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Extraction of phosphorus and struvite production from the anaerobically digested organic fraction of municipal solid waste

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Abstract

In this work a first attempt was carried out to recover phosphorus from the organic fraction of municipal solid waste (OFMSW) and to transform it into a fertilizer. Recovery of phosphorus was carried out by the electrodialytic process combined with struvite formation. Experiments were carried out in an electrodialytic cell, using either distilled water or nitric acid, and extraction times ranged from 1 to 16 days. During these experiments phosphorus was solubilised from a real industrial waste and separated from metal contaminants using electromigration. The extraction step was then followed by batch chemical precipitation tests to yield struvite.

Phosphorus extraction from the waste was up to 43 % in the electrodialytic treatment and its precipitation as struvite reached efficiencies close to 100 %. The electrodialytic process effectively separated Ca, Cd, Pb, and Cu from the phosphorus fraction, but was not as effective in separating Zn. Struvite still contained $0.6 - 1.4$ g kg^{-1} of Zn, which restricted its agronomic application to some cultures.

This works shows that phosphorus can be extracted from digestate of OFMSW using the electrodialytic process and afterwards can be precipitated as struvite, a slow release fertilizer. Despite this work being only a first attempt to recover phosphorus from digestate of OFMSW and still requires optimisation, the potential of the process was demonstrated, which means digestate of OFMSW currently represents a so far under-explored secondary source of phosphorus.

1

Keywords

1. Introduction

Anaerobic digestion of municipal solid waste (MSW) is a current practice in Europe, allowing for the recovery of the energy contained in the organic fraction of MSW (OFMSW) through biogas generation. In 2013 there were 166 anaerobic digestion plants across 15 European Union member states, with a total capacity of 5.7 Mtonne [1]. Usually, these facilities can handle either source segregated bio-waste or the organic fraction recovered from MSW after mechanical sorting. The sludge-like residue remaining after anaerobic digestion process is called digestate. The processing techniques applied to digestate are solid/liquid separation (e.g. centrifugation), followed by mixing the solid fraction with carbon-rich material to achieve an optimum C/N ratio and finally composting. In case source segregated biowaste is used as feedstock for the anaerobic digestion process the resulting compost has a higher quality and, depending on the national regulations, might be sold as "soil improver" or as "organic amendment" [1]. In southern European countries such as Portugal, Spain and Greece, separate collection of biowaste has not been implemented in large scale. In this case, the quality is lower than when source segregated biowaste is used due to the higher percentage of contaminants in the collected waste. The resulting stabilised product is either landfilled or used in non-agricultural applications [1].

The "waste hierarchy" shows that waste recovery and recycling is to be prioritized over landfilling [2]. Digestate of OFMSW contains comparatively high amounts of phosphorus (P) (17 g - 58 g P_2O_5 kg^{-1}; dry weight) [3,4], which are lost when digestates are landfilled. In 2014, phosphate rock was included in the EU Critical Raw Materials list, together with rare earth elements, cobalt and niobium [5], highlighting that the secure and continuous access to P is a growing concern within the EU.

This work explores for the first time the possibility of recovering P from the anaerobically digested OFMSW using the electrodialytic (ED) process combined with struvite formation. In the ED technique, a voltage drop is applied across the waste material and the soluble ions migrate under the electric field towards the electrode of opposite charge, a process denominated electromigration. Phosphorus is present mostly as negatively-charged species [6], and moves to the anode during ED process, while contaminants such as heavy metals are usually positively charged, and migrate to the cathode.

2

Consequently, a P-rich solution virtually free of metal cations and other positively or neutral contaminants is obtained at the end of ED process. The capacity to separate P from the remaining waste material is the major advantage of ED technique, when compared to other processes (e.g. acid/base extraction), and this separation capacity is of great importance when extracting P from a waste of mixed constituents, where different contaminants might be present.

In recent years, the ED process has been extensively investigated to extract P from waste matrixes, namely wastewaters [7,8], sludges from wastewater treatment plant [9–12] and ashes [13–15]. However, most of these studies were limited to the extraction into solution of P using the ED process, and did not pursue the subsequent reuse of the P-rich solution obtained, even though this step is essential to close the P-cycle. The exceptions were the works by Zhang et al. [7] and Wang et al. [10] in which a two-step ED process was conducted on a synthetic wastewater, where P was present in solution. For a real industrial waste, the ED process used by Zhang et al. [7] and Wang et al. [10] cannot be applied due to the presence of suspended solids in high concentration, and because the target elements are not in dissolved form, else are bound to the solid matrix of the waste, and therefore are more difficult to extract. One of the objectives of the current work is applying the ED process to a real waste stream (digestates of OFMSW) and taking the process into the next level, by transforming the extracted P into a fertilizer. The option here explored is the production of struvite ($MgNH_4PO_4 \cdot 6H_2O$), a slow release P-based fertilizer that can be either directly used in agriculture or be used as raw material in the fertilizer industry [16–18]. In addition, since the ED process has never been applied to the digestates of OFMSW, this works aims also to assess the feasibility of using this separation technique with this particular waste material.

In summary, two main research questions are addressed: (i) Can P be extracted from digestate of OFMSW using ED process? and (ii) Can ED successfully separate heavy metals and calcium, so that a high quality struvite can be attained?

2. Materials and Methods

2.1 Digestate of OFMSW

In April 2015, 10 kg of digestate of OFMSW were collected at a mechanical and biological treatment facility in Portugal. This facility receives unsorted waste discarded by households and commercial facilities. The organic fraction is mechanically separated from the remaining waste fractions and undergoes anaerobic digestion. The sample was collected after anaerobic digestion and before composting. Immediately after collection the sample was refrigerated < 4 ºC until use (less than 48 h), was dried in a forced draft oven at a temperature of 105 °C for 24 h, then ground to pass through a 1 mm sieve and stored in closed decontaminated glass containers, at room temperature. The characterization

3

of the sample of digestate of OFMSW was previously carried out in Oliveira et al. [3]. Briefly, the dry sample presented a pH of 7.8, an ash content of 18.55 % and a total P concentration of 8.1 mg g^{-1}. The concentration of calcium and magnesium were 103.7 mg g^{-1} and 12.6 mg g^{-1}, respectively. The digestate of OFMSW presented copper (Cu) concentration of 156.0 mg kg^{-1}, zinc (Zn) was 452.4 mg kg^{-1}, lead (Pb) was 195.9 mg kg^{-1} and cadmium (Cd) concentration was 2.17 mg kg^{-1}.

2.2 Electrodialytic experiments

Electrodialytic experiments were conducted in a stationary (non-stirred) 3-compartment cylindrical Plexiglas laboratorial cell with an internal diameter of 4 cm (Fig. 1). The three compartments were: I – anolyte compartment (L = 5 cm); II – central compartment (L = 10 cm or L = 3 cm, depending on the experiments), where a mixture of the digestate and distilled water (or 1.1 M nitric acid) were added (with a liquid/solid ratio of 2.5); III – catholyte compartment (L = 5 cm). One electrode was placed in compartment I and another in compartment III. The electrodes were platinum coated titanium bars, 3 mm in diameter and 5 cm in length. Ion-exchange membranes separated the compartments: a cation-exchange membrane (CMI-7000S, MEMBRANES INTERNATIONAL INC) was used between compartments II and III and an anion-exchange membrane (AMI-7001S, MEMBRANES INTERNATIONAL INC) was used between compartments I and II. This membrane set-up delays pH changes in the waste material in compartment II, while allowing P and heavy metals to migrate into the electrolytes. A power supply (Hewlett Packard E3612A) was used to maintain a constant current density. In each electrode compartment (I and III), 0.01 M NaNO$_3$ was used as electrolyte and circulated between the compartment and an external reservoir (Erlenmeyer flask) using a peristaltic pump (ISMATECH BVP).

(Figure 1)

Four electrodialytic experiments (**A**, **B**, **C** and **D**) were carried out using different electric current values, pH in central compartment and duration of experiment (Table 1). The first experiments (**A** and **B**) were carried out for a short period of time (1 - 2 d) to allow tuning of experimental conditions. In experiment **B** nitric acid was added to OFMSW digestate and placed in compartment II, while in experiment **A** distilled water was used instead. These first experiments were followed by two more experiments, running for longer periods of time, using also nitric acid (exp. **C**) and distilled water (exp. **D**).

Previously it has been found that acidic conditions favour dissolution of P from digestate of OFMSW [3], so by using nitric acid higher P solubilisation is expected. However, because nitric acid dissociates into H$^+$ and NO$_3^-$ ions, when it is used the electric conductivity (EC) values in the central compartment at the beginning of experiments were much higher in experiment **B** than in experiment **A**. This meant

4

that in order to achieve similar values for the voltage drop in the following experiments a higher current (30 mA) was used in experiment **C**, while in experiment **D** the current passed was 10 mA, keeping the value used in the previous experiments (Table 1).

(Table 1)

Voltage drop and electric current were registered every day during the experiments. The pH and EC were determined in the catholyte and anolyte using a HANNA (Combo) probe. Correction of pH in the catholyte was carried out on weekdays to $pH < 2$ using 1:1 M HNO_3, to prevent precipitation of insoluble substances due to the high pH values arising here. pH was measured daily in the digestate of OFMSW with pH strips (Panreac). In experiment **D** acidification to $pH = 4 - 5$ of digestates took place once, at $t = 10$ d, because the low electrical conductivity at that moment in time did not allow to achieve the set point of 10 mA without acidification. Once a day, 5 mL of anolyte and catholyte were collected, and soluble P and EC were measured in these solutions. This step allowed the calculation of the amount of P transported daily towards the electrolytes.

At the end of experiments, the pH, EC and volume of anolyte and catholyte were registered and samples were taken for determination of soluble P, Ca, Mg and heavy metals (Zn, Cu, Cd and Pb). Electric conductivity and pH were also measured in compartment II (OFMSW digestate) and the material in this compartment was mixed and dried (105 °C) for determination of total P (P_{tot}), sequential P fractionation, Ca, Mg and heavy metals. Ion exchange membranes and electrodes were soaked in 1:1 M HNO_3 during 24 h, and the soaking solution was filtered and stored for analysis of soluble P, Ca, Mg and heavy metals.

Phosphorus solubilised from the digestate of OFMSW in the central compartment and transported into the electrolytes is referred herein as "extracted P", because this is the fraction that will be submitted to precipitation processes to yield struvite. Extraction efficiency of P is defined as the percentage of the initial mass of P in the digestate of OFMSW that is found in the electrolyte solutions at end of the ED experiments, calculated as:

P extraction efficiency (%) = (mass of P in electrolytes at the end of electrodialytic step) / (mass of P in the digestate at the beginning) *100

2.3 Struvite Precipitation

Batch experiments aiming at P precipitation as struvite were conducted with the anolyte solutions resulting from ED experiments **C** and **D**.

The anolyte solutions at the end of the ED experiments were transferred to a 500 mL beaker, with a

5

magnetic stirrer. While stirring, hexahydrate magnesium chloride ($MgCl_2 \cdot 6H_2O$) was added as Mg source, the pH was quickly adjusted to 9 using 5 M NaOH solution, and then ammonium chloride (NH_4Cl) was added as nitrogen source. The amounts of magnesium and nitrogen were calculated to set the molar ratio Mg:N:P at 2:2:1. After 60 min with slow stirring, agitation was halted and the suspension filtered through a 0.45 μm membrane filter (Whatman ME25/21ST) to separate the precipitate. The filtered solution was kept for further analysis. The harvested precipitates were dried at 50 °C and analysed using an X-ray Diffractometer (XRD, Rigaku Geigerflex, JP) with a Cu anode, operating at 45 kV and 40 mA. The patterns were collected in the 4 – 80 °2theta range (0.02 °2theta s^{-1} step-scan, and 1.5° min^{-1}). The precipitates were also analysed using scanning electron microscopy coupled with energy dispersion spectroscopy (SEM-EDS) using Hitachi S4100 equipped with EDS – Rontec.

Precipitation efficiency of P was defined as the percentage of P precipitated from solution (measured as the difference between the initial and the final concentration) in relation to the initial P in solution, calculated as:

P precipitation efficiency (%) = ($[P]_{initial} - [P]_{final}$) / $[P]_{initial}$ * 100

2.4 Analytical methods

Total P (P_{tot}), sequential P fractionation, Ca, Mg and heavy metals were measured in digestate of OFMSW before and after ED step. Total P (P_{tot}) was measured by shaking 1.0 g of incinerated digestate of OFMSW (1 h at 550 °C) with 0.5 M sulphuric acid for 16 h. After shaking, the solutions were centrifuged at 5000 rpm for 10 min and the supernatant analysed using the ascorbic acid colorimetric method [19]. The sequential P fractionation procedure followed was proposed by Hedley et al. [20] as described in Siebers et al. [21]: 0.5 g of dried digestate of OFMSW was placed in a flask and 30 mL of extractant was added. Then, the solution was shaken for 18 h at 120 rpm and, finally, centrifuged and filtered with qualitative paper, before P analysis. The fractionation process involved four sequential extraction steps: 1) extraction of P with distilled water (H_2O-P); 2) extraction of P with 0.5 M $NaHCO_3$, pH = 8.5 ($NaHCO_3$-P); 3) extraction of P with 0.1 M NaOH (NaOH-P); and 4) extraction of P with 1 M H_2SO_4 (H_2SO_4-P) [21]. The corresponding putative P forms obtained from each extracting solution are as follows: (i) easily exchangeable and solution P (step 1), (ii) labile inorganic, organic and some microbial P (step 2), (iii) inorganic and organic P forms sorbed and/or fixed by aluminium and iron oxide minerals as well as P forms in humic and fulvic acids (step 3) and (iv) P associated with Ca and Mg minerals (step 4) [21]. Each extract was analysed for inorganic P (P_{ino}) content using ascorbic acid colorimetric method and P_{tot} content after digestion with potassium persulfate and sulphuric acid. Organic P (P_{org}) concentrations were calculated as the difference between P_{tot} and P_{ino}. Calcium, Mg and heavy metals were measured in accordance with the procedure described in John et al. [22] (in triplicate): 0.5 g of dried digestate of OFMSW were placed into a digestion tube and 5 mL of concentrated nitric

6

acid (65 %) and 10 mL of hydrogen peroxide 30 % were added. The tubes were heated in a block digester (SCP Science) at 120 °C until solution turned pale yellow or clear. Then the digested samples were filtered through 0.45 μm filter (SCP Science) into 50 mL volumetric flasks for further analysis.

The Ca, Mg and heavy metal content in the solutions (anolyte, catholyte, membrane and electrode cleaning solutions, digested samples and solution after struvite precipitation) was measured by atomic absorption spectrometry (Perkin Elmer AAnalyst 300) and P_{tot} in solution was determined by the vanadomolybdophosphoric acid colorimetric method [22] at a wavelength of 470 nm (spectrophotometer HITACHI: U-2000). All concentrations are given on a dry weight basis.

3. Results and discussion

3.1 Phosphorus extraction using ED process

3.1.1 Phosphorus distribution at the end of ED

By applying an electric field to the digestate of OFMSW it is expected that charged P species will move from the central compartment, across the ion-exchange membranes, towards the electrode of opposite charge. The distribution of P in the electrodes, ion-exchange membranes, electrolytes and OFMSW digestate sample at the end of ED experiments is presented in Fig. 2. The mass balance shows that between 92 % and 109 % of the P initially in the digestate of OFMSW was recovered at the end of the ED experiments. These values are acceptable, considering the heterogeneous characteristics of digestate of OFMSW and the analytical procedures involved. No P was detected in the cathode compartment and P either stayed in the central compartment (II) or moved across the anion-exchange membrane into the anolyte (I), indicating it is present in this system as negatively charged compounds. Experiments **A** and **D** were carried out at pH values between 5 and 7 while experiments **B** and **C** at pH values between 1 and 3 (Fig. 3). Given the pKa of phosphoric acid (2.12, 7.2 and 12) at the pH range of the experiments, P is expectedly present mostly as $H_2PO_4^-$ and HPO_4^{2-} in experiments **A** and **D** and as $H_2PO_4^-$ and H_3PO_4 in experiments **B** and **C**. Of these substances only H_3PO_4 is non-ionic. The remaining P-forms are negatively charged and moved towards the anode, into the anolyte.

No P was found at the surface of the electrodes, but a residual amount was found at the ion-exchange membranes, which is explained by these membranes being in physical contact with the digestate of OFMSW.

(Figure 2)

7

3.1.2. Phosphorus transport into the anolyte during ED

The evolution with time of P in the anolyte solutions is shown in Fig. 3. The amount of P removed to anolyte was higher in experiments with distilled water (exp. A and D) than with acid (exp. B and C) during the first 2 days of ED extraction. This result was not anticipated. In fact, a previous study by Oliveira et al. [3], showed a dependence of solubilised P (from OFMSW) with the pH, in which more acidic conditions were found to favour the solubilization of P: while 90 % of P was solubilised at pH range of 1.2 – 1.5, solubilisation decreased to 60 % at pH range 2.0 – 4.2, and a further decrease to 20 % occurred when the pH increased to 4.9 – 5.6. For even higher pH (above 7) P solubilisation becomes less than 10 %. So the higher transport rates of P into the anolyte in the experiment at higher pH were unexpected. A possible explanation is that since under acidic conditions larger amounts of ions are present in the central compartment (solubilization from the sample itself and ions from the acid dissociation) most of the driving force of the electric field is used in the initial stage to transport other ions, rather than P. After day 7 the concentration of P in experiment **C** (with acid) reached values near those achieved in experiment **D** (with water).

The practical result was that P in the anolyte was consistently higher in experiments with distilled water (exp. **A** and **D**) than in experiments with nitric acid (exp. **B** and **C**), for the same experimental time. This means that while acidifying a sample might increase dissolution of P from the waste [3], the presence of other dissolved substances hinders P transport into the anolyte. So in case more ions are present (acidic conditions) longer times and higher currents are required.

(Figure 3)

In experiment **C** the voltage increases systematically after day 3, reaching the maximum allowed by the equipment around day 10, after which the experiment was halted because it was no longer possible to maintain the current at the pre-defined value. This increase in voltage drop was probably due to an increased resistance at the cathode/catholyte interface due to the formation of a whitish/orange precipitate at the surface of the cathode. Analysis of the precipitate collected from the cathode surface at the end of the experiment indicated the presence of Ca and Mg compounds, which are major constituents of digestate of OFMSW. The precipitate did not form however in experiment **D**, and it was possible in this case to sustain a constant extraction of P during the time of the experiment (t = 16 d). In experiment **D** a decrease in voltage drop after 10 d (from about 39 V to 21 V) is attributed to the addition of nitric acid in the central compartment at day 10, which increased the amount of ions in solution and lowered pH from 6 to around 4.5, favouring additional dissolution of P.

8

3.1.3 Extraction efficiency

Phosphorus extraction efficiency from digestate of OFMSW was: 43 % in exp. **D** (16 d); 28 % in exp. **C** (10 d): 8 % in exp. **A** (1 d); and 0.3 % in exp. **B** (2 d). As the shorter experiments were carried out to tune operating conditions, results and discussion will focus on the longer experiments, **C** and **D**.

The best extraction result of 43 % was obtained after 16 d of ED, in a digestate sample mixed with distilled water (L/S ratio of 2:5) and presenting an initial pH of 6.3. The sample was slightly acidified after 10 d of ED, lowering pH to circa 4.5.

The maximum P extraction herein is lower than in other previously reported works (Cordell et al. [23] summarized many systems with recoveries over 80 %). For example, Zhang et al. [7] also studied the two-step process, and Fukumoto and Haga [8] reported an almost 99 % P recovery. So the question is why the P recovery from this system is so limited, leaving more than 50 % of P in the waste.

The first observation is that in the cited experiments the sample submitted to ED treatment is obtained after a solid/liquid separation process, with the liquid fraction being used. Opposite to these previous studies, the aim of the current research is to use the solid fraction, after the solid/liquid separation. While the liquid fraction contains most of the easily soluble P, the solid fraction (from where the P is most difficult to extract) is the one targeted in the current research. Phosphorus speciation in digestate of OFMSW shows that the P fraction extractable with water (step 1 of the extraction procedure) is less than 10 % (Fig. 4), supporting the considerations that most soluble P had been taken with the liquid fraction during the solid/liquid separation. It is also noteworthy that about 60 % of P is associated with Ca and Mg minerals (extraction step 4) and with the residual fractions, being most difficult to extract. The labile inorganic, organic and some microbial P extracted in step 2 represented 22 %, and the P forms sorbed and/or fixed by aluminium and iron oxide minerals extracted in step 3 was almost 10 %.

The second observation is that the waste source used herein is different from other reported studies. Digestates from OFMSW likely comprise: (i) end-products of the anaerobic digestion, including cells of the microorganisms that carried out the digestion; (ii) organic matter recalcitrant to biological decomposition; and (iii) various inorganic materials that were not separated from the organic fraction due to inefficiencies of the mechanical sorting. So this sample is quite different from other solid samples undergoing ED process (such as incineration ashes), in which the organic matter was previously destroyed. The presence of organic matter in the digestates is likely to make extraction more difficult, as some P might be intrinsically part of the microorganisms: in cell membranes (where phosphate groups are linked to chains of fatty acids), in DNA and RNA (where phosphate forms the "backbone" of the double helix and single helix) and in energy molecules (such as ATP and ADP) [24]. Organic P in the digestate of OFMSW represents 8.6% of P_{tot}, with the remaining 82.8 % being P_{ino} and 8.6 % residual P (Fig. 4). There are a few results on P-extraction from organic wastes, such as the ones carried out by Ebbers et al. [9], in which a sewage sludge from wastewater treatment facility was ED treated in a similar

set-up (3 compartments) and the P removal was 20 % - 40 %. Guedes et al. [12] also report P-extraction efficiencies from sewage sludge ranging approximately from 5 % to 78 % but in this case a different ED cell configuration was used (2 compartments). The results obtained in this work show similar extractions for P but were carried out without stirring the sample. This means that there is still great possibility for improvement, and as optimisation proceeds higher extractions are expected, making it possible to up-scale the process. Future optimisation is discussed further in the conclusion section.

In experiment **C** (carried out at lower pH) practically all the P associated with Ca and Mg minerals and the residual fraction had disappeared by the end of experiment. In experiment **D**, the acidification of digestate at t = 10 d resulted also in a decrease of P forms associated with Ca and Mg minerals and residual fraction, but to a less extent than that verified in experiment **C**, as pH was not as low.

Given that > 60 % of P is present as Ca and Mg minerals and residual fraction, acidification is essential to comprehensively extract P from the digestates. In addition to acidification, longer experimental times may also be required to increase the more easily and labile P forms in digestate and enhance its extraction: the presence of a significant amount of water-bound P in the waste digestates at the end of experiment **C** indicates that this experiment should have been prolonged to achieve higher extraction efficiencies. As discussed above, experiment **C** was stopped at day 10 because of the appearance of a precipitate in the catholyte, that increased the cell resistance and did not allow the passage of electric current.

The results obtained herein are promising, having achieved 43 % of P extraction from digestates of OFMSW. Nevertheless, these are only a preliminary assessment of the recovery of P from digestate of OFMSW using ED process and highlight the need to further optimise the system.

(Figure 4)

3.2 Heavy metals distribution at the end of ED

Heavy metals are undesirable contaminants commonly found in MSW. Unlike orthophosphate (negatively charged), heavy metals are positively charged, meaning they will migrate towards the cathode side, away from compartment I where P accumulates. However, depending on the composition of the digestate of OFMSW and on experimental conditions (e.g. pH) metal complexes bearing different electric charges might be formed. In case these complexes are negatively charged they will be transported to the anolyte, together with P. Cu, Zn, Cd and Pb are heavy metals commonly found in municipal waste and therefore were selected in this work for further assessment. The distribution of these metals in the different compartments of the ED cell at the end of the experiments is shown in Fig. 5.

10

(Figure 5)

Under the experimental conditions tested in this work, Cu and Pb were not transported to the anolyte and mostly remained in the digestate of OFMSW in compartment II (> 97 %), while a residual amount was moved into the catholyte (< 3 %). Cadmium was almost completely extracted from digestate of OFMSW into the catholyte in experiments **C** and **D** (95 % - 100 %). No Cd was found in the anolyte compartment, to where P was moved, meaning that similarly to Cu and Pb, experimental conditions were also successful in separating Cd from P. In addition, it was found that longer times of experiment increase the mobilization of Cd to the catholyte. By contrast, Zn was transported into the anode compartment (anode+anolyte): 16 % in exp. **A**, 1 % in exp. **B**, 7 % in exp. **C** and 4 % in exp. **D**. The increase of Zn mobilization towards the catholyte seems to be related to the lower pH of digestate of OFMSW and with longer times of experiment (exp. **B** and **C**).

In general, the heavy metals were either transported towards the catholyte or remained in the central compartment, whereas the P was transported towards the anolyte, supporting the P separation objective. The exception was Zn, which partly moved towards the anode compartment together with P, and whose impact on the quality of the struvite obtained is discussed in the next section.

3.3. Production of struvite

The recovery process was based on the precipitation of P in the form of struvite ($MgNH_4PO_4\cdot6H_2O$) from the anolyte solutions obtained at the end of ED experiments **C** and **D**. The harvested precipitates were labelled "precipitate **C**" and "precipitate **D**", according to the anolyte solution used. The concentration of P and Zn in solution before and after the precipitation process is shown in Table 2. The precipitation process successfully removed 94.9 % of the P in solution in experiment **C** and 99.3 % in experiment **D**.

(Table 2)

Results of the X-ray diffraction (XRD) of the precipitates are shown in Fig. 6. The pattern (position and intensity of the peaks) matches the struvite standard, confirming the formation of struvite crystals during the precipitation process. No extra/minor phases were detected. In an earlier work precipitation of struvite directly from digestates of OFMSW had failed due to the presence of large amounts of Ca [3]. In the current work, Ca was separated from P by ED technique (being a cation, Ca moved to the catholyte), so that the reactions leading to struvite precipitation successfully occurred (Fig. 5).

(Figure 6)

SEM-EDS analyses (Fig. 7) reveal the presence of elongated crystals (irregular in the case of precipitate **D** and more orthogonal in precipitate **C**), in which the major elements are Mg, P and O (EDS spectrum), consistent with struvite composition. The shape variations found between precipitates **C** and **D** are caused by slight differences in the precipitation conditions, such as agitation speed or room temperature, or to different composition of the solutions.

(Figure 7)

Struvite is a slow release fertilizer. However, the use of recovered struvite for agricultural application requires some precautions related to the presence of contaminants. Considering the difference between Zn in solution before and after precipitation (Table 2), estimated Zn levels in struvite were 1429 mg kg^{-1} for experiment **C** and 585 mg kg^{-1} in struvite for experiment **D**. Zinc is a desirable micronutrient for soils, and the current European fertilizer regulation, Directive 2003/2003/EC [25], does not impose any maximum limit for Zn in fertilizers. However, limit values exist for Zn in fertilizers in Portugal and in other countries, as shown in Table 3. Comparing Zn levels in struvite in the current work against the Portuguese limit levels shows that struvite **C** is within the limits of a class III fertilizer (crops not used for food nor fodder) and that struvite **D** is within the limits of Class II A (tree and shrub crops including orchards, olive groves and vineyards, and forestry). Nevertheless, limit values in other countries are exceeded (Table 3). Therefore, it is recommended that future works address the optimisation of Zn separation during ED treatment. Possible ways to separate Zn include modelling Zn speciation to identify complexes likely to be present in the sample as negatively charged species (which are now being transported to the anolyte together with P) followed by control of pH to avoid the formation of such complexes. Such optimization of Zn separation will increase the potential of struvite recovered from the anaerobically digested OFMSW to be used as a fertilizer in the European framework.

(Table 3)

3.4. Overall P recovery from digestate of OFMSW

The recovery process tested in this work is a two-step sequential process; the first stage consists of P solubilisation and extraction from the waste into a solution (using the ED process), followed by the removal of P from solution by precipitation (as struvite). The overall recovery of P from digestate of

12

OFMSW was calculated by multiplying the efficiencies achieved in each step. In experiment **C** (with acid) the overall P recovery was 27 %, while in experiment **D** (with distilled water) the overall efficiency reached 43 %. It was also found that the ED step was the one limiting the overall P recovery which means the optimization of the process is essential in order to extract more P from the digestate of OFMSW.

4. Conclusions

The recovery of P from digestate of OFMSW using a combination of the ED process with struvite formation was investigated in this work. The first research question that was addressed was if P could be extracted from digestate of OFMSW using the ED process. This work demonstrated that during the ED step, the separation of P from digestate of OFMSW into the anolyte was achieved with an efficiency of 43 %, at a pH between 4.5 and 6.3, after 16 d. More than 50 % of P still remained in the waste, and a discussion was carried out on why extraction values were lower than in other studies. Two explanations were put forward, the first being that the solid fraction of the waste was used as input in the ED process, as opposed to other studies which used only the liquid fraction. The second explanation relates to digestates being the output of an aerobic digestion process where P is a constituent of the structure of microbial cells, which makes P extraction difficult without the previous destruction of the organic matter.

After crossing of the results of ED experiments with P speciation (before and after ED) several options were put forward for increasing extraction efficiencies to higher levels in future research. These include:

(i) stirring of the digestates during the ED extractions. The stirring will favour ion solubilisation in the central compartment and consequently increase their transport across the ion-exchange membranes, towards the electrode of opposite charge. Even though the consumption of energy will increase, it is expected that stirring will considerably reduce treatment times and increase separation efficiencies of P, allowing for higher recoveries of this nutrient from the waste.

(ii) acidification of the digestate in order to extract P bound to Ca and Mg minerals and in residual fractions, which represents more than 60 % of P_{tot}; preferably, this acidification might be induced by the electrodialytic process itself, due to the water electrolysis taking place at the anode ($2H_2O \rightarrow 4H^+ + O_2$), thus avoiding the need to add external acids; however, pH should be kept higher than 1.5, because at such pH the dominant species is the non-ionic H_3PO_4, which will not electro-migrate. So a balance must be found between a pH which enhances dissolution and one that promotes the appearance of charged P forms, in order to allow transport into the anolyte.

(iii) increasing of voltage drop across the cell to increase the driving force for the electromigration. An acidification of the sample might increase dissolution of P from the waste as well of the other susbstances

13

that could hinder P transport into the anolyte. So in case more ions are present (acidic conditions) longer times and higher currents are required.

(iv) acidification of the catholyte in order to prevent the formation of Ca and Mg precipitates that increase the ED cell resistance and hinder the extraction process.

(v) provide a previous elimination of the organic fraction of digestate to allow extraction of the last 8.6% of P present in digestates as P_{org} and achieve extraction efficiencies close to 100 %; It is necessary to screen available options to achieve this, and each viable option should be assessed in terms of efficiency and for energy-intensity.

The second research question was if ED process was able to separate heavy metals and Ca, so that a high quality struvite is attained at the end. The results point out to a partial success. The ED process proved effective in separating Cd, Pb, and Cu from the P fraction, but was not as effective in the separation of Zn, which partly moved towards the anode and precipitated in the struvite, restricting its application to some cultures. Electrodialytic process was also successful in separating Ca from P, therefore allowing the successful formation of struvite, as originally intended.

Despite this work being only a first attempt for the recovery of P from digestate of OFMSW using ED process and struvite precipitation, the potential has been demonstrated, which means digestates of OFMSW represent a so far under-explored secondary source of P. Economically viability of the process is a crucial point that needs to be assessed in the future.

Acknowledgements

14

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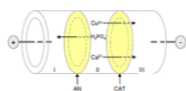[11]   R. Parés Viader, P.E. Jensen, L.M. Ottosen, J. Ahrenfeldt, H. Hauggaard-Nielsen, Electrodialytic

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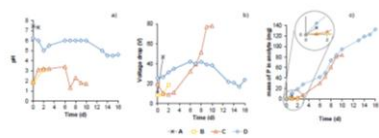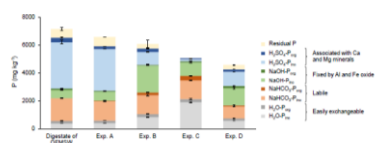
17

List of Figures

18

Fig. 2 Distribution of P at the end of ED experiments, as a percentage of the total P in the digestate of OFMSW at the beginning (AN-membrane: anion-exchange membrane; CAT-membrane: cation-exchange membrane)

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19
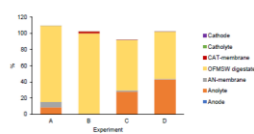
Fig. 3 Evolution with time of (a) pH, (b) voltage drop across the cell and (c) P transported into the anolyte, during ED experiments

Fig. 4 Sequential P fractionation of digestate of OFMSW before and after ED experiments

Fig. 5 Distribution of Ca and heavy metals (copper, zinc, cadmium and lead) in the electrodes, electrolytes, ion exchange membranes and digestate of OFMSW at the end of experiments, as a percentage of the total heavy metals in digestate of OFMSW at the beginning
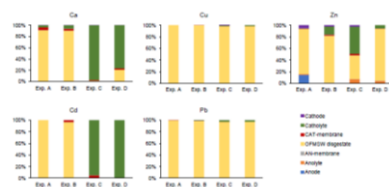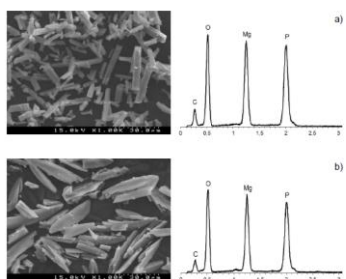
Fig. 6 X-ray diffraction patterns of the precipitates obtained: (a) precipitate **C**; (b) precipitate **D**

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23
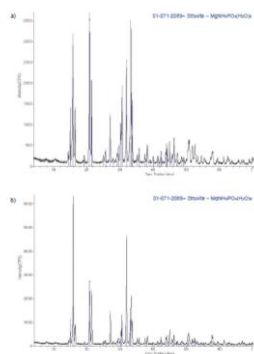
Fig. 7 SEM-EDS of the precipitates obtained: (a) precipitate **C**; (b) precipitate **D**

List of Tables

25

Table 1 Experimental conditions in ED experiments.

Table 2 Concentration of P and Zn in anolyte solutions resulting of experiments **C** and **D** before and after struvite precipitation.

Table 3 Limit values for zinc in fertilizers.

List of Tables

25

Table 1

Exp	mA	Length of compartment II (cm)	Suspension fluid	pH of digestate's at t = 0	EC of the digestate's at t = 0 (mS cm^{-1})	Voltage drop at t = 0 (V)	Duration (d)
A	10	3	Distilled H$_2$O	7.4	6.8	10.4	1
B	10	10	1.1 M HNO$_3$	1.8	>20	8.8	2
C	30	10	1.1 M HNO$_3$	1.9	>20	19.5	10
D	10	10	Distilled H$_2$O	6.2	5.8	25.7	16

Table 2

Exp	Precipitation Step	P in solution (mg L^{-1})	Zn in solution (mg L^{-1})
C	Before	204.7	1.8
	After	10.5	0.1
D	Before	272.0	1.3
	After	1.9	0.1

		P in solution (mg L^{-1})	Zn in solution (mg L^{-1})

Table 3

Country / Region	mg Zn kg^{-1} (dw)
Portugal [26]	
Class I - Agriculture, maximum fertilizer application of 50 t ha^{-1}	200
Class II - Agriculture, maximum fertilizer application of 25 t ha^{-1}	500
Class IIA - Tree and shrub crops including orchards, olive groves and vineyards, and forestry	1000
Class III- Crops not used for food or fodder	1500
Spain [27]	
Class A	200
Class B	500
Class C	1000
Italy [1]	500
The Netherlands [1]	290
EU eco-label for soil improvers and growing media [1]	300