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Alternating pulse approach for electrochemical production of struvite as an option for phosphorous recovery from wastewater

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Water pollution is a concern, as sewage water contains phosphates that come from different sources, generating eutrophication in bodies of water. There is also an overexploitation of phosphorous, which has a huge relevance due to its use in agriculture. Traditionally, different physical or chemical treatments have been used to remove pollutants from water, some of which use a sustainable management approach focusing on nutrient recovery, rethinking wastewater treatment as resource recovery. Recent developments have used chemical precipitation as an alternative, by adding different metals to yield a slow-release fertilizer. There is considerable literature on struvite production with magnesium added or obtained by electrochemical methods; the latest methods offer the advantage of providing the magnesium from a sacrificial magnesium electrode in a system with low energy consumption, avoiding the addition of chemicals. Although this may be a good alternative, passivation occurs in the anode, causing loss of efficiency in the system. Considering all these factors, this paper examines the influence of different variables such as the concentration of nutrients, distance between electrodes, current density, and frequency of electrical pulses in the efficiency of the system to remove P-PO_4^{3-} and N-NH^{4+} for the production of struvite. On the whole, the results show that the current influences the promotion of Mg^{2+} release and prevents its excess at 53 mA, and that the optimal frequency of 0.0005 Hz is important to avoid passivation and increase the removal of nutrients from water.

Introduction

Phosphorous is widely used in agriculture due to it being a key nutrient for plant growth.[1] Phosphorus in water originates from various sources, including rocks, soil erosion, agricultural runoff, and discharges from municipal and industrial wastewater.[1,2] Values lower than 25 mg P L^{-1} are considered naturally derived, but those above 50 mg P L^{-1} are attributed to anthropogenic influence. Sewage, for example, contains phosphates from human sources, detergents, food waste, food additives, and various other products, and 2 g P per person per day is the average release.[2] The transference of phosphorous from the ground to water, *i.e.*, from agricultural systems to surface waters, can reduce water quality by increasing the possibility of eutrophication in water bodies.[2]

When there is an imbalance between the concentration of nutrients and the ecological characteristics in bodies of water, it promotes the growth of aquatic plants and algae.[3] This changes the flora and fauna in aquatic systems, reducing their diversity and promoting de-oxygenation on surface waters.[1]

The importance of controlling phosphorus, preventing the compound from reaching bodies of water and aquatic systems, is important for their management, recovery and restoration, thus preventing eutrophication.[4] Several treatments have been used for the removal of phosphorous from wastewater, for example, biological processes,[4] wetlands, chemical coagulation, precipitation with compounds like iron, or by ion exchange technologies.[3]

In addition to the removal of phosphorus, another concern is its scarcity, and it is important to ensure its long-term availability. Phosphorous is one of the essential elements for food production, and it is a non-renewable resource; its availability is critical.[5,6] The number of phosphorous reserves is decreasing, as well as the presence of impurities in them is increasing.[7]

One recent objective has been the recovery of nutrients during wastewater treatment by recycling the resources available in it, which are considered pollutants. This initiative is driven by economic and environmental motivations, promoting the recovery and recycling of resources, the reuse of water, and

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the development of strategies to start a sustainable management of wastewater. One option to achieve this is using a resource recovery strategy.[4,8]

There are several approaches in the search for methods to remove and recover nutrients as nitrogen; some examples are solid-phase adsorbents,[4] ion-exchange processes, magnetic microsorbents, urine separation in domestic water, or other stages in treatment plants.[1] Another alternative is removal employing salts by transferring dissolved ortho-phosphates to their particulate form; by adding metals (*e.g.* iron or aluminum), a new precipitate is formed and typically recovered in a separation process due to its low solubility.[4,9]

Phosphates can be precipitated in wastewater, this being an alternative removal and recovery method.[7] Recently, the development of methods to recover phosphorous from different sources, including wastewater, has gained more interest in the effort towards phosphorous sustainability.[3,4,10]

Among the strategies for phosphorus recovery, some of the most common are chemical precipitation with iron or aluminum, forming phosphates; crystallization or precipitation with calcium or magnesium; membrane or ion exchange technologies; and extraction from incineration ashes.[11]

Important savings in the water and agricultural sectors can be made if some methods are found to develop sustainable sources of phosphorus.[11] One of them is the recovery of ochre saturated with phosphorus and its use as a slow-release fertilizer.[11,12]

Another alternative for the recovery of phosphorus is by precipitation of struvite (magnesium ammonium phosphate, $MgNH_4PO_46(H_2O)$).[11] The recovery of nutrients in the form of struvite is widely used due to the great amount of phosphorus and nitrogen present in water and the low quantity of impurities during its formation, and its recovery by sedimentation is not complicated.[13] Since 2006, struvite has been listed by the Regulation of European Chemicals Agency as a non-hazardous compound; it is used as a commercial fertilizer.[13]

One of the advantages of this process is that it allows the recovery of phosphates and ammonia at the same time, when these compounds and Mg^{2+} are present in equimolar concentrations,[14] following the reaction:

$$Mg^{2+} + NH_4^+ + PO_4{}^{3-} + 6H_2O \rightarrow MgNH_4PO_46(H_2O) \quad (1)$$

This process occurs in two steps: the first is nucleation, where the combination of ions generates crystals with an embryonic pattern.[13] Sometimes, the nucleation happens spontaneously, but it can be stimulated by the addition of seed crystals like sand grains;[15] the seeds stimulate the formation by increasing the thermodynamic driving force.[16] After the nucleation process, the growth of crystals occurs.[13,17]

The optimal range of pH for struvite crystallization is between 7 and 11, and its formation occurs when the Mg^{2+}, $PO_4{}^{3-}$ and NH^{4+} concentration product is higher than the solubility product (K_{sp}).[18] According to several studies, the optimal temperature for struvite production is from 25 to 35 °C, and higher temperatures (60 °C) improve the dissolution of Mg^{2+} ions, but this increase reduces the yield in the production of struvite. The presence of ions influences the formation of struvite. For example, the presence of an appropriate amount of K^+ ions improves the formation of struvite at pH 7, due to the greater thermodynamic driving force. In contrast, higher concentrations generate salts such as $Ca_3(PO)_2$ and $MgKPO_4$.[16] Other ions that negatively influence the formation of struvite are Ca^{2+}, Na^+, K^+, $CO_3{}^{2-}$ and HCO,[3–13] which act as competitive ions, generating impurities in the resulting salts.[16] It also has been demonstrated that struvite precipitation is slow, taking even three months at environmental temperature.[16]

In order to achieve the formation of struvite, it is necessary to supply magnesium to the system. MgO, $MgSO_4$ and $MgCl_2$ are the most common salts employed for this purpose, sometimes by automatized systems.[10,19] As a result of the development of strategies to improve the production of struvite and reduce the cost of supply and transportation of chemical reagents, an electrochemical struvite precipitation has been studied.[5,14] In these experiments, a sacrificial magnesium electrode was employed to obtain Mg^{2+} ions,[14,19,20] showing that it is suitable economically and technically.[19]

Electrochemical precipitation of struvite by electrolysis is possible with low energy consumption at pH 7. When the pH near a magnesium electrode employed as an anode was high enough, struvite was obtained.[20] Due to the acidic conditions produced by electrolysis, it is not necessary to adjust pH,[19] thus reducing cost.

In this approach, when Mg electrode is used as a sacrificial anode,[19,21] there are several processes to explain the formation of Mg^{2+}. One such process occurs in several steps, the first of which is magnesium being oxidized in the anode following eqn (2) and (3), where the rate of reaction is controlled by eqn (2): [22]

$$Mg \leftrightarrow Mg^+ + e^- \quad (2)$$

$$Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + 0.5H_2 \quad (3)$$

Another process is the direct oxidation to Mg^{2+}:

$$Mg \rightarrow Mg^{2+} + 2e^- \quad (4)$$

An alternative proposal is the formation of an intermediate, in this case Mg^+, followed by the further formation of Mg^{2+} ions:[23]

$$Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + \tfrac{1}{2}H_2\uparrow \quad (5)$$

In all of the proposed pathways, the result is that Mg^{2+} ions are released to the solution, providing the ions required for struvite formation. The oxidation of Mg occurs spontaneously, but to maintain the production of struvite over time, an overpotential is required.[19,23,24]

Other advantages of the use of magnesium electrodes are its fast dissolution, increasing the speed of precipitation, and at the same time, the low energy demand for its release, this because of its non-galvanic corrosion.[19] Unfortunately, the analysis of Kékedy-Nagy and co. on the consumption of energy required in electrochemical processes shows that it is higher than that required by biological or chemical processes.[23]

After the liberation of Mg^{2+} into the solution, the process continues to follow the reaction in eqn (1) for the crystallization of struvite, first by nucleation and then growth of struvite crystals.[20] However, this process occurs when the pH near the electrode is high enough due to the reduction of water or dissolved oxygen at the cathode;[20] at pH between 7.5 to 9.3, the purity of struvite increases.[21]

Also, it is possible to generate $Mg(OH)_2$ film in the electrode surface, which can lead to electrode passivation; this process takes place between −1.5 and 0.9 V *vs.* ENH.[19] In the same manner, $Mg(OH)_2$ is obtained by spontaneous reaction of the Mg plate with the ammonium dihydrogen phosphate solution, when the conditions in solution are from acid to neutral pH.[23] The problem associated with these films is the inefficiency in charge transport, and it has been reported that their composition is nesquehonite ($MgCO_3 \cdot 3H_2O$), elemental aluminum and some struvite.[19]

A problem associated with the formation of a passivation layer in the anode, forming a film, is that it reduces the dissolution of the Mg plate, and different strategies have been used to reduce the formation of this layer.

To avoid the passivation process, one approach is to apply a higher potential than the pitting potential (−1.5 V *vs.* ENH in Hug and Udert's experiment).[19] Likewise, in electrochemical processes used for other applications, it has been proven that the use of alternating pulses has increased efficiency, for example, in the electrocatalytic synthesis of disulfide[25] and dye removal by electrocoagulation,[26] achieving long-term stability in the electrochemical system[27] and higher performance against direct-current systems.[26] Those studies also provided information about the importance of the application of the right frequency.[27]

The aim of this work is the study and optimization of the concentration, distance between electrodes, current applied and different frequencies for the application of the alternating pulses, in order to improve the performance of the conventional electrolysis method and increase the yields in struvite production and removal of ammonia and phosphorus.

Experimental

The study was performed with 0.25, 0.05 or 0.005 mol L^{-1} solutions of $NaNH_4HPO_4 \cdot 4H_2O$ in 1 g L^{-1} of NaCl (J. T. Baker) used as a synthetic medium.

Analytical techniques

Quantification of $P\text{-}PO_4{}^{3-}$ was performed by molybdenum blue method[28] according to NMX-AA-029-SCFI-2021. N-NH_4 was quantified by spectrophotometric method at 410 nm.[29] Mg^{2+} determination was performed by titration with ethylenediaminetetraacetic acid (EDTA) with the technique reported in NMX-AA-072-SCFI-2001. Linear regression plots are presented in SI. Conductivity and pH were determined with an Apera PCO60 Multiparameter.

Changes in electrode mass (Δm) were measured by the difference between initial mass m_{Mg0} and the mass at the end of the experiment m_{Mgt}:

$$\Delta m = m_{Mg0} - m_{Mgt} \tag{6}$$

The magnesium (Mg^{2+}) theoretical yield was calculated by the third law of Faraday, as presented in the following equation.

$$m = \frac{E_q}{F} It, \tag{7}$$

where E_q/F is the electrochemical equivalent (1.044 g A^{-1} h^{-1}), I is current intensity in A, and t represents the time in hours.

Struvite purity was calculated by determining the amount of ammonia in a sample of the recovered powder from the precipitate, dissolved in HNO_3 and following eqn (8):[19]

$$\%_{\text{struvite}} = \frac{\text{mol}_{\text{NH}^{4+}} \times \text{PM}_{\text{struvite}}}{m} \times 100, \tag{8}$$

where $\text{mol}_{\text{NH}^{4+}}$ is the number of mols of ammonia; $\text{PM}_{\text{struvite}}$ is the molecular weight of struvite (245.41 g mol^{-1}) and m represents the total mass of the precipitate powder in g;

$$\%_{\text{DM}} = \frac{\left(\#\text{mol}_{\text{PO}_4^-} - \#\text{mol struvite}\right) \times \text{PM}_{\text{DM}}}{m} \times 100, \tag{9}$$

where $\%_{\text{DM}}$ represents the percentage of dimagnesium phosphate in the sample; #mol struvite is the number or moles of struvite determined analytically (equal to moles of NH_4); m is the mass of the precipitate in grams; and PM_{DM} is 120.28 g mol^{-1}.

Electrochemical studies

Voltammetric study. Linear voltammetry was performed using a potentiostat galvanostat BAS Epsilon, in a 0.005 mol L^{-1} solution of $NaNH_4HPO_4 \cdot 4H_2O$ in 1 g L^{-1} of NaCl using Mg plate as a working electrode, Ag|AgCl|KCl 3 mol L^{-1} as reference and a Pt wire as an auxiliary electrode, at 1 mV s^{-1} for the Mg plates and at 0.166 mV s^{-1} for the study of the electrodes used in the experiment for struvite production. To remove oxygen from the solution, it was bubbled for 5 minutes with nitrogen gas prior to the experiments, and a nitrogen atmosphere was kept during the experiments. Prior to each voltammogram, the working electrode (to study the electrode material) surface was sanded with 1000 grit sandpaper, rinsed with distilled water, and sonicated for 5 minutes and instantly immersed in the solution.

Electrochemical reactor setup. The electrolytic cell was an acrylic container with length of 7 cm, width of 7.5 cm and height of 5 cm, along with 2 × 5 cm electrodes of magnesium AZ31B (94–97% Mg, 2.5–3.5% Al, 0.6–1.4% Zn, 0.2–1% Mn) or stainless steel (316), operating with a volume of 150 mL. Constant agitation was kept at 200 rpm during the experiments.

A reference electrode of Ag|AgCl|KCl 3 mol L^{-1} was set up with a multimeter to determine the potential values at the working electrode, under different applied currents (see the SI for the setup of the electrochemical cell for measurement of potential). Operation of the electrochemical cell was performed with a power supply.

Conventional electrochemical system for struvite production. In the case of the conventional system, it employed a Mg electrode as anode and a stainless-steel electrode as cathode, both 2 x 5 cm. Three different concentrations of $NaNH_4HPO_4 \cdot 4H_2O$

were studied: 0.25, 0.05, and 0.005 mol L^{-1}, and two distances between electrodes were used, 3 and 5 cm. The system was monitored for 6 hours, determining the following parameters: removal of $N\text{-}NH^{4+}$ and $P\text{-}PO_4^{3-}$ every 30 minutes, change in mass of the anode at the beginning and at the end of the experiment, mass of the powder recovered, and Mg^{2+} in solution.

Alternating pulses. To analyze the effect of polarization, the electrochemical cell described in a later section was employed, but in this case, Mg plates were used in both electrodes. The frequencies studied were 10, 1, 0.1, 0.01 and 0.001 Hz. The system followed the same parameters as those in the experiment described in the previous section.

X-ray diffraction (XRD). Powder X-ray diffraction measurements of the materials were carried out using Cu kα radiation in the 2θ range of 20–80° (wide-angle) on a D8 Advance Bruker diffractometer.

Electrical consumption

The consumption of electric energy (EC) in kW m^{-3} was determined with the following equation:[19]

$$\mathrm{EC} = \frac{P \times t}{V \times 1000}, \tag{10}$$

where P is the potential in W, t is the time in h, and V is the volume in m^3;

$$P = V\int_{t1}^{t2} I\mathrm{d}t. \tag{11}$$

Results and discussion

Voltammetric study of Mg electrode

In order to understand the interaction between the electrode and the synthetic solution at different potentials, linear voltammetry was performed. Through this, it was possible to elucidate the electrochemical reactions occurring at the magnesium electrode in the media, by associating the obtained data with physical changes occurring in the electrode surface during the experiment and contrasting it with the reliable information from studies performed by other researchers, such as Hug and Udert (2013).[19]

Four different stages were observed in the electrode surface; the voltammogram is presented in Fig. 1, and images of the electrode are presented in SI. In the beginning, an almost constant current was observed in the experiment, from −1.65 to −1.20 V *vs.* Ag|AgCl|KCl 3 mol L^{-1}, when the electrode was polarized. After that, in the region from −1.20 to −0.90 V *vs.* Ag|AgCl|KCl 3 mol L^{-1}, the formation of bubbles was observed on the electrode surface; the voltammogram showed an abrupt change in current at 0.091 V *vs.* Ag|AgCl|KCl 3 mol L^{-1}, which is associated with pitting potential, according to other authors.[19,30]

Then, from −0.90 to −0.53 V *vs.* Ag|AgCl|KCl 3 mol L^{-1}, the electrode surface changed from a smooth surface to a rough aspect, with a sudden formation of pits, while the amperometric behavior showed a stable behavior in this potential region and an abrupt change in current at −0.91 V (0.305 μA).

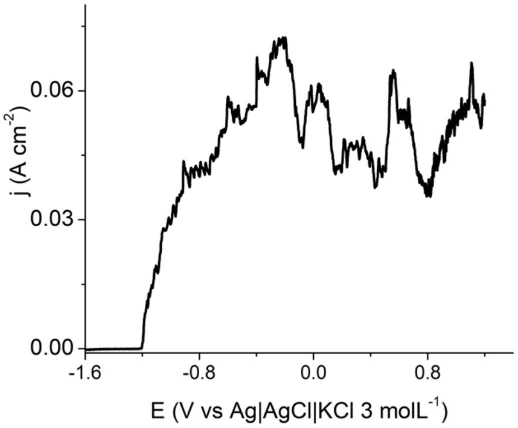

Fig. 1 Linear voltammogram of 0.005 mol L^{-1} of $NaNH_4HPO_4 \cdot 4H_2O$ at pH 7.5. Working electrode Mg plate, auxiliary electrode Pt wire, and reference electrode Ag|AgCl|KCl 3 mol L^{-1}, at 0.1 mV s^{-1}. Starting from open circuit potential.

Beyond the potential of −0.53 V, the formation of a white crystalline solid was noticed on the electrode surface, similar to that obtained by Hug and Udert (2013).[19] The crystalline solid is associated with the formation of struvite.[31] At these potentials, the current variation remains lower than 0.160 μA.

Finally, in potentials above −0.40 V, a white film is observed covering the entire electrode surface; this film increases in thickness with the potential. With this increase, the result is the passivation of the electrode surface, which other authors refer to as the second passivation process.[19] The differences in the electrode changes and the formation of this film are directly associated with the greater change in current at −0.4 V, with 0.317 μA.

Even though some peaks in the current are observed and changes in behavior continue occurring in the voltammogram beyond these potentials, the objective of this study was to find the experimental conditions suitable for struvite formation, and according to the results, its formation occurs at 0.52 V *vs.* Ag|AgCl|KCl 3 M. Further potentials can increase the energy consumption and reduce the yield in the removal of pollutants and production of struvite.

Change in operation from potentiostatic to galvanostatic mode. To identify the values of current to be applied with a source power, the values of potential in the system were measured using a reference electrode plugged to the working electrode, as shown in SI. The currents applied in the experiment were 5, 45, 53 and 61 mA. During the operation, P and N were determined as $P\text{-}PO_4^{3-}$ and $N\text{-}NH^{4+}$; the obtained results are presented in Fig. 2.

This test revealed that when higher currents are employed, the removal of $P\text{-}PO_4^{3-}$ and $N\text{-}NH^{4+}$ increases, which is associated with the greater release of magnesium from the anode. The higher values obtained include the removal of 80.85% $N\text{-}NH^{4+}$ and 90.85% of $P\text{-}PO_4^{3-}$ at 62 mA. This agrees with the finding regarding the change of the anode mass, which is increased at higher values of current; these results are presented in Table 1. The same effect is reported by Zhang *et al.* (2019);[31] in our study,

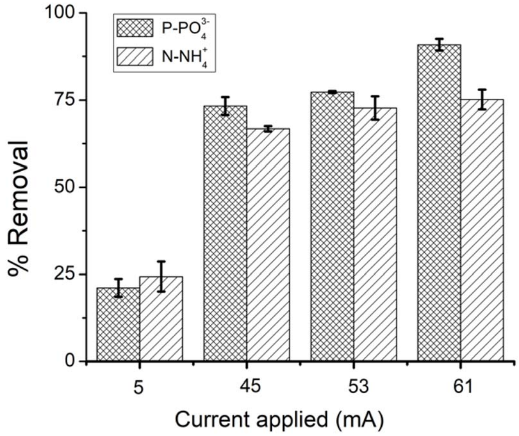

Fig. 2 Percentage removal of P-PO$_4^{3-}$ and N-NH^{4+} at different current intensities in 0.005 mol L^{-1} of NaNH$_4$PO$_4$·4H$_2$O, after 6 hours of operation in the electrochemical reactor.

an increase in the mass of the powder recovered in the electrochemical cell was also observed, which could be associated with the formation of Mg salts between them, like struvite.

During these tests, it was possible to notice the formation of a passivating layer in the electrode surface in all the cases, consistent with previous studies.[19] The formation of a passivating layer is a disadvantage for the process due to its presence reducing the electroactive area, negatively impacting the yield of the process.

When currents greater than 5 mA are applied, the resistance in the electrode surface remains constant, between 3 and 4 Ω in the first 180 minutes; after that, it increases, reaching 14 Ω in 360 minutes in all the cases (45, 53 and 61 mA), which is associated with the formation of a passivation layer on the surface; similar results were reported by Chen *et al.* (2021).[33] Additionally, the values of electrical consumption were 0.21, 9.45, 13.83 and 15.87 kW m^{-3} for the currents of 5, 45, 53 and 61 mA, respectively, showing a correlation of the energetic consumption with higher currents (presented in the SI), due to the compensation of the system that is needed to maintain the same current, increasing the power consumption.[32]

Building upon the analysis of other variables, the conductivity of the solution and Mg^{2+} ions were determined in the system. The conductivity value remained constant during the 360 minutes of experiment when 5 mA was applied; in this case, the lower current shows that when this energy is applied, there is no excess of Mg^{2+} ions dissolved in the solution, while it is detected in the other cases after 180 minutes of experiment. This fits previous findings where higher current densities lead to higher concentrations of Mg^{2+} ions;[33] it was observed that the presence of the ion also improves the conductivity.

To distinguish the effects of different currents applied, a statistical analysis (ANOVA) was conducted using Tukey's test to determine the significant differences between them. This analysis made it possible to establish that the best result is obtained when 61 mA is applied. However, while at this current the removal is highest, with values above 80%, the oxidation of Mg^{2+} is not optimal due to the elevated levels of Mg^{2+} ion detected, indicating an excess of magnesium (157.50 mg L^{-1}), which is an unintended effect in the process; for this reason, this current was not chosen as the best option (table with statistical analysis is presented in SI).

After eliminating the currents 5 mA and 61 mA, it was possible to establish that better results are obtained at 53 mA, which gives higher removal percentages and lower amounts of residual components; thus we set the current at this value for subsequent experiments.

Results obtained at 53 mA showed that during the first 180 minutes, P-PO$_4^{3-}$ is removed faster; this can be due to the formation of magnesium phosphate, an intermediate. The removal of P-PO$_4^{3-}$ and N-NH^{4+} reached the same value around 180 minutes and remained almost consistent, as shown in Fig. 3; during the experiment, the values of pH remained slightly basic, with values close to 9.

Distance between electrodes and nutrient concentration. Once the current intensity was established in the previous section as 53 mA, we analyzed the effect of other system variables, such as the concentration of nutrients (0.250, 0.050 and 0.005 mol L^{-1}), the distance between electrodes (3 and 5 cm), and their influence in the percentage of removal of N- NH^{4+} and P-PO$_4^{3-}$, using the following equations (eqn (8) and (9)) to estimate the effects of the factors in the removal of the nutrients.

The results showed that the influence of distance does not significantly change the performance of the system, and for this reason, 5 cm was selected. In contrast, the concentration has an influence in the removal of both nutrients; in this case, the optimal condition was 0.005 mol L^{-1}.

Polarization of electrodes as an alternative to avoid passivation. Once the conditions for the best performance of the electrochemical cell were established, including concentration

Table 1 Comparison of theoretical and experimental changes in the mass of Mg anode at different currents[a]

	Anode mass change, g		Solids produced, g			
i, mA	Theoretical	Experimental	Experimental	Theoretical	Current efficiency	Mg^{2+}, mg L^{-1} CaCO$_3$
5	0.031	0.021 ± 0.003	0.162 ± 0.007	0.316	39.85	ND
45	0.282	0.128 ± 0.002	1.398 ± 0.004	1.841	14.06	87.5 ± 2.17
53	0.330	0.161 ± 0.005	1.630 ± 0.021	1.841	11.26	70.04 ± 3.23
61	0.382	0.207 ± 0.007	1.716 ± 0.008	1.841	17.09	157.50 ± 4.74

[a] Theoretical values of changes in anode mass were calculated using eqn (4).

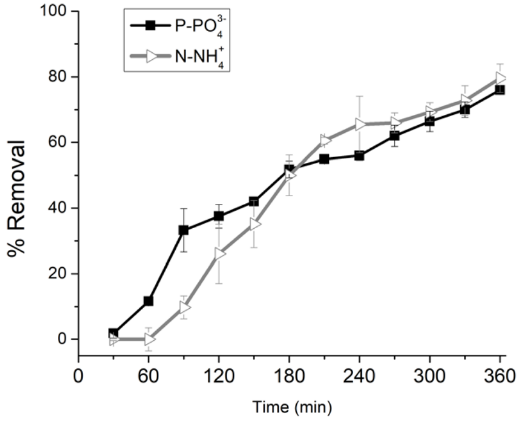

Fig. 3 Changes in the percentage of removal of P-PO$_4^{3-}$ and N-NH^{4+} by an electrochemical process at 53 mA in a solution 0.005 mol L^{-1} of NaNH$_4$PO$_4$ over 6 h.

and distance between electrodes; we addressed a serious limitation, the formation of film in the anode. This passivating layer is formed by the salts produced by the occurring chemical and electrochemical reactions.

An alternative solution was the polarization of electrodes, employing magnesium electrodes for both the anode and cathode. To investigate the influence of frequency on the removal of contaminants, different experiments were conducted, and the results are presented in Table 2.

Previous reports have shown that applying alternating pulse current prevents passivation and reduces energy consumption by reducing the resistance generated by the film formed in the electrode in an electrocoagulation process.[34] The most striking result was that at lower frequencies (0.01 Hz), the removal rates increased for both P-PO$_4^{3-}$ and N-NH^{4+}; another important effect noticed was that higher values of Mg^{2+} were obtained when no polarization was applied (0 Hz).

In our experiment, it was also possible to notice that the amount of solid recovered, which is associated with the amount of struvite synthesized, also increases at lower potentials. In these studies, the best results were obtained when the frequencies of 0.01 and 0.001 Hz were applied. In these cases, the amount of recovered solid obtained from the precipitation content of struvite was obtained using eqn (8).[35] Once we obtained the percentage of struvite, this value was used to determine the percentage of dimagnesium phosphate (DM) in the precipitate, following eqn (9).

Table 2 Effect of frequency in the percentage of removal of N-NH^{4+} and P-PO$_4^{3-}$, Mg^{2+} concentration, and solid recovered in a solution 0.005 mol L^{-1} NaNH$_4$HPO$_4$ at 53 mA and 5 cm of distance[a]

Frequency, Hz	Removal, % P-PO$_4^{3-}$	Removal, % N-NH^{4+}	Mg^{2+}, mg L^{-1} CaCO$_3$	Solid formed, g
0.1	16.67	5.78	ND	0.11
0.01	64.75	58.41	14.00	0.29
0.001	86.89	83.02	28.00	0.51
0	98.14	98.33	106.31	0.68

[a] ND, not detectable; 0 Hz is the treatment presented in the latter section, without polarization.

Table 3 Effect of frequency on the percentage of species generated in the solid recovered from a solution 0.005 mol L^{-1} NaNH$_4$HPO$_4$ at 53 mA and 5 cm of distance between electrodes[a]

Frequency, Hz	Struvite	MgHPO$_4$	Mg(OH)$_2$, MgO and others
0	23.02	6.18	70.80
0.01	51.18	47.88	0.94
0.001	75.51	22.16	2.33

[a] The treatment of 0 Hz is that presented in the latter section, without polarization.

As expected, the analysis performed and the calculations using eqn (8) and (9) showed the presence of different species when different frequencies are applied; results are presented in Table 3. In the case of 0 Hz (conventional electrochemical system), struvite purity is 23.02%; at 0.01 Hz, it is 51.18%; and at 0.01 Hz, it is 75.51%.

To verify the results, the precipitate was analysed by X-ray diffraction. The plots are presented in Fig. 4. Diffraction patterns show characteristic peaks corresponding to struvite[36] (PDF 71-2089), as indicated by the reference file; the similarity between the reference and the solid obtained at different frequencies are 70.37% for 0.01 Hz; 74.04% for 0.001 Hz and 66.66% for 0 Hz. Through this analysis, it was possible to notice that at 0.01 Hz, there were more intense and defined bands, indicating the best crystalline arrangement and lower amount of secondary species in the solid. Matching with the purity values calculated by the chemical approach (eqn (8) and (9)), these

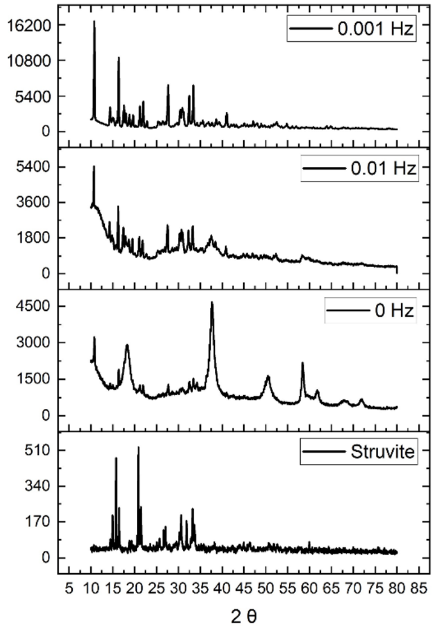

Fig. 4 X-ray diffractogram of the solid samples obtained at 53 mA and at 0.01 Hz, 0.001 Hz and 0 Hz and the struvite pattern.

observations allow us to prove that by alternating pulses, it is possible to increase the purity and reduce residual Mg^{2+} in the solution; the passivation layer was also reduced on the surface of the electrode. These observations have further strengthened our confidence in the use of alternating pulses by polarizing the electrodes, leading us to optimize the frequency in the system.

Study of frequency in the efficiency of the system. To optimize the frequency, three intermediate values near the best frequency obtained in the previous section were studied; in this case, 0.01 and 0.002 and 0.0005 Hz were tested, and results of their effect in the removal of nutrients is presented in Fig. 5.

Results presented in Fig. 5 show that at lower frequencies, the removal of nutrients increases. This effect is associated with the extended liberation of Mg^{2+} from the anode into the solution when the anode is polarized for longer periods of time. Also, the amount of Mg^{2+} remaining in the solution is higher at lower frequencies, showing that oxidation of the sacrificial anode is not efficient at lower potentials. Meanwhile, the highest purity of struvite is obtained at 0.0005 Hz. The visual appearance of the electrodes after treatment also has important differences; the passivating film in the electrode is thinner and homogeneous at 0.0005 Hz.

Given that our findings on the passivation of the electrode are based on observations of the electrode surface, to provide further details, an electrochemical study was performed using the electrodes operated in the electrochemical reactor with alternating pulses and in a traditional way; results are presented Fig. 6. In this plot, it can be observed that when no pulses are applied, during the first 6000 s, the current is low, indicating higher resistance in the electrode to the charge transfer, which can be associated to the passivating film on the electrode surface. This resistance is mitigated after 6500 s with the increasing current. In contrast, in the electrode employed with alternating pulses, the current is higher, which is associated with a lower resistance, and at 1500 s, the change in current increases, reducing the time significantly in comparison with the other experiment, proving that through alternate polarization, passivation in the electrode was reduced significatively.

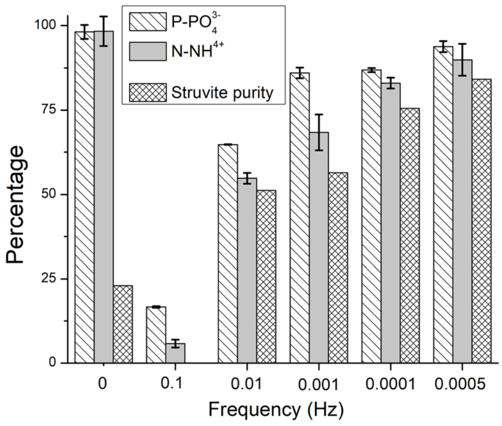

Fig. 5 Effect of frequency in the removal of N-NH^{4+} and P-PO_4^{3-} and purity of struvite in the solid recovered, in 0.005 mol L^{-1} of $NaNH_4HPO_4$ with 1 mg L^{-1} of NaCl at 53 mA.

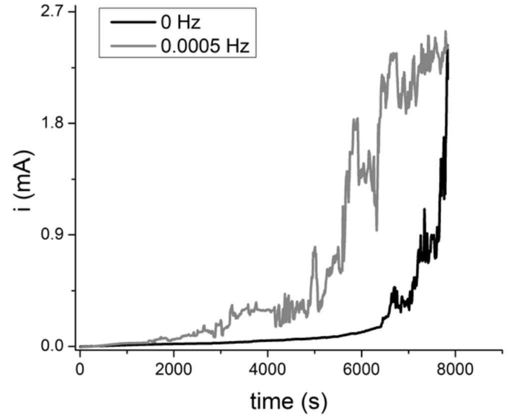

Fig. 6 Linear polarization study: working Mg electrodes operated in the electrochemical reactor at 0 Hz and 0.0005 Hz over 6 hours, in a potential window from −10 to 10 V *vs.* Ag|AgCl|KCl at 0.166 V s^{-1} in 0.005 mol L^{-1} $NaNH_4HPO_4$.

Conclusions

The experiments carried out allowed us to identify the optimal potential for the operation of a potentiostatic system in which the release of Mg^{2+} ions into the media is enough for the process, but the excess of the ions is controlled. This occurs between −0.52 to −0.42 V *vs.* Ag|AgCl|KCl, and in the case of the galvanic system, a current of 53 mA was found to be ideal for this process. With the objective of removing N-NH^{4+} and P-PO_4^{3-} with the simultaneous formation of struvite, different conditions were studied, such as the distance between electrodes, concentration of the media, and ideal current in order to achieve the highest removal of pollutants and a higher yield in the synthesis of struvite, and avoid the excess of Mg^{2+} ions in solution. Taking these points into account, it was found that the distance between electrodes does not influence the results and was fixed at 5 cm, while the optimal concentration of the media was 0.005 mol L^{-1}.

We have obtained an optimal frequency by alternating pulses using magnesium electrodes as the anode and cathode, contributing to reducing the problem associated with the passivation layer and the excess of Mg^{2+} in the solution, showing that between the frequencies of 0.0005 to 0.01 Hz, 0.0005 Hz stands out as the optimal choice. By applying this frequency, the removal of P-$PO_4^{3-}$is 93.74% in comparison with the traditional system where the removal is 98.14%; similarly, the N-NH^{4+} removal is 89.92% for the pulsed system and 98.33% for the traditional system. Different favorable phenomena occur as advantages of the pulsed system: First, magnesium is not released in excess, with the values reduced from 70.04% to 35.00%, thus avoiding the pollution of water from the added metal. Second, the purity of struvite increases to 84.19%. Finally, passivation of the electrode is reduced. This increases the life of the electrode and the efficiency of N and P removal. Although this study demonstrates the efficiency of the pulsed electrochemical process at a laboratory scale, additional tests are required to understand the mechanism involved and to scale up the system.

Author contributions

The experiments were performed by E. Rodriguez Nuñez under the supervision of A. Cardenas, who designed and directed the research. G. Aguilar Vazquez, A. Sosa and R. Nava contributed to data analysis and discussion. All authors reviewed and approved the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available as SI.

Supplementary information includes the schematic representation of the electrochemical cell, images of the working electrode at different potential zones, a detailed ANOVA analysis, and the linear regresions used for the quantification of ammonia and phospates. See DOI: https://doi.org/10.1039/d5ra02880a.

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Notes and references

1 S. Burke and N. Preedy, in *Phosphorus in Environmental Technology: Principles and Applications*, ed. E. Valsami-Jones, IWA Publishing, 1st edn, 2005, vol. 4, pp. 120–146.

2 A. M. Farmer, in *Phosphorus in Environmental Technology: Principles and Applications*, ed. E. Valsami-Jones, IWA Publishing, 1st edn, 2005, vol. 4, pp. 174–192.

3 F. A. Khan and A. A. Ansari, *Bot. Rev.*, 2005, **71**, 449–482.

4 G. B. Douglas, M. S. Robb, D. N. Coad and P. W. Ford, in *Phosphorus in Environmental Technology: Principles and Applications*, ed. E. Valsami-Jones, IWA Publishing, 1st edn, 2005, vol. 4, pp. 291–320.

5 M. K. Perera, J. D. Englehardt and A. C. Dvorak, *Environ. Eng. Sci.*, 2019, **36**, 511–529.

6 D. Cordell and S. White, *Sustainability*, 2011, **3**, 2027–2049.

7 P. G. Koutsoukos and E. Valsami-Jones, in *Phosphorus in Environmental Technology: Principles and Applications*, ed. E. Valsami-Jones, IWA Publishing, 2005, vol. 4, pp. 193–248.

8 L. Aljerf, *J. Environ. Manage.*, 2018, **225**, 120–132.

9 G. Tchobanoglous, F. L. Burton, H. D. Stensel, *Metcalf and Eddy, Wastewater Engineering: Treatment and Reuse*, McGraw-Hill Education, 4th edn, 2003.

10 Y. Jaffer and P. Pearce, in *Phosphorus in Environmental Technology: Principles and Applications*, ed. E. Valsami-Jones, IWA Publishing, 1st edn, 2005, vol. 4, pp. 402–427.

11 IWA Publishing, *Phosphorus in Environmental Technology*, ed. E. Valsami-Jones, 2004.

12 L. D. Hylander and G. Simán, *Biol. Fertil. Soils*, 2001, **34**, 42–48.

13 A. Siciliano, C. Limonti, G. M. Curcio and R. Molinari, *Sustainability*, 2020, **12**(18), 7538.

14 I. Wu, A. Teymouri, R. Park, L. F. Greenlee and A. M. Herring, *J. Electrochem. Soc.*, 2020, **166**, E576–E583.

15 K. Moriyama, T. Kojima, Y. Minawa, S. Matsumoto and K. Nakamachi, *Environ. Technol.*, 2001, **22**, 1245–1252.

16 X. Hao, C. Wang, M. C. M. Van Loosdrecht and Y. Hu, *Environ. Sci. Technol. Libr.*, 2013, **47**(10), 4965–4966.

17 A. G. Jones, *Cristallization Process Systems*, Elsevier, London, 1st edn, 2002, vol. 1.

18 Q. Guan, Y. Li, Y. Zhong, W. Liu, J. Zhang, X. Yu, R. Ou and G. Zeng, *J. Environ. Manage.*, 2023, **344**, DOI: 10.1016/j.jenvman.2023.118383.

19 A. Hug and K. M. Udert, *Water Res.*, 2013, **47**, 289–299.

20 S. Ben Moussa, G. Maurin, C. Gabrielli and M. Ben Amor, *Electrochem. Solid-State Lett.*, 2006, **9**(6), c97–c101.

21 X. Zhou and Y. Chen, *Environ. Sci. Pollut. Res.*, 2019, **26**, 2435–2444.

22 K. Rajaniemi, T. Hu, E. T. Nurmesniemi, S. Tuomikoski and U. Lassi, *Processes*, 2021, **9**, 1–13.

23 L. Kékedy-Nagy, M. Abolhassani, S. I. Perez Bakovic, Z. Anari, J. P. Moore, B. G. Pollet and L. F. Greenlee, *J. Am. Chem. Soc.*, 2020, **142**, 18844–18858.

24 D. J. Kruk, M. Elektorowicz and J. A. Oleszkiewicz, *Chemosphere*, 2014, **101**, 28–33.

25 L. E. Sattler, C. J. Otten and G. Hilt, *Chem.—Eur. J.*, 2020, **26**, 3129–3136.

26 M. Eyvaz, M. Kirlaroglu, T. S. Aktas and E. Yuksel, *Chem. Eng. J.*, 2009, **153**, 16–22.

27 C. Schotten, C. J. Taylor, R. A. Bourne, T. W. Chamberlain, B. N. Nguyen, N. Kapur and C. E. Willans, *React. Chem. Eng.*, 2021, **6**, 147–151.

28 S. R. Crouch and H. V. Malmstadt, *Anal. Chem.*, 1967, **39**, 1084–1089.

29 J. I. Pacheco Conde, *UniversidadMayordeSanAndres*, 2018.

30 N. Song, A. Atrens, D. Stjohn, J. Nairn and Y. Li, *Corros. Sci.*, 1997, **39**, 855–875.

31 Z. Zhang, L. She, J. Zhang, Z. Wang, P. Xiang and S. Xia, *Chemosphere*, 2019, **226**, 307–315.

32 P. Atkins, *Physical Chemistry*, Oxford University Press, 10th edn, 2014.

33 R.-F. Chen, T. Liu, H.-W. Rong, H.-T. Zhong and C.-H. Wei, *Membranes*, 2021, **11**, 594.

34 X. Mao, S. Hong, H. Zhu, H. Lin, L. Wei and F. Gan, *J. Wuhan Univ. Technol., Mater. Sci. Ed.*, 2008, **23**, 239–241.

35 X. Ye, Z.-L. Ye, Y. Lou, S. Pan, X. Wang, M. Ku. Wang and S. Chen, *Powder Technol.*, 2016, **295**, 16–26.

36 A. Whitaker and J. W. Jeffery, *Acta Crystallographica B*, 1970, 1429–1440.