

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

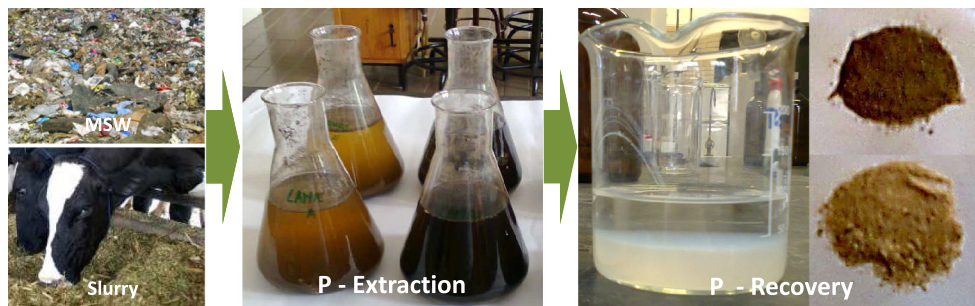
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**Abstract** Phosphorus is a vital cell component and an essential and irreplaceable element. Yet at the current rate of exploitation, the phosphate's reserves will be fast depleted. Dairy cattle slurry and digestates from anaerobic digestion of municipal 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 HNO<sub>3</sub>, 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 h for dairy cattle slurry and 48 h 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.

## Graphical Abstract



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## 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].

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

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

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

The phosphorus recovery from waste streams to be used as a fertilizer or as a raw material for the fertilizer industry

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

In this work we target for the first time the extraction and recovery of phosphorus from the organic fraction of municipal solid wastes after anaerobic digestion. In addition, we also test the extraction from another waste: cattle yard slurry. We aim to investigate the influence of pH on phosphorus release overtime and identify the conditions that optimise extraction. Another objective is to promote the precipitation of phosphorus from solution in the form of a phosphorus-rich precipitate which might be used in place of synthetic fertilizers or as a raw material for the fertilizer industry.

## Materials and Methods

### Dairy Cattle Slurry and MSW Digestates

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

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

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

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

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

### Characterization of Waste Samples

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

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

### Selection of the Phosphorus Extractants

Initially both organic acids and mineral acids were considered as possible extractants. Sulfuric acid is cheaper, but

it causes the formation of gypsum in high quantities [9]. The formation of gypsum is not of interest, because when handling the remaining material an increased volume needs to be disposed of. Since struvite precipitation occurs in the presence of nitrogen (ammonium), nitric acid was selected to acidify the solution, thus avoiding the introduction into the system of yet another anion (e.g.  $\text{Cl}^-$ ) that might eventually interfere with the precipitation process. Selection of citric acid was based on previously reported experiments for other wastes [14].

### Phosphorus-Extraction Experiments

Extractions experiments were made (in duplicate) using 40.0 g of dry sample and 1000 ml of extractant ( $\text{HNO}_3$  or NaOH at different concentrations) at a liquid to solid ratio (L/S) of 25 for 48 h. The experimental conditions are shown in Table 1. One preliminary experiment with citric acid and extractions with distilled water were also carried out, for comparison purposes.

To assess the phosphorus release over time samples were collected at 0, 2.5, 24 and 48 h and centrifuged at 10,000 rpm for 20 min. The supernatant was then filtered (0.45 µm filter, SCP Science) and analysed for soluble phosphorus by ICP-OES. At the end of experiments the concentrations of Ca, Mg, K, Cu, Zn, Cd and Pb in solution were measured using atomic absorption spectrometry and the ammonium concentration ( $\text{NH}_4$ ) was measured by the Nessler method, as described in [27].

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

### Phosphorus Precipitation

Precipitation experiments were conducted with 100 mL of extraction solutions resulting from experiments A1 and

A2 (dairy cattle slurry) and B1 and B2 (MSW digestates), after filtering through Whatman 0.45  $\mu\text{m}$  membrane filters. Each experiment was made at the conditions leading to struvite formation, that is  $\text{pH} = 8.0$  and a molar ratio  $\text{Mg:N:P}$  of 1:1:1. The solutions were stirred and the  $\text{pH}$  value was quickly adjusted with 5 M NaOH, followed by addition of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) as nitrogen source. Afterwards, the mixture was slowly stirred (magnetic stirrer) for 1 h. At the end the precipitate formed was separated by filtration and the phosphorus remaining in solution was measured using the vanadomolybdophosphoric acid colorimetric method [26]. The harvested precipitates were dried at 35  $^\circ\text{C}$  for 72 h and then analysed by X-ray Diffraction (XRD) and Scanning Electron Microscopy coupled with Energy Dispersion Spectroscopy (SEM–EDS). The XRD analysis of the precipitates was carried out on a Rigaku Geigerflex (JP) with a Cu anode operating at 45 kV and 40 mA. The patterns were collected in the 10–80 $^\circ$   $2\theta$  range (0.02 $^\circ$   $2\theta$   $\text{s}^{-1}$  step-scan, and 3 $^\circ/\text{min}$ ). SEM was carried out using a Hitachi S4100 equipped with EDS—Rontec.

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

## Results and Discussion

### Physical and Chemical Characterization of Dairy Cattle Slurry and MSW Digestates

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

Given that in the EU on person produces on average 481 kg of MSW a year [29], of which roughly 45 % is organic waste with 70 % water content, and that during anaerobic digestion there is a reduction of roughly 70 % in the dry mass of waste, we can estimate that per each person

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

Parameter	Dairy cattle slurry	MSW digestates	Limiting values [30]
Physical and chemical characteristics			
Fresh sample			
pH ( $\text{H}_2\text{O}$ )	8.2–8.3	8.9–9.0	–
Conductivity ( $\text{mS cm}^{-1}$ )	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 ( $\text{H}_2\text{O}$ )	6.6	7.8	–
Conductivity ( $\text{mS cm}^{-1}$ )	8.60 $\pm$ 0.18	5.22 $\pm$ 0.04	–
Macro elements			
Total P ( $\text{mg g}^{-1}$ dw)	4.04 $\pm$ 0.08	8.11 $\pm$ 0.25	–
Ca ( $\text{mg g}^{-1}$ dw)	142.82 $\pm$ 3.85	103.68 $\pm$ 3.64	–
Mg ( $\text{mg g}^{-1}$ dw)	4.04 $\pm$ 0.13	12.59 $\pm$ 0.39	–
K ( $\text{mg g}^{-1}$ dw)	13.70 $\pm$ 3.28	9.38 $\pm$ 0.19	–
Heavy metals			
Cu ( $\text{mg kg}^{-1}$ dw)	42.41 $\pm$ 0.95	156.04 $\pm$ 3.77	1000
Zn ( $\text{mg kg}^{-1}$ dw)	177.71 $\pm$ 5.51	452.44 $\pm$ 15.59	2500
Pb ( $\text{mg kg}^{-1}$ dw)	16.69 $\pm$ 1.89	195.86 $\pm$ 8.55	750
Cd ( $\text{mg kg}^{-1}$ dw)	1.64 $\pm$ 0.07	2.17 $\pm$ 0.33	20

0.36 kg of phosphorus will appear in MSW digestates per year. This is equivalent to a small city of 100,000 inhabitants potentially recovering 36 tonnes of phosphorus per year, or a larger city with 3.4 million inhabitants (e.g. Madrid, Berlin) potentially recovering over one thousand tonnes of phosphorus per year.

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

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

### Phosphorus Extraction from Dairy Cattle Slurry and MSW Digestates

Nitric acid ( $\text{HNO}_3$ ) and sodium hydroxide (NaOH) were used to investigate the effect of pH in phosphorus extraction from dairy cattle slurry and MSW digestates.

The extraction from these wastes into solution over time is presented in Fig. 1. For both wastes extractions were higher when  $\text{HNO}_3$  was used than when NaOH or water, expressly indicating that base extraction was not effective and the release of phosphorus from both wastes was better at lower pH values.

In the case of dairy cattle slurry the phosphorus extracted with acid reached between 90 and 100 % of total phosphorus

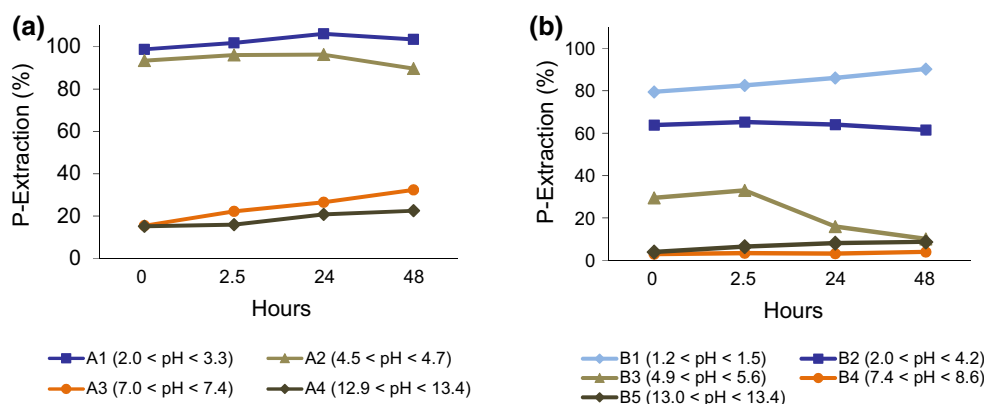
(A1 and A2), with the differences between the two experiments being relatively small. This means it is not necessary to lower the pH from the original value (around 7) to 2 to get good extractions, and the process can be conducted with similar success at pH 4.5 (reducing the need for the acid reagent).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

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

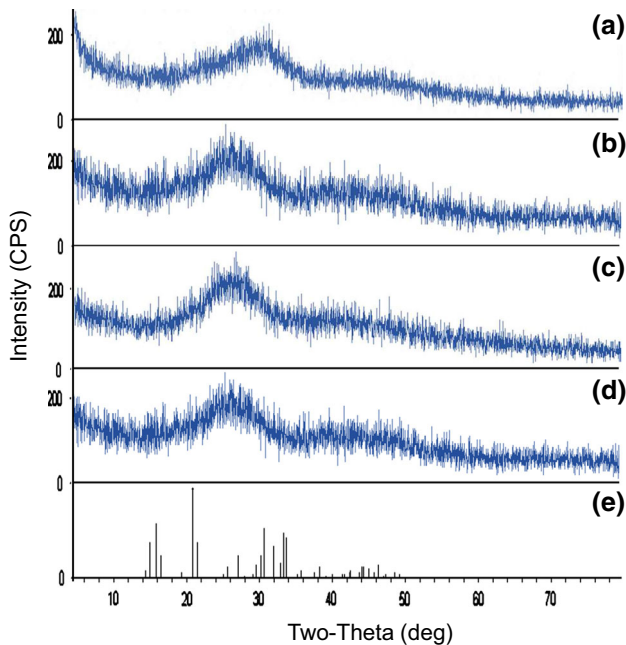
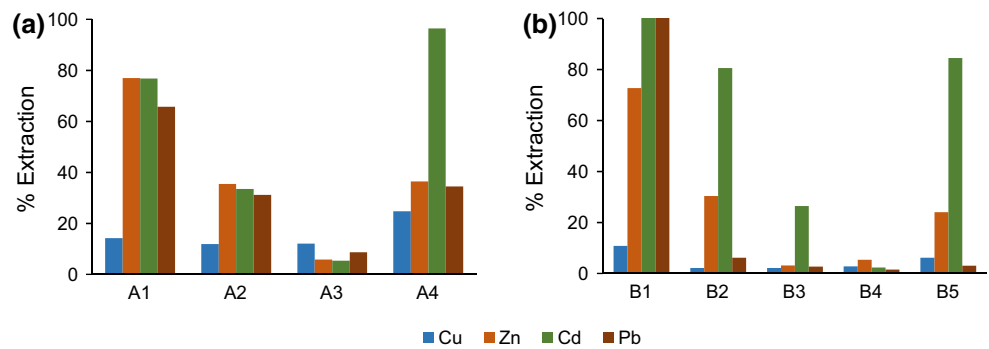
The phosphorus extracted with NaOH was very low and did not exceed 22 % for dairy cattle slurry and 9 % for MSW digestates. The results obtained in this study are lower compared with the investigation made by Stark et al. [11] were the phosphate release from dried sludge at 1 M NaOH (corresponding to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

According to results above we assume that acid extraction of phosphorus could be applied to other organic

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



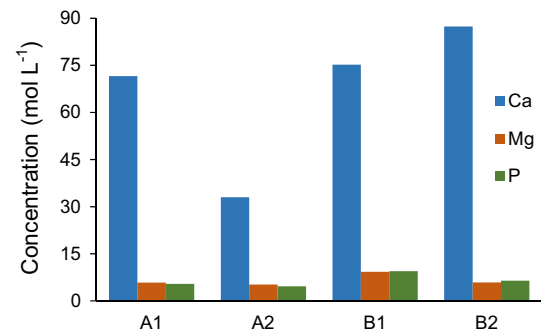
**Fig. 2** Heavy metals in solution after the extraction step, as a percent of the initial mass of each metal in the waste: **a** Dairy cattle slurry; **b** MSW digestates



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

wastes. However, the origin of the waste should be considered because in case the waste has undergone biological treatment prior to the acid extraction then phosphorus might be more difficult to extract and consequently lower pH might be required.

Biswas et al. [7] and Cohen [8] stated that the extraction efficiency of phosphorus increase with the extraction time. As illustrated in Fig. 1, phosphorus extraction in dairy cattle slurry was almost immediate when the sample come into contact with acid, and the amount of solubilised phosphorus did not increase significantly overtime. Xu et al. [6] investigated the effect of extraction time from sewage sludge ash, achieving more than 95 % of extraction after 120 min of reaction. These results are in accordance with the ones presented here and the acid soluble nature of



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

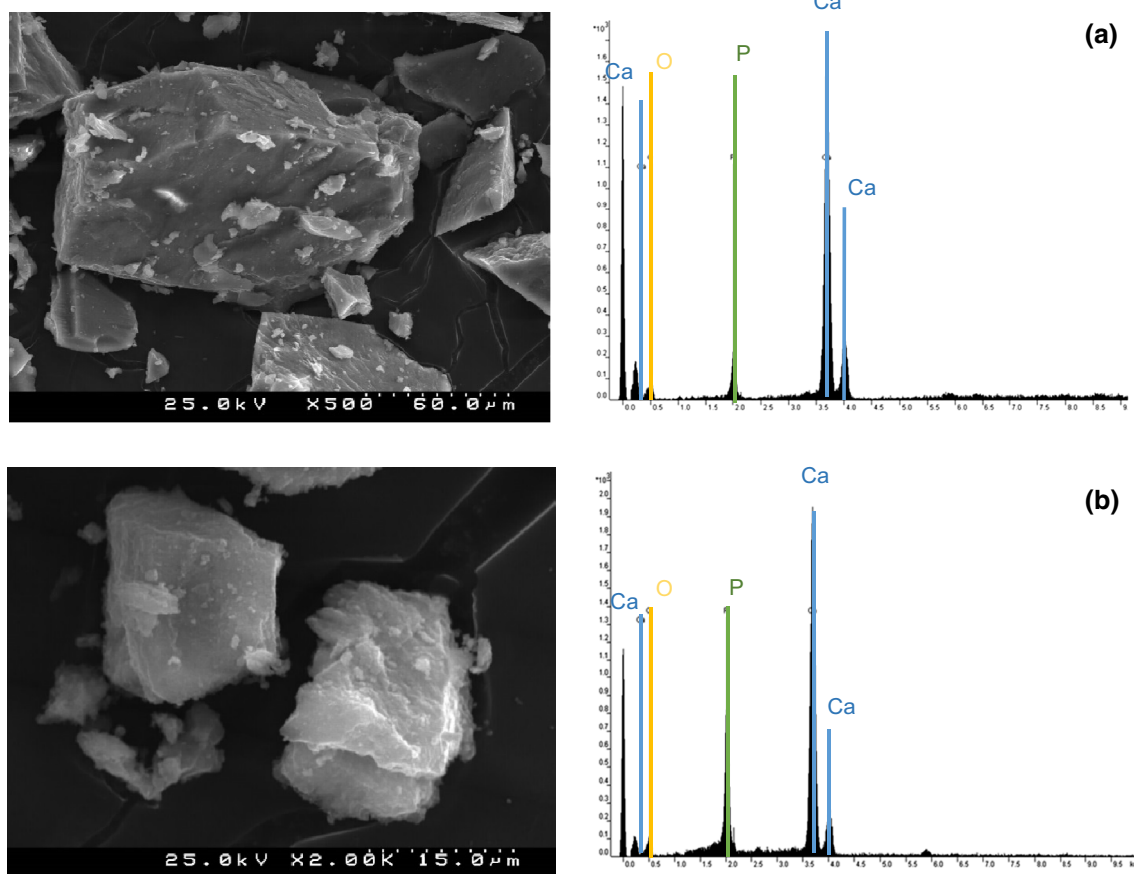
the waste materials can be responsible for the rapid phosphorus extraction.

### Influence of pH on Heavy Metals Extraction

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

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

Around pH 7 (A3 and B4) the solubility of all the metals decreased considerably, while increasing at lower and higher pH values, and this is related to the variation of metal speciation with pH, in which charged metal hydroxides are formed at higher pH and metals ions at lower pH. Due to the polar nature of the water molecule



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

these charged ions and compounds formed at low and high pH are more easily extracted than neutral species.

### Recovery of Phosphorus as a Precipitate

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

The reduction of phosphorus in solution after the precipitation experiments was  $94.0 \pm 0.3 \%$  in A1 and  $97.8 \pm 0.1 \%$  in A2 (dairy cattle slurry). In the MSW digestates precipitation experiments the percentage of phosphorus removed was  $95.8 \pm 0.8 \%$  in experiment B1 and  $99.2 \pm 0.01 \%$  in experiment B2. Jin [28] obtained about 80 % phosphate removal efficiency for a dairy cattle slurry sample in which phosphorus was extracted by microwave-based thermochemical pre-treatment with  $H_2SO_4$  and HCl. Burns and Moody [15] reported a reduction of 91 % of phosphorus in solution when using swine

slurry during laboratory and field tests. Our results overcome these values. The results of XRD carried out on the precipitate are shown in Fig. 3a–d, indicating that in the harvested precipitates there were no crystalline phases present.

Le Corre et al. [32] reported that the struvite crystal growth can be affected significantly by the presence of calcium in solution and that above a molar ratio of Ca:Mg of 1:1 the formation of amorphous calcium phosphate occurs. The concentration of calcium and magnesium compounds in extraction solutions A1–A2 and B1–B2 are shown 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 large excess of calcium when compared to magnesium.

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

Similarly to struvite, calcium phosphate, can be used as phosphate fertilizer in agriculture [14, 12] or as raw material for fertilizer industry. However, the use of

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

## Conclusions

In this work two different wastes were evaluated for the recovery of phosphorus: MSW digestates, arising from the anaerobic digestion of municipal solid wastes and dairy cattle slurry. The concentration of phosphorus in the MSW digestates was 0.8 % (dry weight) and in the dairy cattle slurry 0.4 % (dry weight). These levels are low compared with values reported for ash residues (8–10 %) because as organic materials are destroyed during the combustion process phosphorus becomes enriched in the ash. Nevertheless, given the large amounts of MSW digestates and dairy cattle slurry wastes arising annually it is worthwhile considering these wastes for phosphorus recovery. When trying to extract phosphorus from the wastes using nitric acid ( $\text{HNO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ), 100 % of the phosphorus contained in dairy cattle slurry could be extracted into solution after only 2.5 h at a pH of 4.5. For MSW digestates the maximum extraction was 90 % at pH below 2, indicating that even though phosphorus concentration is higher in this residue, phosphorus is not so easily extracted and the extraction process needs to be carried out at a pH below 2. For both wastes extractions were higher with  $\text{HNO}_3$  than with  $\text{NaOH}$  or water, expressly indicating that base extraction was not as effective to release the phosphorus.

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

and this should be taken into account when considering phosphorus-recovery from wastes.

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