanotti, M.B., Saint,  
333 C.P., Ok, Y.S.: Phosphorus Recovery and Reuse from Waste Streams. *Adv. Agron.* (2015).
- 334 13. Kalmykova, Y., Fedje, K.K.: Phosphorus recovery from municipal solid waste incineration fly ash.  
335 *Waste Manag.* 33, 1403–10 (2013).
- 336 14. Szogi, A.A., Vanotti, M.B., Hunt, P.G.: Process for removing and recovering phosphorus from animal  
337 waste. U.S. Patent 8673046, (2014).
- 338 15. Burns, R.T., Moody, L.B.: Phosphorus recovery from animal manures using optimized struvite  
339 precipitation. *Proc. Coagulants Flocculants Glob. Mark. Tech. Oppor. Water Treat. Chem.* 1–7 (2002).
- 340 16. Schuiling, R.D., Andrade, A.: Recovery of Struvite from Calf Manure. *Environ. Technol.* 20, 765–768  
341 (1999).
- 342 17. Liu, Y., Kwag, J.H., Kim, J.H., Ra, C.: Recovery of nitrogen and phosphorus by struvite crystallization  
343 from swine wastewater. *Desalination.* 277, 364–369 (2011).
- 344 18. Vanotti, M.B., Szogi, A.A., Hunt, P.G.: Extraction of Soluble Phosphorus from Swine Wastewater. In:  
345 *American Society of Agricultural Engineers.* pp. 1665–1674 (2003).
- 346 19. Kalmykova, Y., Harder, R., Borgstedt, H., Svanäng, I.: Pathways and Management of Phosphorus in  
347 Urban Areas. *J. Ind. Ecol.* 16, 928–939 (2012).
- 348 20. Matsubae-Yokoyama, K., Kubo, H., Nakajima, K., Nagasaka, T.: A material flow analysis of phosphorus  
349 in Japan: The iron and steel industry as a major phosphorus source. *J. Ind. Ecol.* 13, 687–705 (2009).
- 350 21. Ott, C., Rechberger, H.: The European phosphorus balance. *Resour. Conserv. Recycl.* 60, 159–172  
351 (2012).
- 352 22. Rodrigues, J., Oliveira, V., Lopes, P., Dias-Ferreira, C.: Door-to-Door Collection of Food and Kitchen  
353 Waste in City Centers Under the Framework of Multimunicipal Waste Management Systems in Portugal:  
354 The Case Study of Aveiro. *Waste and Biomass Valorization.* DOI: 10.1007/s12649–015–9366–3. IN  
355 PRESS. (2015).
- 356 23. Quina, M.J., Lopes, D.V., Cruz, L.G., Andrade, J., Martins, R.C., Gando-Ferreira, L.M., Dias-Ferreira,  
357 C., Quinta-Ferreira, R.M.: Studies on the chemical stabilization of digestate from mechanically  
358 recovered organic fraction of municipal solid waste. *Waste Biomass Valoriz.* (IN PRESS) (2015).
- 359 24. Rittmann, B.E., Mayer, B., Westerhoff, P., Edwards, M.: Capturing the lost phosphorus. *Chemosphere.*  
360 84, 846–853 (2011).
- 361 25. Muster, T.H., Douglas, G.B., Sherman, N., Seeber, A., Wright, N., Güzükara, Y.: Towards effective  
362 phosphorus recycling from wastewater: Quantity and quality. *Chemosphere.* 91, 676–684 (2013).

- 363 26. John, P., Combs, S., Hoskins, B., Jarman, J., Kovar, J., Watson, M., Wolf, A., Wolf, N.: Recommended  
364 Methods of Manure Analysis. (2003).
- 365 27. APHA: Standard Methods for the Examination of Water and Wastewater. Published by American Public  
366 Health Association, American Water Works Association and Water Environment Federation,  
367 Washington, DC, USA (1998).
- 368 28. Jin, Y., Hu, Z., Wen, Z.: Enhancing anaerobic digestibility and phosphorus recovery of dairy manure  
369 through microwave-based thermochemical pretreatment. *Water Res.* 43, 3493–3502 (2009).
- 370 29. Eurostat: Municipal Waste. <http://appsso.eurostat.ec.europa.eu/nui/submitViewTableAction.do> (2015).  
371 Accessed 25 June 2015.
- 372 30. MAOTDR: Decreto-Lei nº 118/2006 de 21 de Junho. *Diário da República - I Série-A.* (2006).
- 373 31. Ferreira, C; Ribeiro, A.B.; Ottosen, L.M.: Treatment of MSW fly ashes using the electro-dialytic  
374 remediation technique. In: Brebbia CA, Kungolos S, Popov V, I.H. (ed.) *Waste Management and the*  
375 *Environment II.* pp. 65 – 75. Wit Press, UK (2004).
- 376 32. Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A.: Impact of calcium on struvite crystal size,  
377 shape and purity. *J. Cryst. Growth.* 283, 514–522 (2005).
- 378