# Recovery of phosphorus from digestates of municipal solid wastes using electrodialytic extraction and chemical precipitation

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## Abstract

The main purpose of this work is to evaluate the possibility of recovering phosphorus from municipal solid waste digestate by combining the electrodialytic process with the production of struvite. Four electrodialytic experiments were carried out to extract phosphorus from the organic fraction of municipal solid waste, after anaerobic digestion using either distilled water or nitric acid, and extraction times ranged from 1 to 16 days.

The results showed that of the phosphorus present in the waste 43% was extracted after 16 days, and 94-99% of the phosphorus extracted was subsequently recovered as struvite, using a precipitation process. The electrodialytic process not only separated phosphorus from the waste but it was also capable of excluding undesirable heavy metal contaminants and calcium (which hinders struvite precipitation). The results obtained in this work are promising and the production of a secondary fertilizer was a success, indicating that combining the electrodialytic process with struvite precipitation makes a viable method for phosphorus recovery. By studying the potential of municipal solid waste digestate as a secondary source of phosphorus to support plant and animal production, this work expects to makes a contribution to closing the cycle of this nutrient in the framework of a circular economy.

## Keywords

Electrodialytic process, MSW, Digestates, Phosphorus recovery, Struvite.

# 1. Introduction

The sustainable use of phosphorus is crucial for the continued growth of society because this nutrient is essential for food production. Phosphorus is obtained mainly from phosphates rocks and the main producers in the world are China (45%), Morocco and Western Sahara (14%) and United States of America (12%) (Jasinski, 2015), whereas Europe is almost entirely dependent on exporter countries (Cordell et al., 2011). Moreover, at the current rate of use, known phosphorus reserves might be depleted in the next 50 to 100 years (Cordell et al., 2009). Given the high economic and social importance of phosphorus and the high risk associated with its supply, phosphate rock is now included in the "EU Critical Raw Materials" list, together with rare earth elements, cobalt and niobium, highlighting that the secure and continuous access to phosphorus is a growing concern within the EU. Thus, it is crucial to found secondary sources of phosphorus for guarantee the continuous supply of this nutrient.

Recently, the electrodialytic (ED) process has been referred as a promising technique to extract phosphorus from water, wastewater and waste matrixes, such as sewage sludge and their ashes (Ebbers et al., 2015; Guedes et al., 2015, 2014; Ottosen et al., 2014). However, most of these studies were limited to the extraction into solution of phosphorus using the ED process, and did not pursue the subsequent reuse of the phosphorus-rich solution obtained, even though this step is essential to close the phosphorus cycle. One unexplored possibility is to use the phosphorus-rich solutions from the ED process to produce struvite, a slow release phosphorus-based fertilizer that can be either directly used in agriculture or be used as raw material in the fertilizer industry (Karunanithi et al., 2015; Rahman et al., 2014; Xu et al., 2012).

The main purpose of the present work is to evaluate the possibility of recovering phosphorus from municipal solid waste (MSW) digestate by combining the ED process with the production of struvite.

# 2. Materials and methods

## 2.1 Source of MSW digestate

The MSW digestate was collected in April 2015 from a Mechanical and Biological Treatment facility, in Portugal, receiving unsorted MSW. At this facility the organic fraction is mechanically separated (from the remaining MSW) and is sent to the anaerobic digester. The sample used in this work consists of the industrially centrifuged residue resulting from the anaerobic digestion. Then sample was dried in a forced draft oven at a temperature of 105 °C, grounded through a 1 mm sieve and stored in closed glass containers, at room temperature. The characterization of the sample of digestate of OFMSW was previously carried out in Oliveira et al. (2016).

## 2.2 ED experiments

ED experiments were conducted in a 3-compartment cylindrical Plexiglas laboratorial cell with an internal diameter of 4 cm. One electrode was placed in anolyte compartment and another in catholyte compartment. Ion-exchange membranes (CMI-7000S and AMI-7001S, MEMBRANES INTERNATIONAL INC) were used to separate the compartments and power supply (Hewlett Packard E3612A) was used to maintain a constant current density. In each electrode compartment, 0.01M $NaNO_3$ was circulated between the compartment and an external reservoir using a peristaltic pump (ISMATECH BVP). Four ED experiments were carried out using different lengths of the central compartment, electric current values, pH in central compartment and duration of the experiment (table 1). At the end of ED experiments, the soluble and total phosphorus, Ca, Mg and heavy metals (Zn, Cu, Cd and Pb) were measured.

**Table 1.** Experimental conditions in electrodialytic experiments.

| Exp | mA | Length of central compartment (cm) | g of MSW digestate (dry weight) | Suspension fluid | Liquid/Solid | days |
|---|---|---|---|---|---|---|
| A | 10 | 3 | 10 | Distilled $H_2O$ | 2.5 | 1 |
| B | 10 | 10 | 35 | 1.1 M $HNO_3$ | 2.5 | 2 |
| C | 30 | 10 | 35 | 1.1 M $HNO_3$ | 2.5 | 10 |
| D | 10 | 10 | 35 | Distilled $H_2O$ | 2.5 | 16 |

## 2.3 Struvite precipitation

Batch experiments aiming at phosphorus precipitation as struvite were conducted with the anolyte solutions resulting from ED experiments C and D. A magnesium source was added ($MgCl.6H_2O$), the pH was quickly adjusted to 9 using 5M 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. 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 45kV and 40 mA. The patterns were collected in the 4 – 80 °2theta range (0.02 °2theta $s^{-1}$ step-scan, and 1.5° $min^{-1}$).

## 2.4 Analytical methods

Total phosphorus, calcium, magnesium and heavy metals were measured in MSW digestate before and after ED experiments in accordance with the procedure described in John et al. (2003) (in triplicate). The 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 total phosphorus in solution was determined by the vanadomolybdophosphoric acid colorimetric method (John et al., 2003) 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 distribution at the end of ED experiments

The distribution of phosphorus in the electrodes, ion-exchange membranes, electrolytes and MSW digestate suspension at the end of ED experiments is presented in Figure 1. No phosphorus was detected in the cathode compartment and phosphorus either stayed in the central compartment or moved across the anion-exchange membrane into the anolyte, indicating it is present as negatively charged compounds (such as $H_2PO_4^-$ and $HPO_4^{2-}$, given the pH range). No phosphorus was found at the surface of the electrodes, but a residual amount was found at the membranes, which is explained by the membranes being in physical contact with the compartment where phosphorus was found. Phosphorus extraction efficiency (amount of phosphorus solubilised from the waste and transported into the anolyte in comparison to the initial phosphorus present) was 43% in exp. D (16 days), 28% in C (10 days), 0.3% in B (2 days), and 8% in A (1 day). The higher phosphorus extraction efficiency attained in this work was 43%, which seems promising since these are the only the first results for MSW digestate using ED extraction.

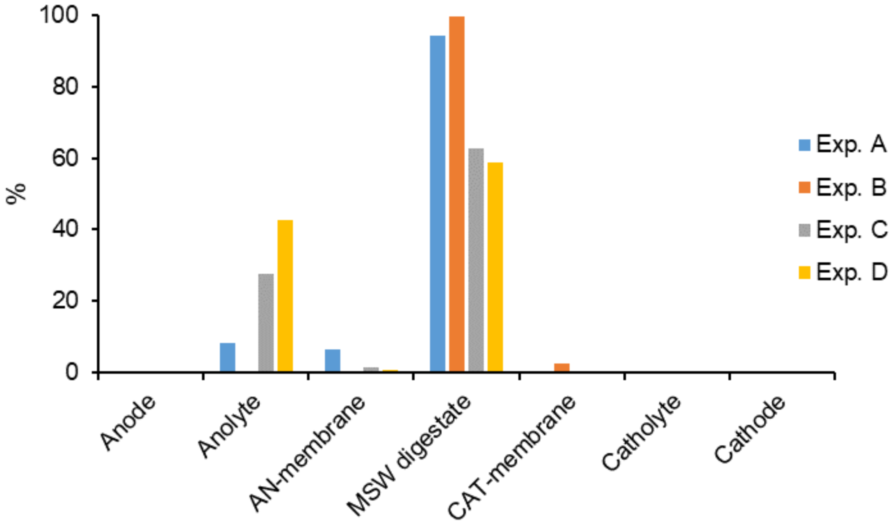

**Fig. 1** Distribution of phosphorus in ED cell compartments at the end of experiments (as a percentage of the total phosphorus in MSW digestate at the beginning)

## 3.2 Heavy metals distribution at the end of ED experiments

Heavy metals are undesirable contaminants commonly found in MSW wastes. Unlike orthophosphate (negatively charged), heavy metals are positively charged, meaning they will expectedly migrate towards the cathode side, away from compartment to where phosphorus is being extracted. Copper, zinc, cadmium and lead are heavy metals commonly found in MSW and were selected in this work for further assessment. Figure 2 presents the experimental data on the distribution of Zn and Cd in the different compartments of the ED cell at the end of the process.

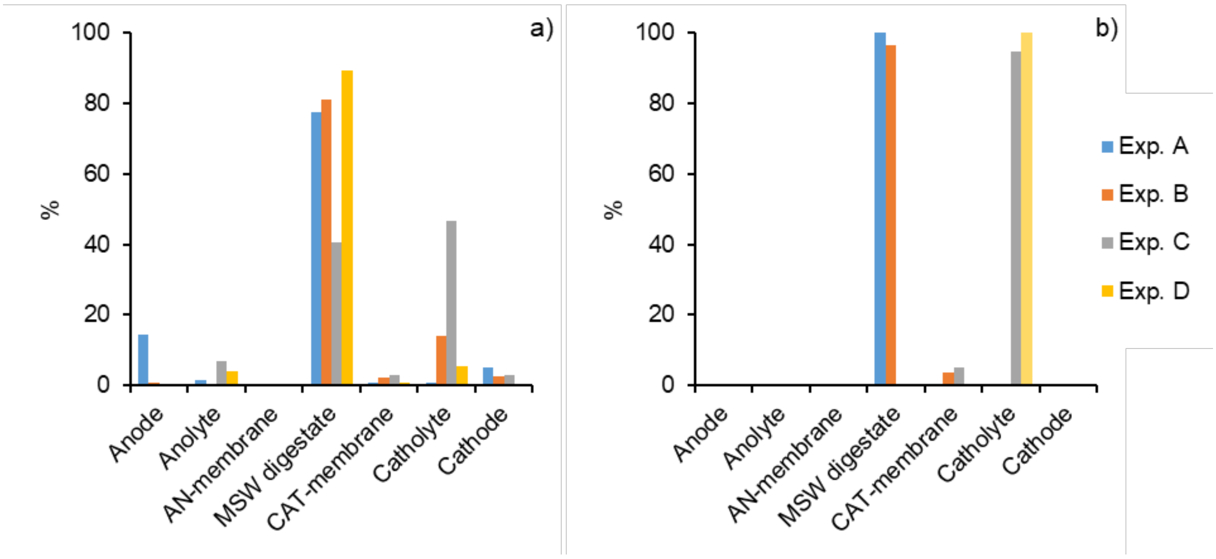

**Fig. 2** Distribution of a) Zn and b) Cd in ED cell compartments at the end of experiments (as a percentage of the total heavy metals in MSW digestate at the beginning)

Cu and Pb do not represent any problem under the experimental conditions tested: they were not transported to the anolyte, and mostly remained in the MSW digestate suspension (> 97%) (data not shown). Cadmium was completely extracted in experiments C and D (Fig. 2a), mostly into the catholyte (95% - 100%). In experiments A and B, above 96% of Cd remained in the MSW digestate suspension. No cadmium was found in the anolyte compartment, to where phosphorus was moved, meaning that similarly to Cu and Pb, experimental conditions were also successful in separating cadmium from phosphorus. By contrast, zinc 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 (Fig. 2b).

### 3.3 Phosphorus recovery as struvite

The recovery process was based on the precipitation of phosphorus in the form of struvite ($NH_4MgPO_4.6H_2O$) from the anolyte solutions obtained at the end of experiments C and D. The precipitation process successfully removed 94.9% of the phosphorus in solution in experiment C and 99.3% in experiment D.

The X-ray diffraction of the precipitates showed that the pattern (position and intensity of the peaks) matches with the struvite standard, confirming the formation of struvite crystals during the precipitation process (Fig. 3). No extra/minor phases were detected. In an earlier work precipitation of struvite directly from a suspension of MSW digestate had failed due to the presence of calcium (Oliveira et al., 2016). In the current work calcium was separated from the phosphorus fraction during the ED treatment (being a cation, calcium likely moved to the catholyte), so that the reactions leading to struvite precipitation successfully occurred.

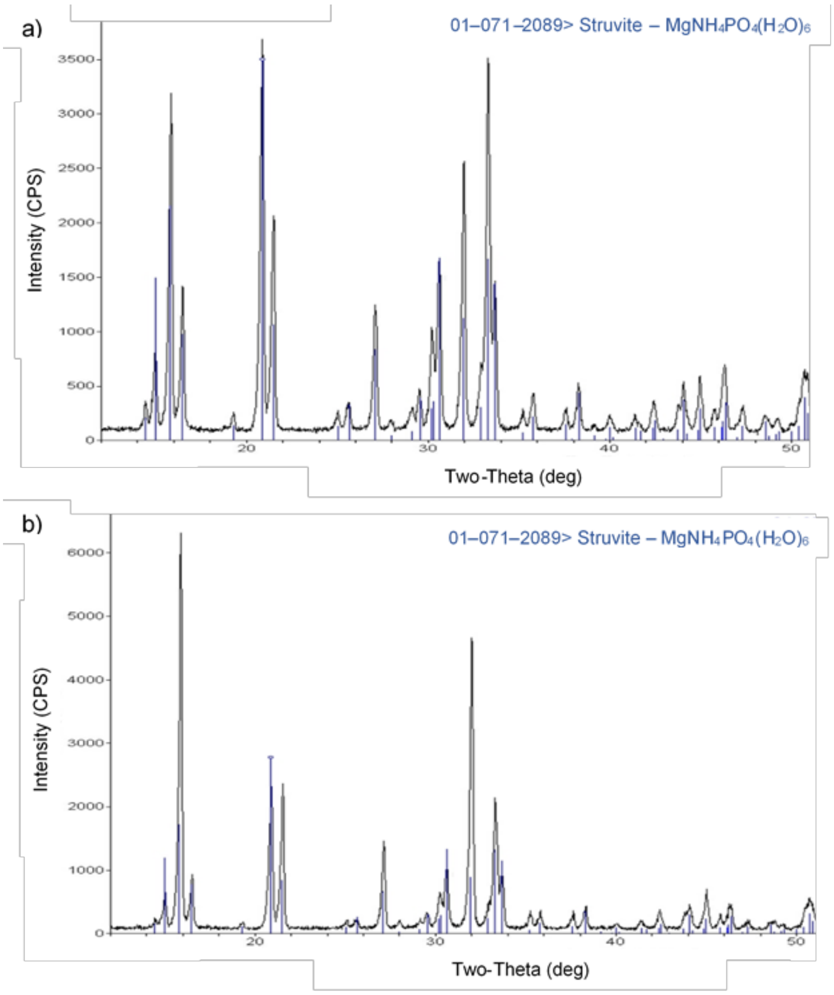

Fig. 3. X-ray diffraction patterns of the precipitates obtained: (a) precipitate C; (b) precipitate D.

## 4. Conclusions

In this work, the phosphorus recovery from MSW digestate was carried out by combining the ED with chemical precipitation as struvite. The results are promising and the production of a secondary fertilizer was a success, indicating that combining the ED with struvite precipitation makes a viable method for phosphorus recovery. Nevertheless, more than 50% of phosphorus still remains in MSW digestates at the end, meaning that optimisation of experimental conditions during ED treatment (pH, electric current and duration) is recommended in further studies to extract and reuse the highest amount possible of this critical nutrient. By studying the potential of MSW digestate as a secondary source of phosphorus to support plant and animal production, this work expects to makes a contribution to closing the cycle of this nutrient in the framework of a circular economy.

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