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Harnessing Electrochemical Processes for Enhanced Struvite Crystallization: A Comprehensive Review

Eko Ariyanto[1], Eka Sri Yusmartini[1,*], Gusmiatun Gusmiatun[2], Fatimah Fatimah[3] Mitayani Purwoko[4]

[1] Department of Chemical Engineering, Engineering Faculty, Universitas Muhammadiyah Palembang, Jln. Ahmad Yani 13 Ulu Palembang, Indonesia.
[2] Department of Agrotechnology, Agriculture Faculty, Universitas Muhammadiyah Palembang, Jln. Ahmad Yani 13 Ulu Palembang, Indonesia.
[3] Departemen of Management, Economic and Business Faculty, Universitas Muhammadiyah Palembang, Jln. Ahmad Yani 13 Ulu Palembang, Indonesia.
[4] Department of Medical, Faculty of Medicine, Universitas Muhammadiyah Palembang, Jln. Ahmad Yani 13 Ulu Palembang, Indonesia

[*] *Corresponding Author: eka.yusmartini@gmail.com*

Abstract

The recovery of nutrients from contaminated water and wastewater can effectively mitigate both the nutrient burden on water resources and the associated environmental issues affecting aquatic ecosystems. This approach presents a valuable solution towards achieving environmental and societal sustainability. Consequently, struvite crystallization technology has emerged as a promising method for nutrient recovery, as the resulting precipitate can be recycled as a natural fertilizer. This review aims to elucidate the characteristics of struvite and provide insight into the fundamental process of crystallization. Furthermore, it comprehensively discusses the various variables that influence struvite crystallization, with a special focus on its application in urine-contaminated water using electrochemical methods. The review also highlights the advantageous on environmental and economic aspects. In addition, the limitations of struvite crystallization technology are examined, and future research prospects are explored, particularly in the context of electrochemical techniques which offer innovative solutions for controlled nutrient extraction. Ultimately, this work serves as a foundational resource for the future utilization of struvite crystallization technology in nutrient recovery, in response to the escalating environmental challenges and depletion of natural resources.

Keywords: Struvite formation, electrochemical process, magnesium anode, struvite crystallization, natural fertilizer

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Pemulihan nutrien dari air dan air limbah yang terkontaminasi merupakan solusi efektif untuk mengurangi beban nutrien pada sumber daya air serta dampak lingkungan yang mempengaruhi ekosistem perairan. Pendekatan ini menawarkan kontribusi signifikan dalam mencapai keberlanjutan lingkungan dan sosial. Teknologi kristalisasi struvite adalah metode yang menjanjikan untuk pemulihan nutrien, karena presipitat yang dihasilkan dapat didaur ulang sebagai pupuk alami. Tinjauan ini bertujuan untuk menjelaskan karakteristik struvite serta memberikan pemahaman tentang proses kristalisasi dasarnya. Selain itu, tinjauan ini secara menyeluruh membahas berbagai faktor yang mempengaruhi kristalisasi struvite, dengan fokus pada aplikasinya dalam air yang terkontaminasi urin melalui metode elektrokimia. Tinjauan ini juga menggarisbawahi keuntungan lingkungan dan ekonomi dari pembentukan struvite. Keterbatasan teknologi kristalisasi struvite juga dianalisis, dan prospek penelitian di masa depan dieksplorasi, terutama dalam konteks teknik elektrokimia yang menawarkan solusi inovatif untuk ekstraksi

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nutrien yang lebih terkontrol. Pada akhirnya, tinjauan ini berfungsi sebagai sumber daya mendasar bagi pengembangan teknologi kristalisasi struvite dalam pemulihan nutrien, sebagai respons terhadap tantangan lingkungan dan keterbatasan sumber daya alam yang semakin meningkat.

Kata Kunci: Pembentukan struvite, proses elektrokimia, anoda magnesium, kristalisasi struvite, pupuk alami

INTRODUCTION

Electrochemical processes have been thoroughly examined and implemented for the purpose of struvite production from urine waste [1]. These processes entail the utilization of electrochemical cells, wherein urine waste is subjected to electrolysis to generate the essential ions required for struvite formation. The primary aim of these processes is to extract beneficial substances from urine waste, like potassium and phosphorus. Shan *et al.* have developed an electrochemical crystallization system in which sacrificial magnesium anodes are used to extract phosphorus and potassium from simulated urine in the form of K-struvite. Wu *et al.* have presented a comprehensive electrodialysis-struvite recovery system that not only concentrates wastewater but also produces struvite in a single unit operation. In a separate study conducted by Jadhav *et al.*, the potential of microbial electrochemical systems (MES) in the treatment of human waste and animal urine to generate electricity and recover resources like struvite was discussed [2,3]. Additionally, various studies have pointed out the significance of magnesium as a sacrificial anode in the electrochemical recovery of nutrients from waste streams through struvite precipitation [4,5].

The electrochemical method is widely recognized for its environmentally friendly characteristics, absence of the need for external pH adjustment, and versatility in various environmental conditions and capacities [1,6,7]. Studies have demonstrated that an electrolysis reactor employing a magnesium anode is an effective approach for treating solutions with acidic, neutral, or alkaline properties that contain ammonia and phosphate [8–10]. Furthermore, electrochemical methods have the advantage of compact size, chemical selectivity, wide applicability, and minimal production of secondary waste, as they directly remove contaminants from water [5,7,11,12].

The formation of struvite crystals in urine waste is influenced by various factors, including pH, molar ratio, current density, voltage supply, stirring speed, reaction time, type of electrode, and distance between electrodes [7,13–15]. The utilization of sacrificial magnesium anodes in electrochemical crystallization systems has demonstrated promising outcomes for phosphorus (P) and potassium (K) recovery in the form of K-struvite [5,15]. Introducing preformed struvite crystals into urine as seed material can enhance the recovery of both P and K [16]. Peptides have been investigated as a means to control and enhance the growth of struvite crystals at neutral pH, thereby improving the efficiency of electrochemical struvite precipitation [5]. Several studies have reported their findings on the composition of precipitates and the role of the magnesium anode in electrochemical reactions, providing valuable insights into phosphorus recovery from wastewater [1,17]. In addition, the addition of sodium chloride to wastewater has been shown to reduce energy consumption and enhance the conductivity of the wastewater during electrochemical struvite recovery. The results revealed a 33.5% reduction in energy consumption under optimal conditions, with the addition of NaCl resulting in the recovery of 84.5% of phosphate and 50% of ammonium species [18].

Electrocoagulation has been recognized as an effective technique for the precipitation of struvite due to its ease of operation, scalability, and cost-effectiveness [19,20]. Several studies in literature have contributed to the development of this urine waste management system. For instance, a metagenomic sequencing analysis study revealed the presence of antibiotic resistance genes in stored urine and struvite samples, highlighting the importance of addressing mobilomes before utilizing struvite as fertilizer [21]. A method involving constant voltage electrolysis with a magnesium anode has been proposed for the crystallization of struvite from anaerobically digested chicken manure slurry, demonstrating effective nitrogen and phosphorus recovery across a wide pH range [22]. Electrochemical methods utilizing sacrificial magnesium anodes have also been developed to recover phosphorus and potassium in the form of K-struvite from simulated urine, achieving optimal recoveries at specific current densities [23]. In-house constructed electrochemical cells have been employed for struvite recovery from sewage wastewater, and the addition of sodium chloride has been found to reduce energy consumption while increasing phosphate and ammonium recovery [7].

Despite its promising process and outcomes, the utilization of urine as a raw material for struvite crystal production presents challenges, particularly concerning the presence of antibiotic resistance genes. Research studies have demonstrated that urine carries a range of microorganisms, viruses, and mobilomes that may harbor antibiotic resistance genes [24–26]. Consequently, it is of utmost importance to investigate the behavior of antibiotic resistance genes in struvite crystals.

Liu *et al.*, [27] stated that fresh urine had a high occurrence of streptococcus phage, whereas stored urine exhibited increased levels of ARGs when compared to both fresh urine and struvite samples. Further, all three samples indicated five resistance genes: *aminoglycosides*, *carbapenem*, *chloramphenicol*, *erythromycin*, and *efflux pump*. Notably, the key pathogens carrying these genes included *Acinetobacter*, *Aeromonas*, and *enterococcus* as reported by Tao et. al., [28]. The presence of carbapenem, aminoglycoside resistance, and efflux pump gene families in struvite suggests the existence of mobilomes loaded with resistance genes, including those associated with last-resort antibiotics. This issue demands attention prior to utilizing struvite as fertilizer [29]. It is recommended to further enhance the struvite production process to minimize mobilomes. The detection of antibiotic resistance genes in stored urine and struvite samples underscores the significance of addressing mobilomes before using struvite as fertilizer. Consequently, additional research is essential to improve the struvite production process and reduce antibiotic resistance genes. Identifying antibiotic resistance genes in stored urine and struvite samples raises concerns regarding the potential transmission of these genes to the environment when struvite is used as fertilizer. Consequently, this study promotes a thorough understanding of the behavior of antibiotic resistance genes in struvite and to develop strategies to minimize their presence prior to its utilization.

KEY STAGES IN ELECTROCHEMICAL PROCESSES

The electrochemical struvite crystallization process comprises several pivotal stages, namely electrode activation, ion migration, nucleation, crystal growth, and harvesting. Commencing with electrode activation, this stage initiates the electrochemical reaction [5,22].

Furthermore, ion migration takes place as the charged ions migrate towards the electrodes. Subsequently, nucleation occurs, wherein the ions aggregate to form small clusters known as nuclei. These nuclei then undergo crystal growth by augmenting in size, resulting in the formation of larger struvite crystals [30–33].

Once the stage of crystal growth has concluded, the struvite crystals may be gathered for subsequent utilization or processing. In the process of electrode activation, an external voltage is employed to facilitate the liberation of ions from the electrodes, thereby establishing a favorable environment for struvite formation [1,34].

Ion migration occurs when ions (Mg^{2+}, NH_4^-, and PO_4^{3-}) that have been released move towards the reaction zone under the influence of the electrical field generated by the electrodes. Within the reaction zone, these ions recombine and undergo nucleation to form struvite nuclei. Following nucleation, crystal growth occurs as additional ions are deposited, resulting in the enlargement of the struvite nuclei [31]. Subsequently, the collected struvite crystals are separated and retrieved from the solution [35]. It is imperative to optimize the electrochemical struvite crystallization process and minimize the presence of antibiotic resistance genes in order to produce an effective fertilizer [36].

The electrochemical precipitation of struvite from wastewater using a sacrificial magnesium anode has been proven to be an effective approach for phosphorus recovery [5,15]. The mechanism behind the release of Mg ions at the magnesium anode in the electrolysis process for struvite crystal formation involves the breakdown of the passivating film on the anode's surface. This film, composed of magnesium hydroxide ($Mg(OH)_2$) and/or struvite, hinders the release of divalent Mg^{2+}ions and reduces struvite precipitation. Additionally, using a dynamic potential, as opposed to a constant potential, enhances the disruption of the passivating film and facilitates the release of Mg^{2+} from the anode, thereby addressing issues related to electrical passivation [22]. Applying a higher voltage helps further break down the passivating film and promote the release of Mg^{2+} [10,15,37,38]. In other words, employing a dynamic voltage with a sinusoidal waveform has been found to significantly boost the release of magnesium ions and improve struvite recovery when compared to a constant voltage.

Nevertheless, there remain challenges that must be addressed to optimize the electrochemical process for the formation of struvite. The electrode materials and operational parameters, as summarized in Table 1, significantly influence the efficiency of struvite crystallization during the electrochemical process, with variations in anode and cathode types, as shown in Table 1, impacting nutrient recovery and crystal purity. One such challenge pertains to the creation of struvite crystals on cathode plates, which can hinder the efficiency of the process and impede the recovery of phosphorus and nitrogen [15]. Furthermore, achieving a higher level of purity in the obtained product is another obstacle [39]. Impurities, including the coexisting ions and organic matter, are potentially and significantly diminishing the quality of the recovered struvite. Consequently, several studies have explored different approaches to enhance the purity of struvite. For instance, utilizing a dynamic voltage waveform instead of a constant voltage can prevent or reduce struvite attachment to the electrode surface. Moreover, optimizing the initial pH and flow rate in the electrolysis process can maximize phosphate removal efficiency while minimizing impurities in the product stream. Low concentration of phosphate in wastewater, which may render struvite precipitation ineffective for phosphorus removal, is an additional challenge to address.

The formation of Struvite in an electrolysis reactor by employing a Magnesium plate is significantly influenced by the electrochemical reactions transpiring at the anode and cathode. Specifically, at the anode, the process of magnesium oxidation occurs, leading to the liberation of Mg^{2+} ions, which can be observed.

Consecutively, the cathodic reaction, as depicted in Equation (2), progresses through the subsequent two steps:

At the anode:

$$Mg \rightarrow Mg^{2+} + 2e^- \quad (1)$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

Reaction (1) and (2) react to become:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (3)$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \quad (4)$$

At the same time, the cathodic reaction, as depicted in Equation (2), progresses through the subsequent two steps:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (5)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (6)$$

When the electrolysis system's solution contains ammonia and phosphate, the Mg^{2+} ions combine with NH_4^+ and PO_4^{3-} ion to form struvite ($MgNH_4PO_4.6H_2O$) at a suitable pH. This can be observed in the following equation:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 2H_2O \rightarrow MgNH_4PO_4.6H_2O \quad (7)$$

FACTORS INFLUENCING THE FORMATION OF STRUVITE CRYSTALS

pH

Solution pH is a substantial factor in the electrolysis process of struvite crystals formation. As hydrogen evolves at the cathode during electrolysis, the solution pH increases and promotes the precipitation of struvite by elevating the concentration of hydroxide ions (OH^-) [40,41]. It is believed that pH 8 to 9 facilitates struvite crystallization due to the slightly alkaline environment [42]. Ariyanto *et al.*, [43] has found that the growth rate of struvite crystals is higher in more alkaline solutions. This is further supported by Moulessehoul *et al.*, [44] that pH 8.5 is the optimal value for struvite crystal growth, resulting in a 98% phosphorus to phosphate conversion rate. In general, the catholyte pH accelerates both the reaction rate of struvite crystals and the efficiency of phosphorus recovery. Furthermore, Wang *et al.*, [37] revealed a significant increase in the reaction rate of struvite precipitation with an increased solution pH. However, extremely high pH levels can negatively affect the purity of struvite, leading to the formation of unwanted by-products. Therefore, it is crucial to control the pH within the optimal range to maximize struvite recovery efficiency and product quality.

The Purity of magnesium anode

The purity of the magnesium anode used in the electrolysis process can have a significant impact on the quality of the recovered struvite crystals [4]. Struvite crystals produced with higher purity magnesium anodes exhibit fewer impurities. Magnesium anodes that contain impurities or contaminants can introduce contamination into the struvite crystals during the electrolysis process [35]. Various studies have highlighted the importance of magnesium anode purity [5,10,14,15,22,45,46]. For instance, Kékedy-Nagy *et al.*, [8] demonstrated that a pure magnesium anode outperforms the AZ31 magnesium alloy in terms of struvite production and current density. Likewise, Robinson Junior *et al.*, [46] increased the applied current in a dual-chamber electrolytic reactor with a magnesium anode which resulted in a 5.7-fold of struvite yield. Kruk *et al.*, [45] also observed that a high-purity magnesium alloy cast anode was effective in producing high-quality struvite.

According to Wang *et al.*, [15], the composition of the electrode, whether it is pure magnesium or a magnesium alloy, has an impact on both the efficiency and mass of struvite produced. In another study, a comparison was made between pure magnesium and an AZ31 magnesium alloy. The results showed that the pure-Mg anode was able to produce approximately 4.5 times more struvite with a current density 2.8 times higher than the AZ31 alloy in a 6-hour batch experiment. Furthermore, the dissolution rate of pure-Mg was found to be higher at 1.2 $mg.cm^{-2}.h^{-1}$, compared to 0.8 $mg.cm^{-2}.h^{-1}$ for the AZ31 alloy [8].

The process by which Mg^{2+} ions are released from the magnesium plate anode is initiated when the Mg^{2+}

ions present on the surface of the magnesium anode undergo oxidation and are subsequently released as Mg^{2+} ions into the electrolyte solution during the electrolysis process. The fundamental reaction for the liberation of magnesium ions at the anode can be represented as follows:

$$Mg \rightarrow Mg^{2+} + 2e^- \quad (8)$$

The standard reduction potential for the mentioned reaction is -2.37 V SHE. This reaction occurs when the magnesium plate, acting as an anode, is submerged in an aqueous solution. As the magnesium atoms present on the plate's surface undergo oxidation, they dissolve into the solution as Mg^{2+} ions. This reaction is then accompanied by the polarization of the Mg anode in ammonia and phosphorus-containing solutions, resulting in the creation of a mixed outer film on the anode surface [5]. This mixed outer film comprises struvite crystals, which are formed through the reaction of magnesium ions with phosphate and ammonium ions present in the solution [8].

Regarding the precipitation of struvite in wastewater treatment, the augmentation of current applied to the magnesium anode facilitates the formation of struvite, while concomitantly diminishing the adsorption of struvite on the anode surface. This phenomenon contributes to the efficient recovery of phosphorus from wastewater.

Cathode material

The selection of cathode material used in the electrolysis process for struvite formation substantially affected the quantity and quality of precipitated struvite as shown on **Table** 1. Several studies have been conducted to investigate this matter. For instance, Cusick and Logan [11] discovered that cathodes made of stainless steel 304 mesh demonstrated higher phosphate removal compared to flat plates. This finding suggests that the surface area and structure of the cathode plate can influence the formation of struvite crystals [11]. In order to enable more adsorption sites for struvite precursor ions (Mg^{2+}, NH_4^-, and PO_4^{3-}), cathodes with a higher specific surface area can be used, thereby facilitating the cathodic deposition of struvite. Consequently, a surface that promotes the nucleation and growth of struvite crystals is advantageous for the overall process [47].

There are various types of cathodes employed in the crystal struvite electrolysis process, including graphite, titanium-based, aluminum, stainless steel, nickel, and carbon-based cathodes. Among these, graphite-based cathodes have been acknowledged for their outstanding performance. Yan *et al*., [48], for instance, discovered that the electronic conductivity of porous graphitized carbon, which has been enhanced, can considerably enhance the electrocatalyst's performance.

Graphite cathodes are known for their smooth surface area, which facilitates the easier recovery of deposited struvite crystals. This is due to their relatively inert nature and good electrical conductivity. Additionally, struvite harvested from graphite cathodes can exhibit high purity, and the cathode itself can be reused, indicating its better operational sustainability [15]. In the electrolysis process, graphite cathodes play a crucial role in efficiently creating high-purity struvite [49]. The researchers discovered that, under optimal conditions, the purity of struvite collected on the graphite cathode surface could reach up to 41.52% [15]. Wang *et al*., [41] demonstrated that electrochemical deposition on a graphite cathode can rapidly form pure struvite at a neutral pH. This finding was further supported by Cusick *et al*., [11] observed that the crystallization of struvite on the cathode of a microbial electrolysis cell depended on the applied voltage and cathode material, with graphite cathodes proving particularly effective. Cusick *et al*., [40] also demonstrated that stainless steel and graphite cathodes were effective in producing struvite in a single-chamber microbial electrolysis cell.

Furthermore, cathodes based on titanium typically exhibit exceptional corrosion resistance, a highly advantageous attribute in the corrosive conditions encountered in electrolysis processes [50]. Moreover, they can be effectively modified with coatings to facilitate the nucleation process and promote the growth of struvite crystals.

Other cathode materials, such as nickel-based cathodes, are widely recognized for their porous structure, which can effectively expand the available surface area for chemical reactions. This unique characteristic holds the potential to significantly enhance the precipitation of struvite crystals and thereby improve the efficiency of nutrient capture from wastewater. In support of this, Wang *et al*., [41] conducted a study demonstrating that the utilization of a nickel cathode within an electrolytic cell promotes the rapid formation of pure struvite at a neutral pH.

Current density

The current density has substantially contributed to the formation of struvite during the electrolysis process. Increased current densities have been shown to enhance the cathodic deposition of struvite, resulting in higher levels of struvite purity and deposition pro-

Table 1. Electrode materials and parameters for struvite crystallization in electrochemical processes

No	Anode Material	Cathode Material	Current Density	Solution, pH, Reactor Type	Results	Ref.
1	Magnesium (Mg) Plate	Graphite	0.01 A	Synthetic wastewater (2.5–3 g/L COD, 100 mg/L NH_4^+, 80 mg/L PO_4^{3-}), pH 7.35, Electro-AnMBR (Anaerobic Membrane Bioreactor with MF Membrane)	26% NH_4^+ and 48% PO_4^{3-} recovery as struvite, 77% struvite purity deposited on cathode, 600 mg of struvite separated from the reactor in one cycle (6 days)	[51]
2	Magnesium (Mg)	$Ti/PtIrO_2$	0.1 A	Synthetic wastewater (10 mg/L PO_4^{3-}, 34.6 mg/L NH_4^+, 0.3 g/L NaCl), pH 8.8, Electrodialysis system with a magnesium anode	65% phosphate removal as struvite (324.4 mg removed), final phosphate concentration in feed < 4 mg/L, estimated cost $31.27/kg of phosphate recovery	[17]
3	Magnesium (Mg) Alloy	Graphite	5.76 A/m²	Synthetic wastewater (39.7 mg/L NH_4^+, 80 mg/L PO_4^{3-}), pH 8.5, Electrochemical reactor with a 500 mL volume, Mg molar ratio of 1.2:1.0, 180 min electrolysis time	91% of undissolved phosphate precipitation deposited on the graphite cathode, struvite purity in deposition reached 41.52%.	[15]
4	Magnesium (Mg)	Stainless Steel (316SS)	5–10 mA/cm²	10 mM $NH_4H_2PO_4$ with NH_4Cl and $(NH_4)_2SO_4$, pH 7, Single-compartment reactor, Pulsating potential (0.1–100 Hz)	96% PO_4^{3-} and 50% NH_4^+ recovery as struvite, increased Mg dissolution by 25.3% (sulfate), energy consumption reduced by 203% (sulfate media)	[1]
5	Pure Magnesium (Mg)	Stainless Steel (316SS)	1.7 mA/cm² (pure Mg), 0.6 mA/cm² (AZ31 alloy)	0.077M ammonium dihydrogen phosphate ($NH_4H_2PO_4$), pH 4.5-6.0, single-compartment electrochemical batch reactor, no pH adjustment	Pure Mg anode produced 4.5 times more struvite than AZ31 alloy, crystalline struvite with elongated needle-shaped morphology and 30 µm particle length	[8]
6	AZ31 Magnesium alloy	Titanium (Ti)	50–200 mA	Synthetic wastewater with 100 mg/L and 10 mg/L PO_4^{3-}, 346 mg/L NH_4^+-N, 3 g/L NaCl, pH 8.8, single-compartment electrolysis reactor (1L volume) with a magnesium anode	Phosphate removal efficiency increased with current, high struvite ($MgNH_4PO_4 \cdot 6H_2O$) formation, lower Mg_2^+ release at high currents.	[5]
7	Pure Mg, AZ31, AZ91D	Titanium (Ti)	100 mA	Synthetic wastewater with 346 mg/L NH_4^+-N, 100 mg/L PO_4^{3-}, 3 g/L NaCl, pH 8.80, single-compartment electrolysis reactor	Pure Mg achieved 98% phosphate removal in 30 min, but AZ31 showed better sustainability with less impurity release	[4]
8	Pure Mg and AZ31 alloy	Stainless Steel (316SS)	Fixed Anode Voltage (-0.8V)	Ammonium Dihydrogen Phosphate (0.077M), pH 4.5, Single-compartment batch reactor with fixed potential	Pure Mg: 38% yield of struvite (3.2g), AZ31: 5% yield (0.5g), with struvite crystal sizes of 73µm (pure Mg) and 44µm (AZ31)	[52]
9	Magnesium (Mg)	Magnesium (Mg)	300 A/m²	Anaerobic bioreactor effluent, pH 8.4, monopolar batch electrocoagulation reactor	97.3% phosphorus recovery, 2.35 kWh/m³ energy consumption	[53]

10	Magnesium (Mg)	Stainless Steel (SS)	2–6 mA/cm^2	Synthetic swine wastewater (PO_4^{3-} and NH_4^+), pH 6.5–8.0, electrochemical batch reactor	94.2% struvite purity at pH 7.0 with a current density of 4 mA/cm^2; effective nutrient recovery and struvite formation	[54]
11	Magnesium (Mg)	Stainless Steel (SS)	~31 V potential	Municipal wastewater pre-concentrated using nanofiltration membranes, pH 8.1–11.2, single-compartment electrochemical reactor	100% PO_4^{3-} and NO_3^- removal, ~30% NH_4^+ removal, ~85% Cl^- removal, magnesium hydroxide and calcium carbonate precipitates	[55]
12	Magnesium alloy	Stainless Steel (SS)	2 mA/cm^2	Swine wastewater, pH 7.8, 1.5 L electrochemical reactor with Mg alloy anode	99% phosphate recovery, >90% ammonia nitrogen removal, 95.7% struvite purity after 45 min reaction	[56]
13	Graphite fiber brush	Titanium mesh (Pt coated)	7.9 A/m^2	10 mM struvite solution (Mg^{2+}, NH_4^+, PO_4^{3-}), 600 mM NaCl, pH 4.4–12.2, Microbial reverse-electrodialysis electrolysis cell (MRESC)	72% phosphate reduction, 7.62 g/m^2/h struvite precipitation rate, hydrogen production rate of 0.71 m^3-H_2/m^3-Van/day	[57]
14	Graphite fiber brush	Stainless Steel (SS 304)	0.5-1.1 V	Synthetic wastewater (60 mg/L P), pH 5.7 to 10.5, two-chamber microbial electrolysis cell (MEC) with a cation exchange membrane	Maximum 99.64% phosphorus recovery efficiency, 99.95% struvite purity, 4.1 kWh/kg-P energy consumption	[58]
15	Magnesium (Mg) Rod	Magnesium (Mg) Rod	2-12 V	Anaerobically digested chicken manure slurry, pH 3.00-7.90, single-compartment reactor with constant voltage electrolytic crystallization	Phosphorus removal rate up to 5.24 mg P h^{-1}cm^{-2}, struvite purity of 98.9% at pH 7.90	[22]
16	Magnesium (Mg)	Carbon plate	15.5 mA	Low-strength wastewater, pH 6.7–9.2, electrochemical constructed wetland (E-CW)	75.8% phosphorus removal, 61.6% struvite recovery, improved microbial community and electroactive bacteria population	[59]
17	Stainless Steel (SS 304)	Titanium (Ti)	10-50 mA/cm^2	Leachate from municipal solid waste (MSW), pH 6.5-8.0, electrochemical reactor	92% ammonia removal efficiency, phosphorus recovery as struvite crystals, high energy efficiency	[60]
18	Platinum-coated Titanium	Platinum-coated Titanium	317 A/m^2	Anaerobic digestion effluent, pH 7.36–8.46, electrochemical reactor with different electrode distances (10, 5, 1 mm)	Phosphate precipitation as hydroxyapatite (HAP) and struvite, energy consumption reduced by 53-64.6% with narrow electrode distance	[61]
19	Titanium (Ti) with Ir-Ru	Carbon cloth (Pt/C)	1.25 to 10 mA/cm^2	Digester centrate from municipal wastewater, pH 6.78–11.37, four-chamber electrochemical membrane system (4C-EMS)	95% nitrogen and 85% phosphorus recovery, 98% reduction in heavy metals in struvite, 8.2 kWh/kg-N energy consumption	[62]
20	Magnesium (Mg) Sacrificial Anode	Titanium (Ti)	40 mA	Supernatant of sludge alkaline hydrolysis, pH 9.0, single-compartment electrochemical reactor	92.3% PO_4^{3-}-P and 50.1% NH_4^+-N removal, struvite precipitation; ammonia further removed in second phase (up to 99% oxidation)	[63]

portion [15]. Wang suggests that cathodes with a high specific surface area, such as graphite cathodes, can offer a greater number of adsorption sites for both the formed struvite and precursor ions, thereby facilitating the deposition process [15].

The studies conducted by Bektaş *et al.*, [64] revealed that an optimal current density of approximately 4 mA/cm² was found to be effective in removing phosphate and ammonium from the solution. Notably, the reaction rate constants for phosphate and ammonium removal exhibited a significant increase with the rise in current density from 2 mA/cm² to 4 mA/cm² [54]. However, further increasing the current density to 6 mA/cm² led to a decrease in the removal rate [64]. This decrease can potentially be attributed to the rapid formation of an insulating layer of precipitates at higher current densities, thereby reducing the mass of Mg^{2+} ions generated from the hydrogen evolution reaction and potentially impacting the efficiency of struvite formation [15].

CHALLENGES IN THE ELECTROLYSIS PROCESS FOR STRUVITE CRYSTAL FORMATION FROM URINE

Struvite precipitation technology facilitates the extraction of nitrogen, phosphorus, and potassium from wastewater streams, thereby enhancing nutrient recovery capabilities. The electrochemical approach employed in struvite formation demonstrates high efficiency in capturing these crucial nutrients and converting them into valuable resources for agricultural and industrial purposes [6,65,66]. Struvite precipitation technology presents a promising solution for nutrient recovery from wastewater, offering both economic and environmental benefits [67]. The integration of electrochemical methods in urine management represents an innovative means to revolutionize nutrient recovery and address the urgent challenges of nutrient utilization and environmental sustainability [66,68–71]

As previously mentioned, the electrochemical method for struvite formation presents a sustainable and efficient approach to nutrient management, thereby reducing dependence on synthetic fertilizers [23,63,66,72]. This innovative technique enables the on-site recovery of nutrients from urine, resulting in minimized environmental impact and contributing to resource conservation by harnessing valuable nutrients.

To date, the process of electrolysis for the formation of struvite crystals from urine encounters various challenges that necessitate attention. One of these challenges pertains to the selection of appropriate anode materials, which are crucial for ensuring efficient phosphorus removal and optimal electrolysis performance. Another challenge involves the optimization of operating conditions, such as pH levels and flow rates, in order to achieve a high efficiency of phosphate removal and to maintain stable struvite formation [73]. Additionally, the management of by-products and potential side reactions during the electrolysis process poses further challenges that must be addressed to ensure the effectiveness and sustainability of struvite formation via the electrochemical process. To overcome these challenges, further research and development are necessary. Moreover, it is crucial to explore the scalability of electrochemical struvite formation in order to determine its feasibility and cost-effectiveness on a larger, plant-scale level. In summary, the electrochemical method for struvite formation exhibits significant potential for nutrient recovery from urine and sustainable nutrient management [6].

Furthermore, the intricate nature of urine composition presents a formidable obstacle, as it is intertwined with the existence of numerous organic and inorganic compounds in urine that have the potential to influence the efficacy of struvite formation and crystal growth. In order to confront this challenge, further research is imperative to comprehend the influence of diverse urine compositions on the electrochemical process, and to devise methodologies that can enhance struvite formation under varying urine compositions.

The variability in the composition of human urine that is determined by diet, hydration levels, and medical conditions, presents a significant challenge for the electrochemical formation of struvite crystals. Addressing this challenge requires extensive research to identify the most favorable operating conditions and to adapt the electrochemical process to accommodate diverse urine compositions. Moreover, the instability of urine composition over time and in varying physiological conditions further complicates the electrochemical formation of struvite crystals.

One innovative approach to address the challenges associated with urine composition in electrochemical struvite formation is the utilization of advanced sensors and real-time monitoring. These sensors can provide continuous feedback on the composition of urine, enabling real-time adjustments to the electrochemical process. Consequently, this allows for more precise control and optimization of struvite formation. The formation of struvite through the electrolysis process entails certain implications, such as the requirement for effective electrode materials and design in order to enhance the efficiency of the electrolysis process. These challenges underscore the necessity for innovative electrode materials and design to enhance the efficiency of struvite formation through electrolysis. In summary, the intricate nature and variability of urine composition pose significant obstacles in the realm of electrochemical struvite formation.

Other aspects such as the control of pH and conductivity are also crucial in the formation of electrochemical struvite. Therefore, it is necessary to carefully regulate the pH and conductivity of the urine in order to facilitate efficient struvite formation through electrochemical methods. Methods and technologies to overcome challenges in pH and conductivity control include the use of pH buffers and conductive additives in the electrolyte, as well as advanced control systems to monitor and adjust pH and conductivity in real time. These innovative approaches can help maintain optimal conditions for struvite formation as well as enhancing the efficiency of the electrochemical process.

In the electrochemical process of struvite crystal formation, there exists a possibility of undesirable by-products being produced. These by-products encompass the generation of hydrogen gas at the cathode and the discharge of toxic substances from the anode. To overcome these challenges, scientists have been conducting investigations into different approaches, such as employing alternative cathode materials to reduce hydrogen gas production and creating protective coatings on the anode to prevent the release of toxic substances. Furthermore, the size of the struvite crystals that are formed during electrochemical precipitation can also have an effect on the separation process.

FUTURE RESEARCH

From a technological perspective, struvite crystallization is evidently effective to recover nitrogen (N) and phosphorus (P). However, in practical wastewater treatment processes, various chemical collaborations may be needed to maximize the desired outcomes. Thus, future research should prioritize the investigation of different combinations of magnesium sources to strike a balance between process cost and product quality. In real industrial crystallization processes, crystals produced through spontaneous crystallization often exhibit poor settleability properties. Therefore, it is crucial to control the ratio of supersaturation in order to avoid the spontaneous nucleation process. A method to achieve this is through supplementation of additional seed materials in order to get a constant size.

Additionally, robust data on struvite crystallization is derived from laboratory-scale experiments. Consequently, there is a lack of necessary data for scaling up these technologies for industrial applications, which requires further expansion. Moreover, other technique to include struvite crystallization for pre-treatment or post-processing has been proven to enhance nutrient recovery. Exploring such aspects can contribute to reducing overall costs without compromising efficiency. For instance, the process of drying struvite crystals is evident to promote sterilization via bacterial inactivation.

Future studies on electrochemical struvite formation should prioritize the development of innovative electrode materials and enhancement of designs to reduce undesirable by-products. There should be a requirement in place to extensively investigate and optimize the regulation of pH and conductivity in the process of electrochemical struvite formation.

High-purity magnesium anodes can serve as a source of Mg^{2+} ions in the crystal struvite electrolysis process. In comparison to the AZ31 magnesium alloy, high-purity magnesium anodes demonstrate superior performance in terms of both struvite production and current density. The utilization of a high-purity magnesium anode plate serves the purpose of preventing the formation of impurities or foreign ions within the struvite crystals. Additionally, carbon graphite can be employed as a cathode in the struvite electrolysis process. This facilitates the enhancement of hydrogen gas evolution efficiency, while simultaneously preventing the discharge of toxic substances. It is worth noting that carbon graphite possesses a relatively smooth surface, thereby enabling the easy retrieval of struvite through scraping. This feature makes carbon graphite a renewable cathode material [15]. The research proposes the use of a cylindrical rod plate as the shape for both the cathode and anode. This choice offers advantages such as improved mass transport and an increased surface area for electrochemical reactions. Consequently, the rate of struvite formation and overall efficiency are augmented.

The process of electrolysis in the crystallizer column involved the strategic placement of electrodes at various stages within the column, aimed at optimizing the formation of struvite crystals. The electrochemical struvite formation process can be further improved through the implementation of advanced control strategies that focus on pH and conductivity. Consequently, additional research is required in order to assess the potential effect of multiple parameters like temperature and flow rate on this process. These investigations are crucial for the optimization of these variables, thus ensuring the attainment of maximum efficiency [8,15].

CONCLUSION

In conclusion, the efficient recovery of nitrogen (N) and phosphorus (P) from wastewater can be considered an effective pathway to address issues related to energy and environmental depletion. The struvite crystallization process particularly the electrochemical deposition method exhibits promising potential in enhancing pure struvite formed at a neutral pH. This technique offers several advantages, such as the utilization of high-purity magnesium anodes and carbon graphite cathodes, enabling the production of high-quality struvite crystals. Moreover, the employment of cylindrical rod plate electrodes and advanced control strategies can optimize the formation process. Overall, the electrochemical deposition method for struvite formation presents several benefits, including the prevention of foreign ions in the crystals, improved efficiency of hydrogen gas production, and the prospect of utilizing renewable cathode materials.

DECLARATION OF COMPETING 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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