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Ammonium and phosphate recovery in a three chambered microbial electrolysis cell: Towards struvite obtaining from livestock manure

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Abstract: Ammonia and phosphate, which are present in large quantities in waste streams such as livestock manure, are key compounds in fertilisation activities. Their recovery will help close the natural cycles and take a step forward in the framework of a circular economy. In this work, a lab-scale three-chambered microbial electrolysis cell (MEC) has been operated in continuous mode for the recovery of ammonia and phosphate from digested pig slurry, to obtain a nutrient concentrated solution as a potential source of fertilisers (struvite). The maximum average removal efficiencies for ammonium and phosphate were 20%±4% and 36%±10%, respectively. The pH of the recovered solution was below 7, avoiding salt precipitation in the reactor. According to Visual MINTEQ software modelling, an increase of pH value to 8 outside the reactor would be enough to recover most part of the potential struvite (0.21 mmol L^{-1} d^{-1}), while magnesium addition to the nutrient recovered solution up to 0.2 mM would enhance struvite production from 5.6 to 17.7 mM. The application of three-chambered MECs to the recovery of nutrients from high strength wastewater is a promising technology to avoid ammonia production through industrial processes or phosphate mineral extraction and close nutrient natural cycles.

Keywords: Struvite, ammonia, phosphate, nutrient recovery, livestock manure, microbial electrolysis cell.

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1. Introduction

Intensive livestock farming is a strategic economic activity in different areas of Europe that generates large amounts of manure. Fertilizing crops with livestock manure is a common waste management practice. Another possibility is to digest the manure anaerobically, recovering energy from waste in the form of biogas [1], with the option of using digestates also as soil fertilizer. Livestock manure can improve soil fertility by adding organic matter and nutrients to soil. However, manure or its digestates usually contain a high concentration of nutrients that hampers their direct application to soils. Uncontrolled applications of slurry to the soil could have negative effects on the environment, such as nitrate groundwater contamination or freshwater eutrophication [2]. Due to environmental concerns, there are legal limitations for the application of livestock manure to soil. These limitations may involve the exportation of livestock manure surplus to distant farmlands, which will increase transportation cost.

An alternative to traditional livestock manure management is the implementation of the circular agrosystems approach. This proposal implies the consideration of livestock manure as a nutrients resource [3], among others, that must be recovered and reintroduced to a closed loop agriculture. There are several technologies that allow closing the nutrients cycle, mainly recovering nitrogen and phosphorus to produce fertilisers, stripping and absorption [4], membrane distillation technologies [5,6], and vacuum

evaporation [7], among others [8]. The combined nitrogen and phosphorus recovery can be achieved by struvite precipitation [9]. Struvite is a salt composed of ammonia, phosphate and magnesium, heptahydrate, which has been described as a slow-release fertiliser. The struvite formation reaction is as follows:

$$Mg^{2+} + NH_4^+ + H_nPO_4^{3-n} + 6H_2O \rightarrow MgNH_4PO_4 + 6H_2O + nH^+ \quad (1)$$

In addition to more conventional nutrient recovery technologies, bioelectrochemical systems (BES) are emerging as candidates for the recovery of multiple resources from wastes [10,11]. BES can be operated as an independent technology, or in combination with other technologies, such as anaerobic digestion [12], allowing for the concomitant recovery of energy or other compounds coupled to nutrient recovery. BES are devices where electrogenic microorganisms catalyse oxidation and/or reduction reactions at an electrode (anode and/or cathode, respectively). BES have been tested with different configurations for ammonia recovery. Ammonia recovery BES are generally based on the migration of ammonium through a cation exchange membrane (CEM) by two-chamber cells coupled to ammonia stripping or hydrophobic membranes [5,12,13]. On the other hand, the recovery of phosphate in BES is performed by precipitation or migration through anion exchange membranes (AEM) [14]. A triple-chamber microbial fuel cell (MFC) has been used for phosphate remobilization from iron phosphate contained in digested sewage sludge [15]. Recently, a four-chamber microbial electrolysis cell (MEC) has been reported to achieve an 80% recovery efficiency of phosphorus in the form of hydroxyapatite [16]. A submersed BES has also been used to recover nutrients from a synthetic solution [17].

Several studies have dealt with the recovery of struvite in BES [18]. Single chamber cells have been tested [19–23], showing that pH buffering may limit the recovery of phosphate [24]. To overcome this limitation, multi-chamber cells have also been developed. The phosphate recovery process improves in double-chamber BES [25], due to the separation between the anode and the cathode. This separation creates an alkaline environment around the cathode, which favours the precipitation and recovery of phosphate [10]. To promote bulk phase struvite precipitation and minimize cathode scaling, a fluidized bed cathode MEC was developed and fed with domestic wastewater treatment plant digestate [26]. Using a magnesium anode, struvite has been recovered in the anode compartment of a MEC fed with digested swine wastewater [27].

These previous studies on BES struvite recovery have shown different drawbacks. On the one hand, struvite precipitates mainly on the cathode, which makes it difficult to recover the salt and reduces cathode performance [21,24]. On the other hand, the presence of organic matter may reduce the purity of struvite, due to salt crystallisation around particles [9]. Hence, the design of BES for nutrients recovery has evolved to three-chamber BES to treat synthetic wastewater [28,29], synthetic urine [30], urine [31,32], domestic wastewater [33] or rejected water from the anaerobic digesters of centralised wastewater treatment plants (WWTPs) [34]. A multiple chamber cell has also been operated with wastewater for the recovery of nutrients to obtain struvite [28].

However, issues such as the low solubility of phosphate in substrates with high organic and solid content must be addressed [35,36]. Furthermore, complex substrates provide a variety of cations and anions that not only compete with ammonium and phosphate for migration across ion exchange membranes but can also affect struvite recovery from the nutrient concentrate solution. In this study, a three-chamber MEC setup is proposed to recover ammonium and phosphate from a high organic and nitrogen strength wastewater (digested livestock manure) providing new insights in these relevant issues. With this configuration, struvite precipitation in the reactor will be avoided, minimising salt precipitation on the electrodes and/or membranes, so that it can be carried out independently of the BES reactor [37]. Furthermore, the struvite obtained will be recovered in a clean solution, free of organic matter.

The aim of this study is to evaluate a three-chamber MEC for the recovery of ammonium and phosphate from livestock manure, to obtain struvite. Continuous assays have been performed under different pH conditions and phosphate concentrations, using digested livestock manure. Visual MINTEQ software has been used to model the struvite formation potential of the concentrate solution obtained with each condition.

2. Materials and Methods

2.1. Experimental set-up

An H-type three-chamber MEC was constructed, which consisted of three 0.6 L glass bottles connected with side openings (Figure 1). A cation exchange membrane (CEM, dimensions: 20 cm^2; Ultrex CMI-7000, Membranes International Inc., Ringwood, NJ, USA) was placed between the side openings of the first and second (or intermediate) bottle (anode and recovery compartments, respectively). An anion exchange membrane (AMI-7100, Membranes International Inc., Ringwood, NJ, USA) with the same dimensions of the CEM was inserted between the second and third bottle (cathode compartment). The recovery compartment was equipped with a magnetic stirrer. A piece of carbon felt (dimensions: 175 cm^2; thickness: 3.18 mm; Alfa Aesar GmbH and Co KG, Karlsruhe, Germany) was used as the anode; and a 304 stainless steel mesh was used as the cathode (dimensions: 156 cm^2; mesh width: 150 μm; wire thickness: 112 μm; Feval Filtros, Spain).

The anode (working electrode) potential was poised to -300 mV by a potentiostat (VSP, Bio-Logic, Grenoble, France) in a three-electrode mode. An Ag/AgCl reference electrode (Bioanalytical Systems, Inc., USA; +197 mV vs. standard hydrogen electrode, SHE) was inserted into the anode compartment of the cell. All potential values in this paper refer to SHE. The potentiostat recorded electrode potentials and current, every 5 min, using a computer with EC-Lab software (Bio-Logic, Grenoble, France).

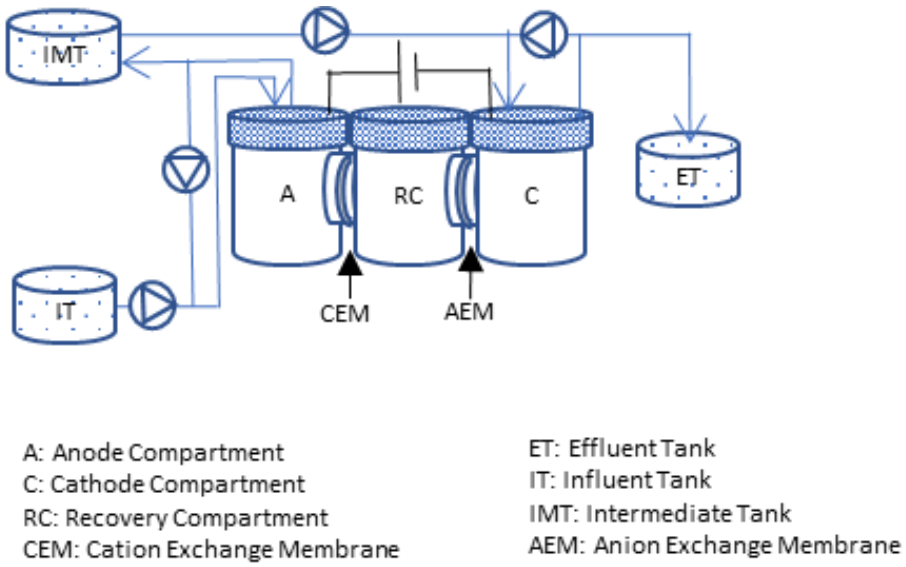

Figure 1. Scheme of the set-up of the three-chambered MEC.

2.2. Feeding solutions

The digestate used to feed the anode compartment of the MEC was collected from a 5 L lab-scale thermophilic anaerobic digester, which was fed with pig slurry. The pig slurry was collected in a farm in Gurb (Catalonia, Spain), sieved (500 μm) and diluted before feeding the anaerobic digester. The digestate was stored at 6º C until its use and sieved (125 μm). The composition of the sieved digestate is summarised in Table 1.

The digestate was fed on the first place to the anode compartment to recover ammonium, and then the anodic effluent was circulated to feed the cathode compartment and

recover phosphate. The catholyte was modified in certain assays to achieve the different conditions tested during the experiment (Table 2). pH was modified in order to assess the effect of this parameter over phosphate solubility. Phosphate is mainly present in the particulate matter of manure and can be released into the liquid fraction as soluble inorganic phosphate by lowering the pH [35]. When acidifying was performed, H_2SO_4 (95-97%) was added to the effluent of the anode compartment before using it as feed to the cathode compartment. Since the phosphate concentration of the substrate that was used in the assays was relatively low (Table 1), KH_2PO_4 was added (16 g L^{-1}) according to Table 2, either in the catholyte or in the anolyte, in order to test in some of the assays a substrate with a higher phosphate concentration.

Table 1. Composition of the digested pig slurry used as substrate (average ± standard deviation). Number of samples, n=8.

Parameter	Unit	Value
pH	-	7.7±0.2
COD	mg L^{-1}	14473±981
Na^+	mg L^{-1}	941±72
NH_4^+	mg L^{-1}	1897±395
K^+	mg L^{-1}	2042±152
Ca^{2+}	mg L^{-1}	407±199
Mg^{2+}	mg L^{-1}	176±77
PO_4^{3-}	mg L^{-1}	143±120
SO_4^{2-}	mg L^{-1}	151±115

The recovery compartment was filled with 600 mL of distillate water, which was replaced after each assay.

2.3. Reactors operation

The anode carbon felt was inoculated with the same digested pig slurry described in Section 2.2, filling completely the anode compartment with digestate. The star-up consisted of operating the MEC in batch mode for one week and then in continuous mode for 3 weeks (data not shown).

After the start-up, the MEC was operated for 115 days in 6 different phases (Table 2), using the substrates amended or not, according to Section 2.2. After each change in feeding conditions, the MEC was operated for at least 4 HRT to ensure steady-state conditions.

The influent solutions from both the anode and the cathode compartments were fed in continuous mode with a pump at 12 mL h^{-1} and mixed by recirculating them by an external pump. Anodic effluent was circulated to feed the cathode compartment and modified when required (Table 2).

The hydraulic retention time (HRT) was 41 h and 36 h for the anode and the cathode compartments, respectively, while the recovery compartment was operated in batch. The organic and nitrogen loading rates (OLR and NLR) of the anode compartment were established at 8.5 kg_{COD} m^{-3} day^{-1} and 0.9 kg_N m^{-3} day^{-1}, respectively. Discrete samples were taken from the anode, cathode and recovery compartments on weekdays. The MEC was operated at room temperature throughout the tests (23±2 ºC).

Table 2. Operational phases of the MEC and modification of the anolyte or catholyte, regarding pH value or phosphate content.

Phase	Period (d)	Anolyte	Catholyte
1	0-16	Not modified	Not modified
2	16-25	Not modified	pH modified to 6
3	25-49	Not modified	pH modified to 5
4	49-73	Not modified	pH modified to 5 Addition of KH_2PO_4 *
5	73-86	Not modified	Addition of KH_2PO_4 *
6	85-115	Addition of KH_2PO_4*	Not modified

* 16 g L^{-1}.

2.4. Analytical methods and calculations

Chemical oxygen demand (COD) was determined in the anolyte and effluent samples. pH was determined in the influents and effluents of the anode and cathode compartments, and in the recovering compartment samples by a CRISON 2000 pH electrode. All the analyses were performed following Standard Methods [38].

Anions (Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) concentrations were measured by ionic chromatography (IC) by an 861 Advanced Compact IC (Metrohm, Switzerland). A Metrosep A Supp 4 (Metrohm, Switzerland) column with a Metrospt A Supp 4/5 Guard pre-column and a CO_2 suppressor were used for anions determination. A Metrohm C4 150/4.0 column (Metrohm, Switzerland) and a Metrosep C4 Guard pre-column were used for cations determination. Prior to the IC analysis, samples were diluted and filtrated with nylon (0.45 mm) and BonElut JR C18 microfilters (Varian, USA).

The current density (A m^{-2}) of the MEC was calculated as the quotient between the intensity recorded by the potentiostat (A) and the area of the anode (m^2). Ammonium, phosphate and COD removal efficiencies were calculated as the ratio of the difference between the anode compartment influent and cathode compartment effluent concentrations and the influent concentration (mg L^{-1}). The recovery rate of the different ions was calculated as the ratio between the mass (mg) of each ion accumulated in the recovery compartment and the elapsed time (d).

A balance of charge was performed to evaluate the number of electrons that were used for ions migration through the CEM and AEM. When calculating charge, Q, a distinction was made between transport of negative charges in the form of electrons through the electric circuit, and transport of positive (Q^+) and negative (Q^-) charges in the form of the dominantly present cations (Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) and anions (Cl^-, PO_4^{3-} and SO_4^{2-}), respectively. Total charge production, Q, expressed in coulombs (C) was determined by integrating current over time. Transport of charges in the form of ions in the system through the membrane, Q^+ or Q^-, expressed in coulombs (C) were determined as follows:

$$Q^+ = \sum_{cat} (x^{cat,t} \cdot V \cdot z^{cat} \cdot F) \quad (2)$$

$$Q^- = \sum_{an} (x^{an,t} \cdot V \cdot z^{an} \cdot F) \quad (3)$$

with $x^{cat,t}$ and $x^{an,t}$ the molar cation or anion concentration of each ion species in the recovery compartment at the end of an experimental run expressed in mol L^{-1} (M), V the recovery compartment liquid volume expressed in litres (L), z^{cat} and z^{an} the valence of the cation or anion species, respectively, and F the Faraday's constant (96 485 C mol^{-1})

2.5. Struvite potential recovery

A theoretical calculation was carried out to evaluate the struvite recovery potential of the solutions obtained in each assay, using Visual MINTEQ (KTH, Sweden, https://vminteq.lwr.kth.se/). Visual MINTEQ (ver. 3.1) is a chemical equilibrium software that allows for the calculation of speciation, solubility, solid equilibrium, and the mineral dissolved phases in laboratory and natural aqueous systems.

Concentrations of the major interest ions present in the solution obtained in each assay (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, PO_4^{3-} and SO_4^{2-}) were introduced in the modelling program, with a temperature of 25 °C. Precipitation and aqueous reactions were provided by the standard databases in the chemical equilibrium program Visual MINTEQ. The sweep utility of the software was employed to calculate the mass of struvite that could be precipitated when increasing pH value between 6 and 11. The same utility was employed to evaluate the amount of struvite obtained when increasing the amount of magnesium present in the solution.

3. Results and discussion

3.1. Performance of the MEC

The current density produced by the MEC in the different phases of operation is shown in Figure S1. Phase 3 and Phase 4 were the periods with a higher average current density, reaching 0.26 A m^{-2} (Table 3), although the differences among the phases were not significantly different. The current densities obtained in these assays are slightly lower than the obtained in previous work performed with similar digested pig slurry and OLR, using H-type cells with adjacent anode and cathode compartments, where 0.35 A m^{-2} were achieved [5]. The increase in distance between the anode and the cathode in this assay, since the recovery compartment was placed between them, may have increased the electrical resistance of the system and reduced in turn the current density [39].

The average COD removal efficiency was in a range of 21-34%, with no significant differences among the different phases (Table 3). This COD removal efficiency is similar to the one reported by previous assays where a MEC was fed with a similar pig slurry digestate [5], and is typical of BES working with complex substrates such as food or agricultural wastes [40].

Table 3. Summary of the main operation parameters of the MEC in the different phases of digestate operation (average ± standard deviation). Phase 1: not amended feeding was used (n=7); Phase 2: catholyte acidified to pH 6 (n=4); Phase 3; catholyte acidified to pH 5 (n=8); Phase 4: catholyte acidified to pH 5 and phosphate amended (n=6); Phase 5: phosphate amended catholyte (n=4); and Phase 6: phosphate amended anolyte (n=7).

Phase	Current density (A m^{-2})	COD removal efficiency (%)	NH_4^+ removal efficiency (%)	PO_4^{3-} removal efficiency (%)
1	0.10±0.06	-	29±14	89±3
2	0.17±0.09	-	16±6	55±1
3	0.26±0.18	21±7	11±2	52±23
4	0.25±0.12	24±7	11±7	17±7
5	0.17±0.09	32±8	7±2	5±5
6	0.21±0.06	34±12	20±4	36±10

- Not determined.

Ammonia removal efficiency during Phase 1, with no substrate modification, was of 29%, slightly higher than the 23% obtained in previous assays performed by Cerrillo et co-workers (2021b) with similar conditions. The phases with acidification of the catholyte (Phase 2, 3 and 4) reduced this removal efficiency to a range of 7-16%, while the amendment of the anolyte with phosphate with no pH adjust (Phase 5), increased the removal efficiency value to 20%. In phases 3 to 5, the ammonium concentration of the cathode effluent was generally higher than in the anode effluent. This fact has been previously reported by other authors when operating three-cambered cells with urine or domestic wastewater, indicating that the AEM allowed the permeation of part of the nitrogen recovered in the intermediate compartment [31,41]. Dissolved ammonia gas can be transported through the AEM as an uncharged species by diffusional forces only, as described before [42].

Regarding phosphate removal efficiency, the higher value with PO_4^{3-} amendment (Phases 4 to 6) was achieved in Phase 6 (36%). In general, the reduction of pH by H_2SO_4 addition decreased PO_4^{3-}removal due to competition with sulphate anions. Previous electrodialysis studies have reported that the PO_4^{3-} removal efficiency decreased due to the coexistence of accompanying ions in the feed solution, especially when competing to SO_4^{2-}, reducing PO_4^{3-} removal efficiency from 50.7% to 29.5% [43].

Other authors have reported the use of three-chambered cells for the recovery and concentration of nutrients. Koskue and co-workers operated a three-chambered cell for ammonia recovery and achieved higher recovery values of 75.5% with synthetic reject water and 53% with real reject water [34]. The use of a complex wastewater with other cations such as Na^+, Ca^{2+}, and Mg^{2+} present in the organic matrix may decrease NH_4^+ removal efficiency, since they would compete with NH_4^+ ions for current driven migration [37]. Besides, the back diffusion of NH_4^+, due to the high concentration in the recovery chamber, can decrease the recovery efficiency. Li and co-workers operated a MEC in batch mode and achieved removal efficiencies from synthetic wastewater of 36 and 30% for NH_4^+ and PO_4^{3-}, similar to the ones obtained in this assay, although increasing the pairs of ion exchange membranes exhibited a higher removal efficiency of 79% and 79%, respectively (Li et al., 2020). Ledezma and co-workers achieved 59.7% removal of the nitrogen from the anodic compartment, and 42.8% of the phosphorus in a MEC supplied with synthetic urine [31].

3.2. Ions accumulation in the recovery compartment

The rate of accumulation of the main ions in the recovery compartment of the MEC system is shown in Figure 2. During the operating period of the system with unmodified digested slurry (Phase 1), no PO_4^{3-} was detected in the recovery compartment, with Cl^- being the dominant anion in the solution. With regard to cations, K^+ (12.6 mg d^{-1}), followed by NH_4^+ (6.8 mg d^{-1}), were the ones that accumulated the fastest. When acidifying the catholyte to pH 6 (Phase 2), to solubilize the phosphate that may be present in the slurry, the increase of SO_4^{2-} in the recovery solution was observed, promoted by H_2SO_4 addition to the catholyte, as well as a slight increase in the Cl^- transfer rate. Both NH_4^+ and K^+ also increased their accumulation rate to 14.0 mg d^{-1} and 19.2 mg d^{-1}, respectively. This increase in accumulation rates may be related to the increase in current density produced in this phase (Table 2). In contrast, PO_4^{3-} remained undetected in the recovery compartment solution, probably due to the increase from 51 to 167 mg L^{-1} of PO_4^{3-} concentration achieved by acidification to pH 6. The acidification of the catholyte to pH 5 (Phase 3) also failed to significantly solubilize PO_4^{3-}, achieving a maximum value of 375 mg L^{-1} in the catholyte. Instead, the accumulation of Cl^- and SO_4^{2-}increased, also accompanied by a greater accumulation of NH_4^+ (39.9 mg d^{-1}) and K^+ (32.4 mg d^{-1}). Since PO_4^{3-} is mainly adsorbed on the particulate matter of pig slurry, and the substrate was sieved before use, it is evident that little PO_4^{3-} to be solubilised remained in the substrate.

The amendment of the catholyte with KH_2PO_4 to simulate a higher PO_4^{3-} content of the substrate (Phase 4) while maintaining the acidification of the catholyte (pH 5), reduced the transfer rate of Cl^- and SO_4^{2-} compared to previous phases, in favour of PO_4^{3-} (51.3 mg d^{-1}), being the most favourable condition of those tested regarding PO_4^{3-} migration. The PO_4^{3-} transfer was slightly reduced (35.7 mg d^{-1}) when the acidification of the catholyte was eliminated (Phase 5), probably due to the decrease in current density of this phase. Finally, the addition of PO_4^{3-} to the anolyte in the form of KH_2PO_4 (Phase 6) maintained the PO_4^{3-} migration achieved in Phase 5. On the other hand, the increase in K^+ in the feeding to the anode compartment caused an increase in the migration of this one (35.2 mg d^{-1}) to the detriment of NH_4^+ (8.5 mg d^{-1}).

Since the current density produced in the MEC affects the migration of ions across the CEM and AEM, these results must also be analysed in the framework of the electrical charge balance, as described in Section 3.2.

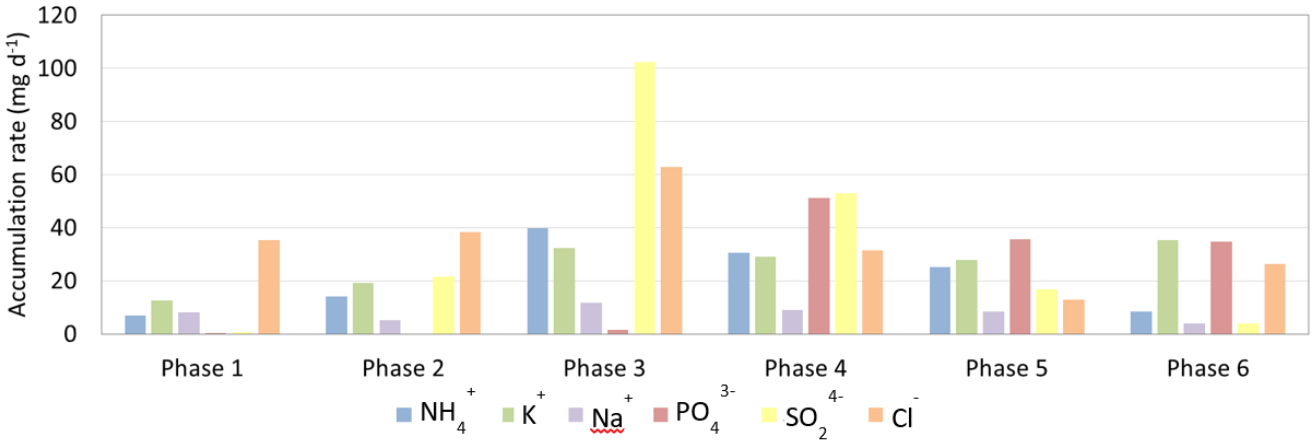

Figure 2. Accumulation rate of NH_4^+, K^+, Na^+, PO_4^{3-}, SO_2^{4-} and Cl^- in the recovery compartment in the different phases. Phase 1: not amended feeding was used; Phase 2: catholyte acidified to pH 6; Phase 3; catholyte acidified to pH 5; Phase 4: catholyte acidified to pH 5 and phosphate amended; Phase 5: phosphate amended catholyte; and Phase 6: phosphate amended anolyte.

3.2. Electrical charge balance

Figure 3 shows the rate of charge transfer in the system, in order to compare the number of electrons transferred from the anode to the cathode, with the number of positive and negative charges migrated through the cation and anion exchange membranes, respectively. As can be seen in Figure S2, the phases with the highest charge transferred have been the two in which the catholyte has been acidified to pH 5. In general, the transport of charges in the form of cations has been slightly higher than that of anions, and also higher than the amount of charge transferred in the form of electrons, except in Phase 2 and 6. This may be due to the diffusion of uncharged species (NH_3), as described before. So, while the migration of anions consumed 95%, 79% and 78% of the electrical charge transferred by electrons in Phases 4 to 6, with PO_4^{3-} amended substrates, cations represented 104%, 133% and 87%, respectively.

NH_4^+ represented 39%, 43%, 42% and 41% of the cations charge content in the recovery solutions of Phases 2, 3, 4 and 5, respectively, with a high competition of K^+, which represented 50%, 33%, 37% and 43% in the same phases. This distribution was strongly affected in Phase 6, with the addition of KH_2PO_4 to the anolyte, causing a decrease of NH_4^+ charge in the recovery solution to 16%, while K^+ one increased to 65%. Although Na^+ has been described as a strong competitor for NH_4^+ migration, due to a similar hydrated radius (0.358 nm and 0.331 nm, respectively) [37,44], in this study Na^+ has represented only between 6% and 17% of the positive charges in the recovery solution. This lower participation in cation migration of sodium may be due to its lower concentration compared to NH_4^+ or K^+ in this substrate (Table 1).

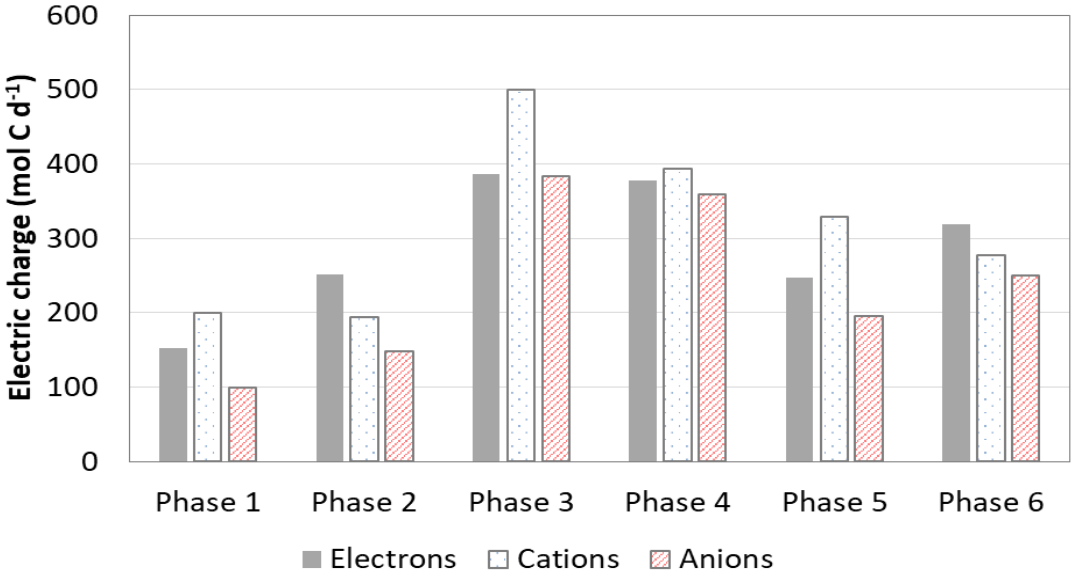

Figure 3. Amount of charge transferred through the electrical circuit (electrons) compared to charge accumulated in the recovery compartment in the form of anions (C^-) and cations (C^+). Phase 1: not amended feeding was used; Phase 2: catholyte acidified to pH 6; Phase 3; catholyte acidified to pH 5; Phase 4: catholyte acidified to pH 5 and phosphate amended; Phase 5: phosphate amended catholyte; and Phase 6: phosphate amended anolyte.

Regarding PO_4^{3-}, this anion accounted for 43%, 56% and 42% of the negative charges that were present in the recovery solution in Phases 4 to 6, respectively, the KH_2PO_4 amended phases. SO_4^{2-} competed strongly with phosphate when the catholyte was acidified in Phase 4, representing 30% of the negative charge of the recovery solution. This proportion decreased to 17% and 3% when acidification step was supressed in Phase 5 and Phase 6, respectively. In the acidified catholyte in Phase 4, most of phosphate is as a monovalent species ($H_2PO_4^-$). SO_4^{2-} has a smaller hydrated radius (rh = 0.23 nm) and a higher valence; thus, it moves across the membrane faster than $H_2PO_4^-$ (rh = 0.302 nm). These facts, added to the increase in SO_4^{2-} concentration in the catholyte due to acidification with H_2SO_4, have decreased PO_4^{3-} removal. The increase in pH of the catholyte in Phase 5 and Phase 6 caused a shift of the $H_2PO_4^-$ anions to their multivalent forms, HPO_4^{2-} and PO_4^{-3}, which have a higher tendency to move across the AEM, reducing the competence of SO_4^{2-} [43].

Thus, the use of a complex substrate, with a wide variety of anions and cations accompanying NH_4^+ and PO_4^{3-}, limits the concentration of the main components of struvite in the recovery solution. However, it must be deciphered whether these companion ions may hamper struvite obtaining when the suitable pH conditions are provided, as will be discussed in Section 3.3.

3.3. Struvite potential recovery

The concentration of the main components of the recovery solution obtained in the intermediate compartment after each assay is shown in Figure 4. Since these solutions were intended to be used to recover struvite, which precipitates at basic pH [9], Visual MINTEQ software was used to estimate the amount of salt that could form in each condition if pH was externally modified (Figure S3). The recovery solution obtained in Phases 1 to 3 would not be suitable for struvite precipitation due to their low content of PO_4^{3-}. However, hydroxyapatite ($Ca_5(PO_4)_3(OH)$) would be recovered in small amounts (<2 mmol L^{-1}) in all the pH range, and brucite ($Mg(OH)_2$) would form at pH values of 10 and 11, thanks to the small amounts of Ca^{2+} and Mg^{2+} present in the solutions.

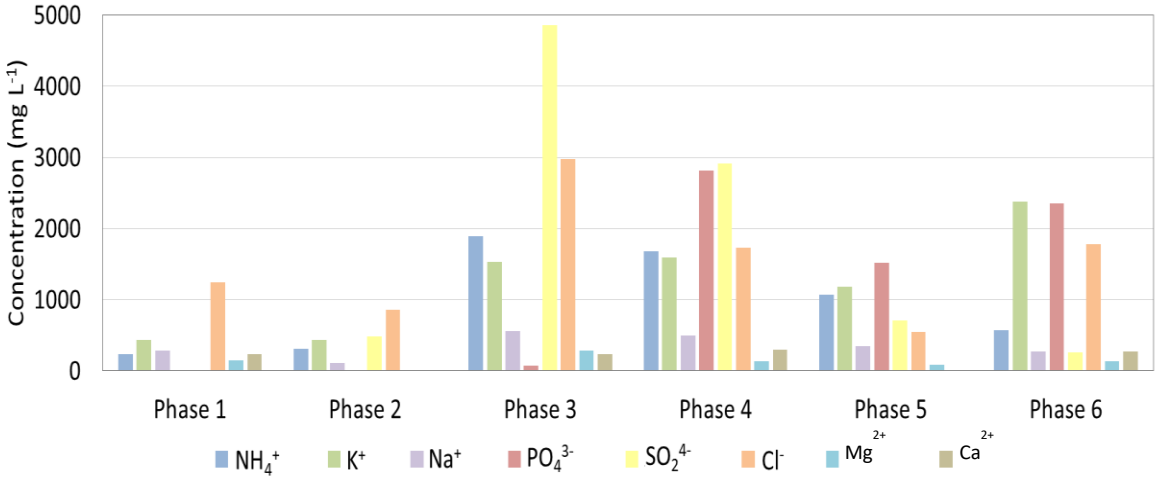

Figure 4. Composition of the main ions in the concentrated solution of the recovery compartment after each condition tested. Phase 1: not amended feeding was used; Phase 2: catholyte acidified to pH 6; Phase 3; catholyte acidified to pH 5; Phase 4: catholyte acidified to pH 5 and phosphate amended; Phase 5: phosphate amended catholyte; and Phase 6: phosphate amended anolyte.

Hydroxyapatite would still form in the solutions recovered in Phases 4 to 6, although struvite would precipitate when increasing the pH to 7, being the main component of the recovered solid. The maximum amount of struvite would be obtained at pH 10 (5.4, 3.7 and 5.6 mmol L^{-1} in the solution recovered in Phase 4, 5 and 6, respectively), although at pH 8 the recovering efficiency would be similar with a lower alkali consumption. The solution recovered in the intermediate compartment has a pH lower than 7, thus avoiding uncontrolled precipitation of struvite inside the reactor, as shown by the mathematical model.

The estimated struvite recovery rate in Phases 3 to 6 at pH 8 would be of 0.24, 0.22 and 0.21 mmol L^{-1} d^{-1}. Added to hydroxyapatite formation, nearly 39% of the phosphate and 14% of the ammonium recovered in the intermediate compartment would be precipitated in a salt that could be used as a fertiliser in Phase 6 (Table 4). Mg^{2+} is clearly the limiting component to increase the amount of recovered struvite, since 99% of this cation is forming precipitates. The external addition of a Mg^{2+} source would enhance struvite recovery, as shown in Figure S4. A concentration of 0.23 mmol L^{-1} of Mg^{2+} in the recovery solution of Phase 6, at pH 8, would increase the concentration of struvite to 17.7 mmol L^{-1}, thus tripling the value obtained with no Mg^{2+} addition. In this case, 84% and 41% of the PO_4^{3-} and NH_4^+ of the recovery solution would be precipitated.

Table 4. Estimation of the fraction of precipitated components on the recovery solution in each phase when adjusting pH to 8. Phase 4: catholyte acidified to pH 5 and phosphate amended; Phase 5: phosphate amended catholyte; and Phase 6: phosphate amended anolyte.

Phase	NH_4^+ (%)	PO_4^{3-} (%)	Mg^{2+} (%)
4	4.5	33.0	99.5
5	4.8	23.6	99.1
6	13.6	38.9	98.9

Struvite recovering outside the MEC by increasing pH is proposed over inside precipitation to increase the practicality of the system. Salt collection in an independent tank is simpler, and scaling is avoided, especially on the ion exchange membranes, which will decrease BES performance [37].

The use of pig slurry or digestate with a high phosphate concentration, instead of KH_2PO_4 amended and acidified, will reduce the amount of K^+ or SO_4^{2-} present in the substrate and their competition with NH_4^+ or PO_4^{3-} in the migration through the CEM and AEM, respectively. This way, the ratio between the later cation and phosphate will equilibrate and enhance struvite recovery. To assure the presence of soluble PO_4^{3-} in the substrate, a solubilisation step may be needed, which will preferably be applied to raw or digested pig slurry previous to any mechanical separation treatment.

4. Conclusions

The suitability of a three-chamber MEC for the recovery of ammonium and phosphate from a high organic and nitrogen strength wastewater (digested pig slurry) has been demonstrated. The maximum average ammonium and phosphate removal efficiencies were 20%±4% and 36%±10%, when the substrate was amended with KH_2PO_4 to simulate a high phosphate content pig slurry. In addition, the COD was reduced by 34%±12%. Ammonium represented a maximum of 43% of the positive charges of the recovered solution, due to strong competition of potassium cations, while phosphate reached a maximum of 56% of the negative charges. The pH value of the recovered solution was kept under 7, avoiding struvite precipitation in the reactor, which represent an advantage over other MEC configurations for struvite recovery that promote struvite precipitation inside the reactor. Visual MINTEQ software showed that increasing the pH value of the concentrate solution to 8 outside of the reactor would be enough to recover most of the potential struvite (0.21 mmol L^{-1} d^{-1}). However, magnesium addition to the recovered nutrient solution up to 0.2 mM would be needed to enhance struvite production from 5.6 to 17.7 mM. Solubilisation of phosphate reveals as a key issue in struvite recovery from livestock manure in BES, since acidification with H_2SO_4 may interfere, on the one hand, with biomass growth in the anode compartment, and on the other hand, with phosphate migration. Phosphate solubilization techniques compatible with BES performance should be evaluated to improve the recovery efficiency of the system. Furthermore, it would be feasible to apply this technology for the treatment of other complex substrates rich in nutrients, mainly those produced in the agro-industrial sector. This way, the recovery of ammonia and phosphate in the form of struvite, a slow-release fertiliser, will help close the nutrients natural cycles.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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