Phosphorus recovery from municipal solid waste digestate aiming at its valorization as a fertilizer

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Resumo

O fósforo (P) é um nutriente essencial para o desenvolvimento das plantas e a produção de alimento. É um dos principais constituintes dos fertilizantes e até ao momento ainda não foi encontrado nenhum outro elemento que o possa substituir. O P é obtido principalmente da rocha fosfatada, que é um recurso não renovável. Isto suscita uma questão fundamental sobre como garantir um fornecimento contínuo de P para a produção de fertilizantes fosfatados necessários para produzir alimento para a humanidade, no futuro. Portanto, é de extrema importância promover a circularidade do P por meio da sua reciclagem e da recuperação a partir de fluxos de resíduos.

O presente trabalho foi desenvido no âmbito de uma tese de doutoramento em que, pela primeira vez, foi explorada a extração de P do digestato de RU utilizando o processo electrodialítico (ED) combinado com a precipitação de estruvite. Este trabalho foi realizado em três etapas: i) extração de P do digestato utilizando o processo electrodialítco; ii) síntese de um biofertilizante – a estruvite secundária, utilizando o processo de precipitação química e, iii) avaliação agronómica da estruvite secundária produzida.

Os resultados mostraram que cerca de 90% do P que está presente no digestato de RU pode efetivamente ser extraído através do processo ED e convertido em estruvite secundária. Esta estruvite secundária apresentou uma elevada qualidade, mesmo quando durante a sua precipitação foram utilizados materiais alternativos em vez de materiais sintéticos. Neste trabalho verificou-se também que a utilização desta estruvite secundária como biofertilizante é semelhante à de um fertilizante sintético comercial. Este biofertilizante livre de contaminantes, produzido à escala de laboratório, amplia assim as possibilidades para a reciclagem do P em larga escala e para a implementação de estratégias eficientes para fechar o ciclo do nutriente P, contribuindo assim para uma gestão mais sustentável dos recursos.

Palavras-chave: Processo electrodialítico, reciclagem de fósforo, estruvite, economia circular, gestão de recursos.

Abstract

Phosphorus (P) is a vital nutrient for plant development and food production. It is a key fertilizer constituent and no feasible substitute has been found yet. P is mainly obtained from phosphate rock, which is a non-renewable resource. This raises the critical issue of ensuring a continuous supply of P-fertilizers to feed mankind in the future. Therefore, it is of utmost importance to promote the circularity of P by recycling and recovering P from waste streams.

The presente research was developed during a PhD thesis, in which the extraction of P from MSW digestate using the electrodialytic (ED) process combined with struvite formation was explored for the first time. This work was carried out in three stages: i) extraction of P from the digestate using the electrodialytic process; ii) synthesis of a biofertilizer – secondary struvite, using chemical precipitation process and, iii) agronomic evaluation of the produced secondary struvite.

The research findings show that up to 90% of P present in MSW digestate could be extracted using ED and converted to secondary struvite. This secondary struvite produced in this work using P recovered from MSW digestate proved to be of high quality, even when alternative materials were used instead of synthetic ones during its precipitation. Also, it was verified that Its action as an effective P biofertilizer is similar to that of a commercial synthetic fertilizer. This contaminant-free biofertilizer, produced at lab scale, widens the possibilities for the large scale recycling of P and for the implementation of efficient strategies to close P-nutrient cycling, thus contributing to a more sustainable resource management.

Keywords: Electrodialytic process, phosphorus recycling, struvite, circular economy, resource management.

Phosphorus (P) is a vital element for human, animal and plant nutrition, being a limited and irreplaceable resource. It is a unique chemical element, as it determines the development of agricultural production, stimulated by the food needs of the world's growing population (Corre et al., 2009). P has important biological functions being the building blocks of DNA, cell membranes, energy-storing ATP, and bones. Thus, it is essential for growth and development of all living organisms and is present in most organic materials (Smol, 2019). Moreover, P is mainly obtained from phosphate rock, which is a non-renewable resource, and cannot be replaced by any other element in biochemical processes, so humans ultimately rely on P availability. Therefore, it is of utmost importance to find other sources of P, such as waste streams, and promote the circularity of P by recycling and recovering.

The municipal solid waste (MSW) digestate is the result of the anaerobic digestion of MSW. It contains P but also contaminants (Table 1), so currently it is mostly sent to landfill. This raised the question of how feasible is the extraction of P from MSW digestate for the production of a high-quality fertilizer?

Table 1. Characteristics of digestate (average±SD; dry weight; data retrieved from Oliveira et al. (2020))

Characteristic	Value
pH	7.67–7.71
Conductivity (mS cm^{-1})	5.72±0.39
Total elements	
P (g kg^{-1})	7.53±0.48
Zn (mg kg^{-1})	351.35±74.39
Pb (mg kg^{-1})	158.57±14.58
Cu (mg kg^{-1})	148.13±21.90
Cr (mg kg^{-1})	34.01±2.06
Ni (mg kg^{-1})	29.30±3.56
Cd (mg kg^{-1})	1.22±0.05

The present research was focused on the extraction of P from MSW digestate using the electrodialytic (ED) process combined with struvite formation. The ED process allows the separation of anions (e.g. PO_4^{3-}) and cations (e.g. metals like Cu^{2+}) present in MSW digestate by selectively transporting them across ion-exchange membranes under the influence of an electric field (Figure 1a). Considering this extraction principle, P extraction experiments were conducted at lab-scale (Figure 1b) attempting to reach three purposes: i) extraction of the P available in the MSW digestate, ii) optimization of the energy performance of the ED process and iii) improvement of ED process, allowing also to recover nitrogen (N) from MSW digestate through a gas permeable membrane (Figure 1c).

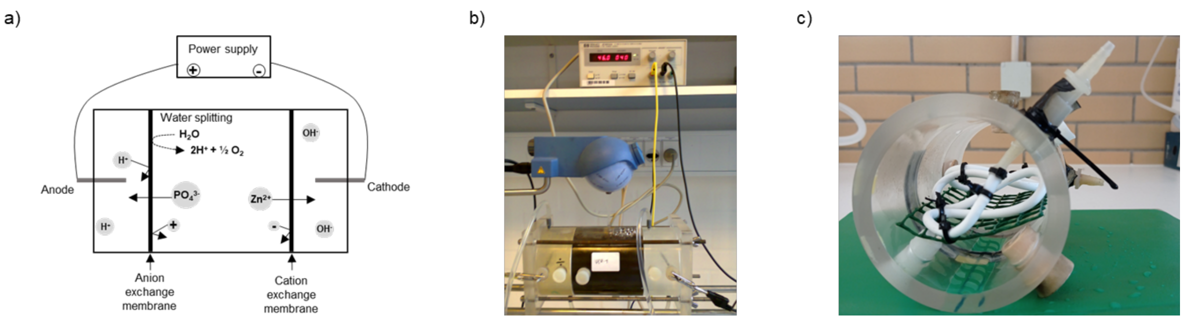

Figure 1. a) Principle of the ED process (Oliveira et al. 2019); b) apparatus used for carrying out the ED P extraction experiments; c) gas permeable membrane (white tube) introduced in the cathode side of the ED cell

Then the ED-extracted P was used for the synthesis of secondary struvite ($MgNH_4PO_4{\cdot}6H_2O$), through chemical precipitation. Struvite is a crystalline substance which is formed under alkaline conditions according to the following reaction (Rahman et al., 2014):

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O + 2H^+$$

Struvite contains 13% of P, 6% of N and 10% of Mg. In waste streams, the content of Mg is generally low, therefore, it should be added (e.g. $MgCl_2$, $Mg(OH)_2$ or MgO) in order to achieve the $Mg:NH_4:PO_4$ molar ratio required for struvite precipitation (Mehta et al., 2015). In the current study, alternative sources of N and Mg needed for the synthesis of struvite were explored, named seawater (as Mg source) and N contained in the MSW digestate itself.

Acting as a slow-release fertilizer, struvite releases nutrients to the soil along the time. The agronomic efficacy of the secondary struvite, obtained using the P extracted from MSW digestate was assessed, first in incubation trials (to study the evolution with time of P in the soil; figure 2a) and then in pot trials (figure 2b), where plant growth in struvite fertilized soils and in soils fertilized with a commercial fertilizer was compared.

a) b)

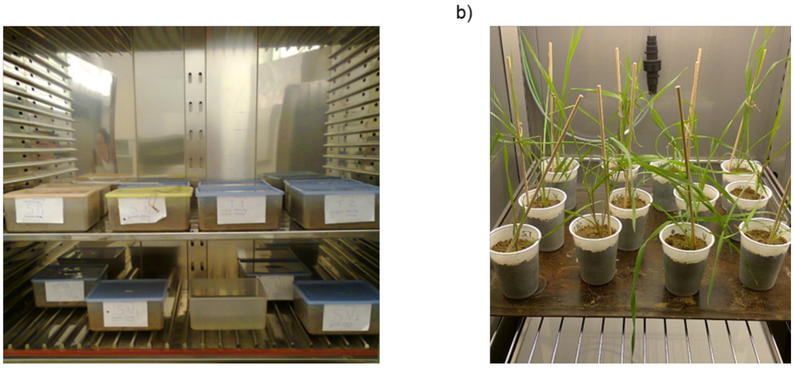

Figure 2. a) Incubation trial and b) pot trial performed to assess the agronomic quality of the secondary struvite

The research findings show that up to 90% of P present in MSW digestate could be extracted using ED and converted to struvite (Oliveira et al., 2018, 2020). Being a negatively charged specie, P moved from the MSW digestate and concentrated in the anolyte solution when a 50 mA electric current (1.0 mA cm^{-2}) was applied. During ED process, the extraction of P was strongly dependent on the pH of MSW digestate, and a low pH (2.5-3.0) was needed to enhance the P solubilization from the MSW digestate. This was achieved by using the electrochemical reaction occurring at the anode (originates H^+ ions), thus avoiding the addition of chemicals. The benefit of this electrochemical reaction was fundamental for the implementation of another strategy for P extraction: a dual-stage approach. In the first stage, the electrode (+) was placed in contact with the MSW digestate, causing a faster acidification of the digestate while P remains in this compartment. When the pH reached 3 in the MSW digestate suspension, the electrode (+) was moved into the anolyte compartment and the solubilized P migrated from the MSW digestate compartment to the anode compartment. This strategy effectively reduced the time required for the ED extraction of P (to 7 days) and consequently decreased the energy consumption (≈30%) (Oliveira et al., 2019).

The extraction of another important nutrient, N, from MSW digestate was also pursued by adding a gas permeable membrane (GPM) to the cathode of the ED cell, while the extraction of P was taking place. N moved from the MSW digestate into the cathode compartment as NH_4^+ (by electromigration), and there it was converted to gaseous NH_3 and collected by the GPM into a clean N solution, leaving behind the heavy metals at the cathode solution. The clean N solution was subsequently used with success as a source of N in the synthesis of secondary struvite. The combination of these two membrane technologies - ED and GPM - for simultaneous extraction of P and N was explored in this work for the first time, and contributed to the sustainability of the synthesis of secondary struvite (Oliveira et al., 2021).

The secondary struvite produced in this work using P recovered from MSW digestate proved to be of high quality, even when alternative materials were used instead of synthetic ones during its precipitation (Oliveira et al., 2021). XRD patterns confirmed that 100% of the precipitate was identified as $MgNH_4PO_4 \cdot 6H_2O$ (Figure 3). It was also found that the secondary struvite action as an effective P biofertilizer is similar to that of a commercial synthetic fertilizer (Oliveira, Horta, et al., 2019).

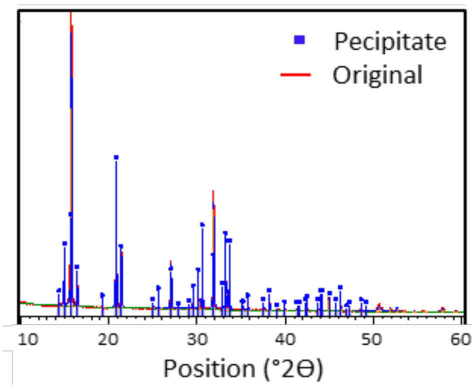

Figure 3. X-Ray diffraction diagram of the obtained secondary struvite with alternative N (recovered from digestate using GPM) and alternative Mg (obtained from seawater) sources (Oliveira et al., 2021)

The major outcome of this work was the proof of concept of an innovative process that combines ED and GPM for the recycling of P from MSW digestate. The contaminant-free biofertilizer, produced at lab scale, widens the possibilities for the large scale recycling of P and for the implementation of efficient strategies to close P-nutrient cycling, thus contributing to a more sustainable resource management.

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References

Corre, K. Le, Valsami-Jones, E. and Hobbs, P. (2009), “Phosphorus recovery from wastewater by struvite crystallization: A review”, *Critical Reviews In*, available at: http://www.tandfonline.com/doi/abs/10.1080/10643380701640573.

Mehta, C.M., Khunjar, W.O., Nguyen, V., Tait, S. and Batstone, D.J. (2015), “Technologies to Recover Nutrients from Waste Streams: A Critical Review”, *Critical Reviews in Environmental Science and Technology*, Vol. 45 No. 4, pp. 385–427.

Oliveira, V., Dias-Ferreira, C., González-García, I., Labrincha, J., Horta, C. and García-González, M.C. (2021), “A novel approach for nutrients recovery from municipal waste as biofertilizers by combining electrodialytic and gas permeable membrane technologies”, *Waste Management*, Vol. 125, pp. 293–302.

Oliveira, V., Dias-Ferreira, C., Labrincha, J., Rocha, J.L. and Kirkelund, G.M. (2020), “Testing new strategies to improve the recovery of phosphorus from anaerobically digested organic fraction of municipal solid waste”, *Journal of Chemical Technology and Biotechnology*, Vol. 95 No. 2, pp. 439–449.

Oliveira, V., Horta, C. and Dias-Ferreira, C. (2019), “Evaluation of a phosphorus fertiliser produced from anaerobically digested organic fraction of municipal solid waste”, *Journal of Cleaner Production*, Vol. 238, p. 117911.

Oliveira, V., Kirkelund, G.M., Horta, C., Labrincha, J. and Dias-Ferreira, C. (2019), “Improving the energy efficiency of an electrodialytic process to extract phosphorus from municipal solid waste digestate through different strategies”, *Applied Energy*, Vol. 247, pp. 182–189.

Oliveira, V., Labrincha, J. and Dias-Ferreira, C. (2018), “Extraction of phosphorus and struvite production from the anaerobically digested of organic fraction of municipal solid waste”, *Journal of Environmental Chemical Engineering*, Vol. 6, pp. 2837–2845.

Rahman, M.M., Salleh, M.A.M., Rashid, U., Ahsan, A., Hossain, M.M. and Ra, C.S. (2014), “Production of slow release crystal fertilizer from wastewaters through struvite crystallization - A review”, *Arabian Journal of Chemistry*, Vol. 7 No. 1, pp. 139–155.

Smol, M. (2019), “Phosphorus extraction and sludge dissolution”, *Industrial and Municipal Sludge: Emerging Concerns and Scope for Resource Recovery*, pp. 657–677.