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A review of chemical and bioelectrochemical process of N, P nutrient recovery as struvite ($MgNH_4PO_4·6H_2O$)

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ABSTRACT

The recovery of nitrogen (N) and phosphorous (P) from wastewater and its conversion to value-added products serve two purposes: satisfying the stringent N, P discharge threshold and meeting the demand for P fertilizers. The driving force for N, P recovery from an increased quantity of discharged wastewater is its environmental impact, on one hand, and the price of inorganic fertilizer and its judicious use, on the other. The available technology for N, P recovery is its precipitation and crystallization as struvite from diversified wastewater sources in several reactor models designed for the purpose. In addition, the electrochemical method of precipitation of struvite is also found to be very effective and novel. The use of electrogenic microorganisms is furthermore favorable to disintegrate the organic matter through the catalytic reaction and a simultaneous recovery of nutrients and the production of bioelectricity can be achieved. The advantage of the electrogenic microorganism method is a high percentage of recovery with good efficiency without the addition of any additional chemicals for pH adjustments. This review describes different aspects of chemical and electrochemical precipitation and the use of microbial electrolysis cell and microbial fuel cell in struvite precipitation from different sources. The critical factors influencing the efficiency and quality of the product are the technique adopted and the interacting process factors such as time and pH. The key differences in each process technology are described in detail with their pros and cons. To conclude, a robust process technology for quality struvite production facilitates its widespread use as a fertilizer.

Keywords: Phosphorus; Wastewater; Struvite; Bioelectrochemical method; Microbial fuel cell

1. Introduction

Sustainable development refers to the all-round development of society by preserving the ‘water–food–health’ chain and the environment for future generations [1]. A growing population has led to an increased demand for agricultural products and water, but at the same time, usable water is being depleted due to pollution. In recent decades, water availability per capita has dropped from 5,000 m^3/y to less than 1500 m^3 due to conflicting demands from different sectors such as industry, agriculture and households [2]. Pollution and overexploitation of groundwater resources have exacerbated the situation [3]. In addition, the non-biodegradable pollutants contaminate water bodies over time. So wastewater treatment plants have become a cost center in industry. As a result, technologies have to be created to convert “waste into value”, resulting

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in a win–win situation, and wastewater treatment plants can help in value generation [4]. A paradigm shift from a linear "use and dispose" approach to a more sustainable circular "use recover and recycle" approach is warranted to address this situation.

Among the various elements present in wastewater, nitrogen (N) and phosphorus (P) are considered valuable as they are the necessary food supplements for all living beings and play a significant role in scientific and horticultural improvement [5]. Soil productivity and overall food security rely on the routine inclusion of minerals accessible to plants, such as N and P [6]. But the excess of N and P introduced into freshwater damages the quality of water and the balance of the ecological system with consequent "eutrophication". This results in the need for additional wastewater treatment, a reduction in diversification of species, and expenditure on water systems. In addition, the accumulation of algae leads to livestock losses and human health problems.

Phosphorus, an essential nutrient, limits biological production due to its limited natural availability. The main source of phosphorus is calcium apatite ($Ca_5(PO_4)_3$(F, Cl, OH)), a mineral. China, the United States, Morocco, and South Africa possess more than 80% of the world's phosphate resources [7]. Several studies have predicted that economically viable phosphate rocks will last just over 100 y at best, and around 50 y at the least [8]. Wastewater is rich in nutrients and excess nutrients can cause eutrophication of water bodies and disrupt the ecosystem balance. Eutrophication has been a growing environmental concern since the mid-20th century [9]. The removal of nutrients such as N and P from the wastewater is therefore essential to keep the water bodies habitable for aquatic life [10]. Given this situation, phosphorus recovery and reuse become necessary to maintain phosphorus supplies, rather than removing it from spent streams. The major source of phosphorus in wastewater is human and livestock effluents as shown in Fig. 1 [11].

Given these facts, the critical recovery of the elements N and P from any water source such as municipal or industrial wastewater and agricultural stream is of great importance for conservation of the limited natural resources. Feasible technology allows for the safe removal of nutrient-rich waste and also helps to secure non-renewable geological P reserves.

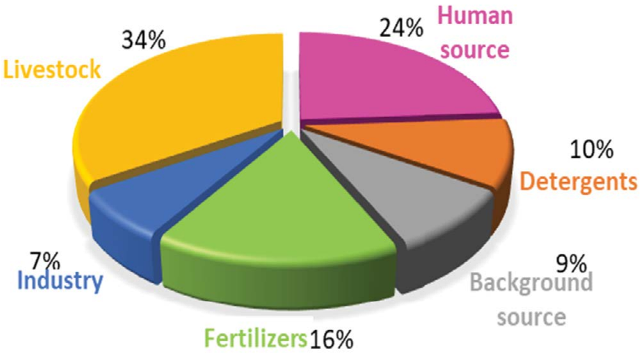

Fig. 1. Sources of phosphorus in the wastewater.

1.1. N, P removal from the waste stream

Traditionally, phosphorus was removed by chemical precipitation or by biological processes. Chemical precipitation of phosphorus is still widely employed for phosphorus removal due to its simplicity of operation and implementation. The resulting sludge is characterized by low bioavailability and the presence of heavy metals that are not suitable for direct use in agriculture [12,13]. In the chemical removal of phosphorus, the feed P is precipitated with iron or aluminum salt. Although this chemical process is technologically simple and also significantly reduces the chemical oxygen demand (COD), high chemical consumption and sludge build-up make it infeasible for regular use [14].

The biological approach uses certain microorganisms that have the ability to accumulate phosphate. The phosphate-accumulating organisms (PAOs) commonly used in activated sludge reactors are *Acinetobacter*, *γ-proteobacteria*, *Candidatus Accumulibacter phosphatis*, *β-proteobacteria*, *Dechloromonas β-proteobacteria*, and *Actinobacteria* [15–17]. This approach is relatively cheaper with minimum sludge volume. However, the biological microorganism processes are less stable and have limited flexibility, and their implementation depends significantly on the wastewater properties [18].

Some of the other nitrogen removal methods in practice are the use of biosolids [19–21], adsorption using zeolites [22], stripping [23]; and chemical precipitation with magnesium (Mg) and phosphate [10,24]. Each technique has its own advantages and disadvantages. This review focuses on the simultaneous removal of N and P from wastewater as moderately insoluble magnesium ammonium phosphate (MAP). This review is based on available literature primarily with regard to optimization of process conditions like pH, concentration of ions, time, supersaturation ratio, nature of influent, and type of the reactor [24].

In contrast, struvite is a difficult substance to handle, especially in wastewater and sludge treatment plants where struvite deposit on pumps, pipes, valves, and centrifuges blocks the flow of the liquid. The growth of this deposit over time leads to an apparent reduction in the flow area of the pipes and equipment, resulting in high pressure drop/resistance. Finally, this leads to high energy consumption and reduction in the capacity of the wastewater treatment plant. The increasing strictness on the limits of effluents and the intensification of waste have increased the cost of treatment, making the recovery of phosphorus in the form of struvite more attractive.

1.2. Struvite as a fertilizer

Struvite has a potential efficiency over conventional fertilizers due to its low solubility [25,26]. Commercially available phosphorus fertilizers are readily soluble and hence a high concentration of applied fertilizers is washed away during rainfall. Struvite, which is a slow-release fertilizer, can minimize the concentration of P absorbed on the soil or released into the land. These advantages could increase the crop yield and reduce the application rate of P, thereby reducing environmental impact [27]. The struvite produced annually from wastewater treatment plants is enough to produce fertilizers that can be applied to several hectares of arable land. Several tonnes of phosphorus as MAP could be produced annually if this struvite recovery process from treatment plants is done on a global scale. It also reduces the extraction of phosphate from rocks by 1.6% [28]. In the last 10 y, struvite precipitation has attracted attention as it is an efficient way of recovering N and P [29]. So the objective of this review is to present the processes involved in the production of the struvite as available in the literature.

In 1998, MAP was first recovered in Japan. It was shown that the chemical costs associated with the treatment and removal of phosphorus can be offset against the value achieved by producing struvite [30]. However, the process is tedious and pumping during the cleaning period is highly prohibited. In 2016, struvite recovery processes have been developed around the world, including Ostara Pearl™, which is used commercially. The product has about 6:29:0 N:P:K value (Mg) and showed some beneficial properties such as the slow release of nutrients and a strong supply of phosphorus. This slow-release fertilizer can increase pH, making it suitable for acidic soils [31]. In terms of phosphorus release, struvite and mono-calcium phosphate (a water-soluble source of phosphorus) do not differ significantly and are generally considered to be fully available to plants.

1.3. Technologies employed for struvite production

As current research focuses on more efficient and energy-conserving methodologies such as electrochemical and bioelectrochemical processes, this review emphasizes the different aspects of these technologies. Fig. 2 shows the technologies adopted for struvite production.

2. Chemical precipitation cum crystallization of struvite

Struvite was first characterized in 1845 by German scientist Georg Ludwig Ulex [de] (1811–1883), who discovered struvite crystals in a medieval midden near Hamburg, Germany. The word "struvite" is derived from the name Von Struve (1772–1851), a geologist. Struvite ($MgNH_4PO_4{\cdot}6H_2O$) is a compound with an equimolar concentration of magnesium, ammonium, and phosphate and six hydrated molecules (water) as indicated in Eq. (1) [32]. It is mildly soluble under neutral and alkaline conditions.

$$\mathrm{Mg}^{2+} + \mathrm{NH}^{4+} + \mathrm{H}_n\mathrm{PO}_4^{n-3} + 6\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{MgNH}_4\mathrm{PO}_4.6\mathrm{H}_2\mathrm{O}{+}n\mathrm{H}^+ \tag{1}$$

Crystallization of struvite is a two-step process made up of nucleation and crystal growth. The nucleation of the crystals requires a state of supersaturation of the solution, which depends on the mass transfer rate through diffusion (intermolecular diffusion). Supersaturation is an equilibrium at which the ionic activity product (IAP) exceeds the solubility product (K_{sp}) and crystallization occurs. IAP can be expressed by Eq. (2). It is also very important for driving the crystallization step [33]. The degree of supersaturation can be derived from the concentration of the solute in a given solution to that of the solubility product. For the crystallization of struvite, the degree of saturation (S) can be obtained from Eq. (3) wherein the concentrations of magnesium, ammonium, and phosphate are taken into consideration [34]. If this supersaturation ratio is greater than 1.0, a faster rate of struvite crystals can be expected [35].

$$\mathrm{IAP} = \left[\mathrm{Mg}^{2+}\right]\left[\mathrm{NH}_4^+\right]\left[\mathrm{PO}_4^{3-}\right] \tag{2}$$

$$S = \frac{f_1\left(\mathrm{NH}_4^+\right) f_2\left(\mathrm{Mg}^{2+}\right) f_3\left(\mathrm{PO}_4^{3-}\right)}{K_{S,O}} \tag{3}$$

where f is the ionic species activity in relation to the struvite components in solution and $K_{s,o}$ is the struvite solubility product.

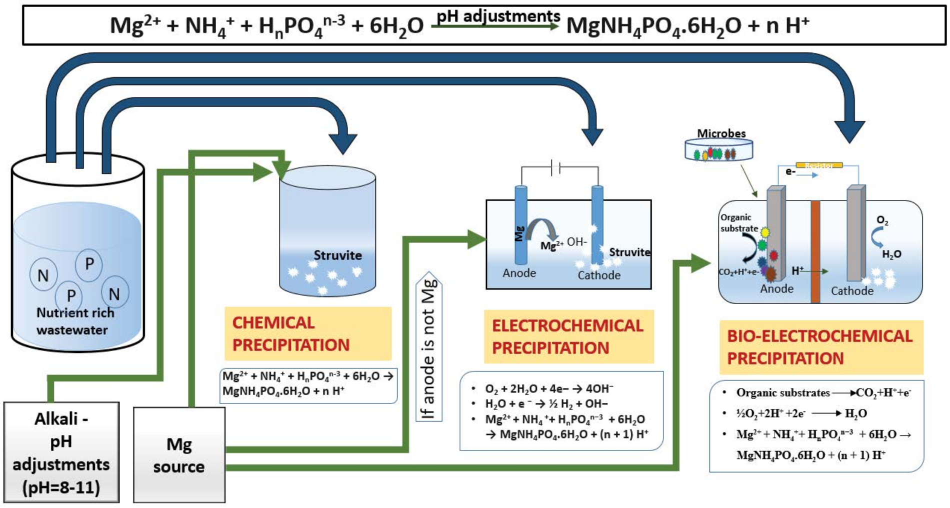

Fig. 2. Schematic representation of struvite production technology.

The next step is nucleation, where the growth of the crystals depends on the integration mechanism due to intramolecular diffusion [36]. In the primary nucleation process, which is either homogeneous or heterogeneous, the internal solution characteristics trigger nucleation. It depends mostly on degree of supersaturation and stirring speed whereas the secondary nucleation arises from external factors such as the presence of some crystal present in auxiliary devices like the vessel surfaces and stirring blades. This will occur even at a lower supersaturation level [37]. Finally, the nuclei are extended to the visible crystals during the step of continuous crystal growth [38]. In homogeneous nucleation, the formation of crystals in a fluid is devoid of other particles or rough surfaces [39].

The free energy required to form a critical nucleus is lowered when there are contaminants in the solution, such as foreign surfaces, resulting in heterogeneous nucleation. Therefore, the maximum level of supersaturation favors homogenous primary nucleation to emerge spontaneously among the many nucleation mechanisms. Yet another critical factor, namely the induction time, is the time it takes for the first stable nucleus to develop. The time to reach the degree of saturation is critical to balance the nucleation characteristics [40,41]. The number of struvite nuclei generated per unit of time and volume is known as the rate of nucleation (J) [42] as shown in Eq. (4).

$$J = A\exp\left[-\frac{16\pi\gamma^3 v^2}{3k^3T^3\left(\ln\Omega\right)^2}\right] \tag{4}$$

where A – kinetic factor; γ – interfacial tension between a crystal and the solution (mJ/m); v – molecular volume (cm^3); k – Boltzmann constant (1.38 J/K); T – absolute temperature (K); Ω – supersaturation ratio

Other than the above factors, several physicochemical parameters also influence struvite formation like solution pH, temperature, mixing ratio, and the magnesium source.

pH plays a significant part in precipitation with struvite. A pH between 7 and 11 is suitable for the precipitation of struvite; however, a value of 7.5–9 is the most acceptable [43]. The pace of pH shift influences crystal development and quality of the precipitated crystals [33]. At pH ≤10, the NH$_4^+$–N content in the precipitate decreases as the pH of the solution rises [44]. Various studies have been done to investigate the influence of pH in the process of removal of N and P [45–48]. During struvite production, pH will be lowered due to the release of protons, thereby improving the solubility of struvite, which is not conducive to the phase of crystal formation [40,41].

Table 1
Properties of struvite

Crystallography	White, inorganic, morphologically orthorhombic crystal
Hardness	1.5–1.7 (Mohs scale)
Thermal decomposition	Dehydration starts at 55°C and becomes anhydrate at 250°C
Specific gravity	1.71
Molecular weight	245.5 g/mol
Solubility product	2.5×10^{-13}

In general, the increase in N and P removal occurs at alkaline pH, but increasing pH values, on the other hand, will decrease the size of the precipitated aggregate [49]. From these factors, it is clear that struvite crystal morphology is influenced by pH. According to Matynia et al. [50], the pH changes from lower (pH = 8) to a higher value (pH = 11), considerably reducing the mean struvite crystal size formed in synthetic solutions. To modify the pH, aeration or chemicals like NaOH and HCl might be used.

The mixing ratios of phosphate, ammonium, and magnesium ions is another critical factor that affects struvite precipitation and crystallization. A wide range of Mg: P ratios were used although the effective ratio was determined to be 1 or 1:2 in the majority of cases. The effect of the Mg:P:N ratio on struvite formation was studied in a series of experiments [51]. In fact, lower Mg:NH$_4$:PO$_4$ ratios (0.5:1:1, 0.8:1:1, 1:1:0.5, 1:1:0.8) decrease the chemical oxygen demand removal rate in comparison to high concentrations like 1.2:1:1, 1.5:1:1, 1:1:1.2, 1:1:1.5 [52]. At last, it is concluded that the unimolar ratio of Mg: P: N would be sufficient for the removal of N and precipitation of struvite. At a pH of around 9.5 and an Mg: P molar ratio of 1:1, the average size of the crystal was smaller. As the Mg:P ratio increased to 1:1.2, the crystal size also increased [53]. Based on the phosphate level in the wastewater, several other researchers discovered bigger crystals with a greater magnesium molar ratio [54,55].

Magnesium is usually the limiting component in the crystallization of struvite, as generally, wastewater contains low concentration of this element. In most cases, MgCl$_2$ is used, as it is the cheapest soluble substance and most available source of magnesium [56]. MgO and Brucite are other sources that are good sources of Mg and also considered as pH-enhancing agents. Some researchers have used MgO and Mg(OH)$_2$ [57]. If magnesium is dosed under the theoretical value of the Mg^{2+}:PO$_4^{3-}$–P molar ratio of 1:1, the system is under optimized conditions for P recovery, but excessive dose does not favor P recovery, as co-precipitation of other compounds can occur [58].

Researchers found that there were no significant variations in ammoniacal nitrogen (N) and chemical oxygen demand between MgCl$_2$ and MgSO$_4$. When MgO was employed as a magnesium source, there was a significant reduction in ammoniacal nitrogen and chemical oxygen demand [51]. Increased total suspended particles due to magnesium hydroxide were also observed, resulting in decreased N removal [59]. MgCl$_2$ as a magnesium source is more acceptable for obtaining the highest efficiencies of nitrogen removal and chemical oxygen demand. As a result, MgCl$_2$ can be recommended as the best alternative for obtaining maximum N removal through wastewater recovery.

Precipitation time is another factor that maximizes the removal efficiency. The reaction time of about 40 min was sufficient for the settling of the formed struvite. It was found that when there was no sufficient precipitation time, phosphate removal efficacy was also poor. There was no appreciable increase in the phosphate recovery percentage after

40 min [60,61]. It was reported that crystals having size of about 20 µm were formed within 10 min of the reaction and a maximum crystal size of 75 µm was achieved after 1 h of mixing. However, a mixing time longer than 60 min broke the crystals [62]. Temperature affects the solubility of struvite [63]. Many researchers have reported on the solubility of struvite at different temperatures as shown in Table 2 [64–66].

The precipitation of struvite at elevated temperatures is not possible because higher the temperature lower the solubility product. In addition, evaporation of ammonia needs to be avoided, which is a serious concern at elevated temperatures. However, temperature also influences the growth of the crystals by influencing the diffusion rate and integration of the surface. The solubility of struvite increases with temperature and hence the precipitation becomes difficult at higher temperatures. Therefore, the optimal temperature for struvite precipitation is in the range of 25°C–35°C in both synthetic liquids and digesters. At high temperatures, diffusion is faster and precipitation occurs almost spontaneously. Newberyite ($MgHPO_4{\cdot}3H_2O$) precipitates more readily at high temperatures than struvite [67]. Fig. 3 depicts the phase changes of struvite under different conditions [68].

2.1. Reactor design

Modeling can be done to analyze the reaction mechanism, and process parameters are considered to predict the performance of the process [69]. Some of the models used for the struvite crystallization are as follows:

- Black box models (BBM), also called empirical models, are only based on experimental findings. For struvite crystallization, BBM uses experimental design techniques such as central composite design [70], Taguchi's design of experiments [71], and Box–Behnken design [72].
- Semi-mechanistic models (SMM) combine the chemical reaction and nucleation descriptive functions [73].
- Thermodynamic models – The supersaturation ratio of solid species in the solution is the basis of the calculations [73].
- Kinetic models.

Table 2
Solubility range for different temperatures

Temperature range	Solubility range	Reference
10°C to 50°C	0.3×10^{-14} to 3.73×10^{-14}	[65]
15°C to 35°C	$10^{-13.17}$ to $10^{-13.08}$	[66]

Different types of reactors [74–85] used for struvite recovery are presented in Table 3. As shown in the table, the type of influent and its chemical composition, reactor model, and applied reaction conditions have a significant effect on recovery as well as crystal size. From the use of different reactors discussed above, the stirred tank reactors and fluidized bed reactors (FBR) are widely used. A stirred tank reactor is a straightforward system that provides homogeneous mixing of wastewater and reactants [86]. In FBR, the central section is used for crystal nucleation and growth favoring the crystallization of struvite. One of the benefits of FBR is the rapid development of crystals as the influent is injected from the bottom and recirculated [87].

In these studies, the main drawback faced is crushing of the crystals to a fine particle. It reduces the efficiency of P recovery. In FBR, the pellet fluidization necessitates a high up-flow velocity, but it resulted in microcrystalline materials with little settling ability. In view of the above drawbacks in the precipitation methods, currently research is focused on electrochemical process for struvite recovery as the main advantage of product recovery in this process is that no chemicals are added for adjusting the pH of the solution. The description of this technique has been presented in the following section. In this technique, the electrochemical reduction of water molecules increases the OH^- concentration near the cathode, which provides desirable pH for struvite precipitation. In addition, if it is constructed as a microbial fuel cell, the simultaneous harvesting of electricity and struvite from wastewater containing N and P can be achieved and regarded as a breakthrough in the struvite recovery process [88]. Fig. 4 shows the trend in yearly publications

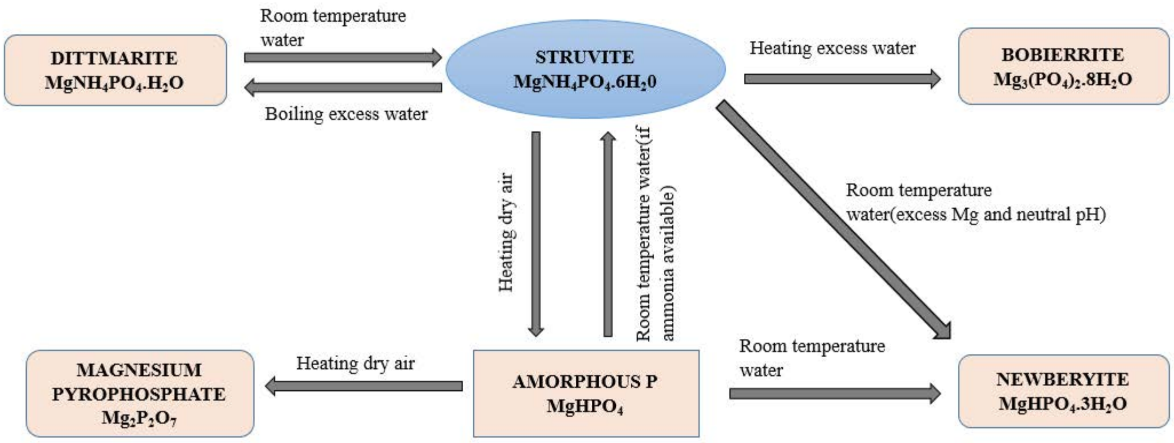

Fig. 3. Phase changes of struvite at different conditions.

Table 3
Summary of struvite recovery from different types of reactors

References	Source	Product	pH	Reactor	Observations
[74]	Municipal wastewater	Struvite	7.9	Rotating algal biofilm reactor	80% P recovery when Mg:P molar ratio is 1.5:1
[75]	Dairy cow urine	Struvite	9.5	Vertical reactor	Orthorhombic crystal or rod shape crystals of struvite with 33.2% phosphate and 27.9% ammonium
[76]	Swine wastewater	Struvite	9.0–10.0	Fluidized bed reactor	Irregular, rectangular, ortho rhombic crystals with 91% PO_4 removal
[77]	Anaerobic digested slurry	Struvite with 88%–90% purity	10	Cone type reactor with aeration	99% of P and 89% of N; at pH = 10; Mg:P = 1.6; N/P = 1.2
[78]	Source separated urine	Struvite with 90% purity	8.6–9.3	Continuous fluidized bed reactor	85% to 99% recovery efficiency of P. During the MAP precipitation, 26% ± 5% of the influent COD and 16% ± 1% of the NH_4^+–N were lost
[79]	Synthetic wastewater	Struvite with mean crystal size 22–41 μm	9–11	Draft tube, mixed suspension mixed product removal type crystallizer	The mean crystal size and homogeneity decreased as the Zn^{2+} concentration increased The size of the struvite crystals was likewise reduced when the pH was raised
[80]	Synthetic solution for batch tests, and centrifuged digested pig slurry for continuous assays	Struvite and other elements (chloride, sodium and potassium)	7–10	Batch experiments and continuous assays in a 20 L lab-scale reactor (isotherm glass reactor with a settling zone)	Optimum pH at 9, and no influence of temperature. High Ca^{2+} reduces the recovery of Mg^{2+} and NH_4^+. The presence of organic matter resulted in the reduction of struvite crystal size
[81]	Source separated urine	Struvite	8–9	Batch reactor with vertical baffles and dual impeller	Optimum pH–8.9. Influence of addition of $MgSO_4$
[82]	Anaerobically digested dairy manure	Struvite and hydroxyapatite	8–9	Batch experiments	Ca^{2+} was the interfering ion HAP precipitated at pH > 9.5–10. Carbonate inhibited calcium phosphates formation
[83]	Aerobically digested swine wastewater	Struvite	8.5–9	Sequencing batch reactor (SBR) and continuous-flow reactor	Computer models (PHREEQC and MINTEQA2) were used for understanding phosphate crystallization. P-removal = 36%–74% and NH_4^+–N removal = 40%–90% through air stripping
[67]	Swine wastewater	Pure struvite	8–9	Plexiglass reactor with an aerator. Consists of two zones: (a) reaction zone and (b) settling zone operated continuous flow model is adopted	Mg: P ratio suitable for enhancing the crystallization of struvite was found to be 0.8–1.
[84]	Swine wastewater	Struvite	8–9.0	Continuous flow reactor	Coarse struvite crystals with an irregular form with 93% PO_4 and 31% NH_4 removal. The Mg: P was maintained to 1.2:1
[56]	Landfill leachate	Struvite	8.0–9.5	Batch reactor	Coarse, irregular crystals with 85.5% PO_4 removal. PO_4:Mg molar ratio is 1:1.1
[85]	Synthetic wastewater	Struvite	8.5–11	Pilot-scale continuous flow reactor	Elongated crystals with 81% PO_4 and 56% NH_4 removal with a 2:1 molar ratio of PO_4: Mg

on the electrochemical and bioelectrochemical recovery of nutrients. In 2012, the research and the related publications were very few, but since then, new methods of extraction and design of reactors are on the rise.

3. Electrochemical technology for struvite recovery

An electrochemical method was implemented for the precipitation of pure struvite ($MgNH_4PO_4{\cdot}6H_2O$) from the mixed ionic solution containing phosphate, ammonium, and magnesium. Due to the reduction of oxygen or water molecules, there is a strong pH increase near the cathodic plate [as shown in Eqs. (5) and (6)] and it is more than enough for the precipitation cum crystallization of struvite [89]. The general chemical reaction of the formation of struvite is shown in Eq. (7) and the basic principle of the electrochemical reactor is depicted in Fig. 5:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{5}$$

$$H_2O + e^- \rightarrow 12H_2 + OH^- \tag{6}$$

$$\begin{aligned} &Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \\ &\quad \rightarrow MgNH_4PO_4 \cdot 6H_2O + (n+1)H^+ \end{aligned} \tag{7}$$

The main advantage of this process is the formation of additional by-products like dittmarite (monohydrate form of struvite) and newberyite deposition. Furthermore, water sanitization can be aided by the oxidation process occurring at the anode plate [90].

3.1. Parameters influencing electrochemical precipitation

Similar to chemical precipitation, this process is also influenced by a few critical factors. They are typically the molar concentrations of ions such as NH_4^+, PO_4^{3-}, Mg^{2+}, and their ionic strength in the solution, pH, and temperature of the system. The ideal pH range reported for struvite formation is between 8.0 and 11.0 [91]. However, its control is varied in different works. Kékedy-Nagy et al. [92] suggested the pH value in the range of 8–10 as optimal. The lower pH (<7.5) decreases the rate of P removal. Anodic corrosion of magnesium releases OH^- ions that could prevent electrochemical oxidation of magnesium. On the other hand,

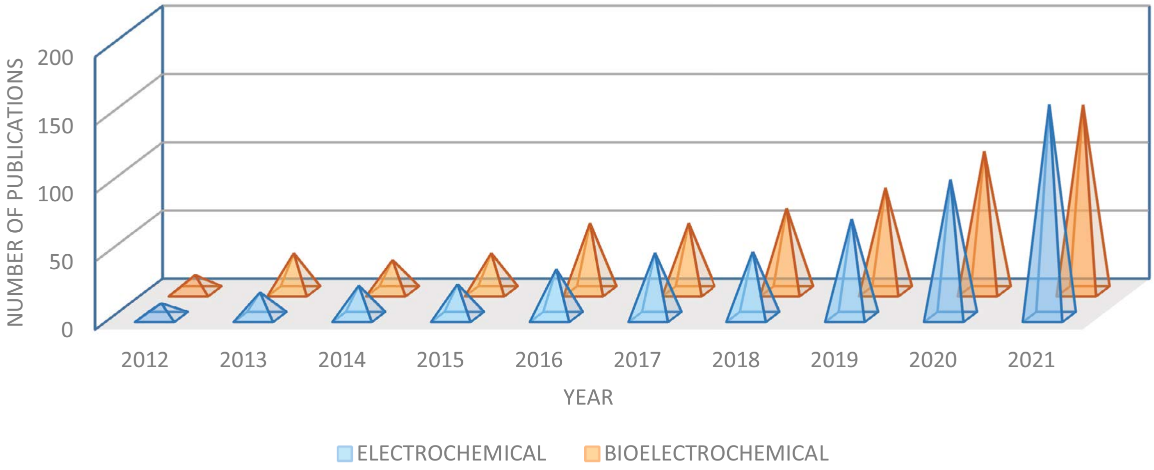

Fig. 4. Reports on struvite recovery using electrochemical and microbial fuel cell technology (Scopus source).

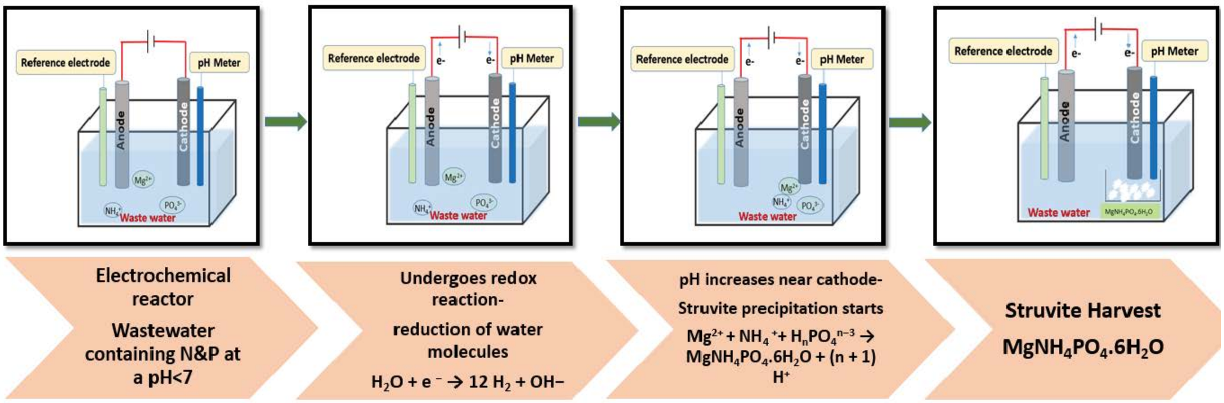

Fig. 5. Basic working principle of an electrochemical reactor for struvite recovery (Schematic representation).

the initial pH itself is maintained above 8.5, so there will not be any change in the final pH and the corresponding phosphate recovery also decreases dramatically. So, alkali wastewater is not a good source for nutrient recovery using electrochemical struvite induction [93].

A pH adjustment is essential for maintaining the concentration of ions above the solubility product (K_{sp}). On increasing the pH from neutral to 9.0, precipitation efficiency is improved with lower content of residual PO_4^{3-}–P (18 mg/L) and above which (pH 10.0), it is greatly reduced [94–97]. It is also be reported that higher pH (pH = 10.0) favored the rate of removal of NH_4^+–N because of which free ammonia escapes, reducing the concentration of NH_4^+–N, and hence reduction of struvite precipitation. From the literature, it was proved that the ideal window for the pure form of struvite recovery is the pH between 9 and 9.5 [93]. The purity of the struvite is affected because of the production of amorphous $Mg(OH)_2$ and $Mg_3(PO_4)_2$.

As reported by Huang, the maximum purity obtained was in the range of approximately 70%–90% with time [98]. This can be explained on the basis of electrolysis reaction, in which the amount of Mg discharged from the anode is proportional to the applied current. Therefore the purity of struvite is affected by the current applied in the system; for example, when the current was increased to a certain extent (40 to 80 mA) in a 2 h process, the purity of struvite increased, but reduced again when the current was further raised to 120 mA. It is concluded that struvite precipitation increased with increasing release of Mg^{2+} ions, leading to an increase in purity [93].

The effect of the nature of the electrolyte on the process was reported by a few researchers. As the electrolyte concentration increases, the removal rate of nutrients also increases. But these effects are not remarkable. Instead, the electrolytes are used to affect the conductivity of the aqueous system. The concentration of electrolyte and conductivity are directly proportional. So an increase in conductivity results in a low energy consumption, which makes the system efficient [99]. The concentration of electrolytes such as NaCl affects the phosphate and nitrogen removal efficiency. The removal rate of ammonia nitrogen is very high when the concentration of chloride ions is high [93]. Even though this improves the release of NH_4–N, there is a reduction of struvite precipitation because of a reduction of NH_4^+–N to N_2 gas by chloride ion.

Liu et al. [100] designed a reactor by optimizing parameters such as reaction time, applied voltage, and the concentration of NaCl. The impact of recycling the dissolved solution on struvite crystallization was also investigated. As anodes, titanium plates coated with iridium oxide were used, while the cathodes were stainless steel plates. The electrolytic reactor was composed of Plexiglas. Phosphate (PO_4^{3-}–P) was dissolved at 49.17 mg/L, while ammonium–nitrogen (NH_4^+–N) was eliminated from the solution. The maximum obtained PO_4^{3-}–P removal efficiency was 79%, and that of NH_4^+–N removal was 53%, respectively [100]. Wang et al. (2010) demonstrated a highly efficient process recovery in a cell with graphite and nickel as anode and cathode, respectively. The reaction was performed at a low voltage and neutral pH [89]. A typical setup has been depicted in Fig. 6. Other than graphite, titanium and various Mg sources are utilized as electrodes.

Huang et al. [98] devised a modified electrochemical approach termed coupled electrochemical process for recovering phosphate as struvite and eliminating ammonia nitrogen from swine wastewater. Magnesium alloy was used as a magnesium source for struvite crystallization by applying a current of 2 mA/cm^2 for 45 min, which resulted in high phosphate recovery efficiency of 99%. Similarly, a comparative study was done with an electrochemical reactor that uses Mg in pure form and its alloy AZ31 as the anode (Fig. 7). The measured Mg dissolution rates for the pure-Mg and AZ31 Mg alloy anodes were 1.2 and 0.8 mg/cm^2·h, respectively [101].

Tan et al. [102] followed a similar approach of using magnesium as the anode in a single-compartment reactor for

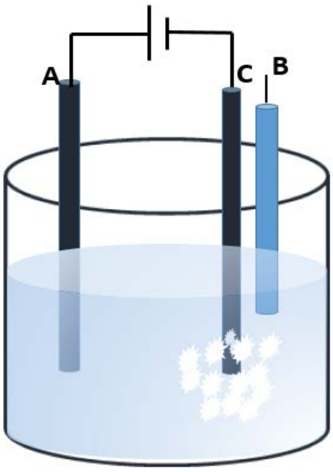

Fig. 6. Schematic representation of experimental electrochemical deposition of struvite. (A) Graphite (Anode), (B) pH meter, and (C)-Nickel (Cathode).

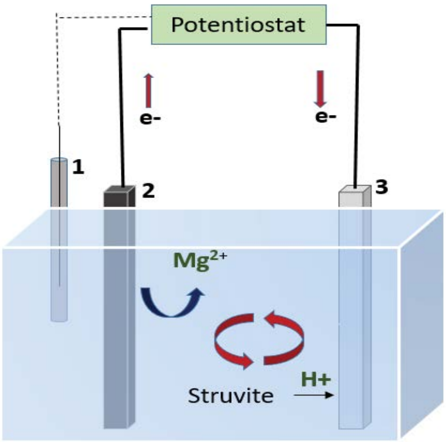

Fig. 7. Schematic diagram of the electrochemical setup. (1) Ag/AgCl-Reference electrode; (2) Mg-Sacrificial Anode; (3) Stainless Steel-Cathode.

recovering phosphate and nitrogen from urine. Phosphate recovery capacity employing a magnesium anode as an electrochemical magnesium dose exceeded 10 mg/P/cm^2·h at a current density of around 14 mA/cm^2 and 20 min anodizing duration. Recovery of ammonium by electrochemical oxidation was achieved with 80% efficiency. In electrochemically assisted struvite formation, magnesium is used as a sacrificial anode to protect the metal from corrosion. Hug and Udert [104] utilized sacrificial magnesium electrode for magnesium dosing and found it to be remarkable that it also reduces the cost of additional dosing. Kruk et al. [103] demonstrated a reactor with 90% purity using sacrificial magnesium anode at a pH between 7 and 9 and P:N molar ratio of 1:1.9. Thus the addition of $MgCl_2$ and $MgSO_4$ or sacrificial magnesium electrodes is found to be useful in this technique, which might be more expensive than using MgO [104].

As an advancement in the field of electrochemistry, ultrasonography was incorporated in the electrochemical reactor. Ultrasound irradiation accelerates the chemical reactions by using sound waves. In this process, the electrodes will be continuously cleaned, which enhances mass transfer and hence the speed of production [105]. In artificial wastewater, the electrochemical production of struvite by using Mg in pure and AZ31 alloy form was investigated and the effect of ultrasound was also analyzed and proved to be very efficient in terms of yield. Furthermore, the application of ultrasonics to the solution boosted the product's mass, as a result of the electrode surface's continual activation by cleaning [106].

Zhang et al. [107] reported a technique utilizing electrochemical acidolysis of magnesite. By dissolving magnesite constantly in the anolyte, the magnesium ions are moved to the cathodic chamber, thereby increasing the pH in the cathodic part and allowing struvite precipitation to occur. As the magnesite dosage and applied voltage increased, the recovery efficiency of phosphate also increased. Li et al. [108] also designed a reactor that uses the electrochemical decomposition of natural magnesite to provide magnesium continuously. The recovery rate of PO_4^{3-} was between 86.6% and 93.3% after a 21-d continuous operation, indicating that the process was stable. When compared to the typical chemical approach, which uses $MgSO_4·7H_2O$ and NaOH, the suggested electrochemical–decomposition process can save up to 60% on phosphate recovery costs.

Bringing novelty to the technology, capacitive deionization (CDI) was used as an electrochemical technique that saves most energy while sacrificing continuity and selectivity. In CDI, water can be deionized by applying a potential difference between the electrodes. The positive and negative ions are separated using an ion exchange membrane and they are concentrated. Based on CDI, Ren et al. [109] developed an electrochemical reactor in which electrolyte cyclic flow was adopted in between the electrode chambers to continuously recover phosphate and ammonium selectively from wastewater. This process enables to repeat of the reaction indefinitely and the long-term stability of the product was confirmed. Table 4 summarizes different types of electrochemical reactors and process conditions adopted [89,98,101–104,107,108,110,111].

Electrocoagulation (EC) is also a technique that is related to the electrochemical principle. EC can remove pollutants from effluents by producing hydroxides by conducting electric current from sacrificial electrodes [112]. Electrocoagulation is a comparatively compact and robust treatment alternative to standard treatment procedures that utilize sacrificial metal anodes, which initiate electrochemical processes, supplying active metal cations for coagulation and flocculation. It has the benefit of not requiring the addition of coagulants to the wastewater, which means that water's salinity does not change after treatment. Though it is a complicated process that involves several pollution removal mechanisms working together, it is highly efficient [113].

Kim et al. [110] employed magnesium-air fuel cell electrocoagulation for struvite recovery as well as electricity production. The removal efficiency of phosphorus from synthetic wastewater was studied by varying the concentration of phosphate and the electrolyte (NaCl). It was found that regardless of the baseline phosphate and NaCl concentrations, the removal of phosphate rises linearly with the Mg:P molar concentration ratio [114]. It has been also used for the removal of COD along with the nutrient recovery from wastewater collected from cheese manufacturing, which is a high-organic, phosphorus-rich residue. This study was done to extract the phosphorus content of whey from sludge and sediment generated using aluminum anode, Ti/RuO_2 cathode. Using this technique, 99.4% of phosphorus was removed, in which 87.4% is in the form of struvite along with the reduction of COD to the extent of 86% [115]. There are other reports available using iron electrodes for the removal of N and P from urine instead of recovery [116,117].

4. Bioelectrochemical methods

Bioelectrochemical systems offer a promising technique for the removal of nutrients from wastewater. A typical unit is presented in Fig. 8 [118]. It consists of two compartments for anode and cathode and is connected using a cation exchange membrane. In the anodic compartment, the wastewater source and the microorganisms are introduced. The electrons formed at the anode flow to the cathode, generating electricity through proton transfer in the cation exchange membrane. The reduction of water molecules results in an increase of pH, which is suitable for struvite formation. The advantage of microorganisms here is the catalytic activity in the decomposition of organics present in the waste, which in turn enhances the content of the N, P. During the electrochemical reaction, bio-hydrogen production is feasible in addition to chemical precipitation at the side of electrodes. The recovery of solid by stripping is normally followed. Generally, these types of reactors are known as microbial fuel cells (MFC) or microbial electrolysis cell models (MEC).

The removal of nutrients from the anode chamber in bioelectrochemical system (BES) is subject to many factors such as the ammonium and phosphate ion concentrations in the wastewater, the pH of the catholyte, the electric current density, the membrane type, and the concentrations of ions

Table 4
Summary of struvite recovery using electrochemical technology

Reference	Source of wastewater	Conditions	pH	Recovery of nutrients percentage
[89]	Synthetic wastewater	- Anode: inert platinum sheet - Cathode: nickel sheet - Electrode spacing of 2.0 cm - 3–12 V DC voltage applied	7.0–7.5	- Removal rate of 94.5%–96.1% of phosphate - 97.1% of struvite precipitation - Presence of calcium ions reduced the phosphate removal efficiency
[104]	Urine	- Flat and rear sides covered electrodes - Anode: magnesium plate - Cathode: steel plate - Inter electrode distance is 5.5 cm - Stirring rate is approximate 275 rpm	9.0–9.4	- 85% of removal efficiency of phosphate - 100% current efficiency - Energy consumption = 1.7 Whg/P
[98]	Swine wastewater	- Combination of two reactors R1 and R2 - Anode of R1: magnesium plate - Cathode of R2: stainless steel mesh plate - R2 has two parallel graphite electrodes - DC power supply of 12 V	7.0–9.0	- 99% of phosphate removal efficiency - Purity of 95.7% for the recovered struvite - Total ammonium nitrogen removal efficiency of above 90%
[102]	Synthetic urine	- Anode: magnesium net - Cathode: titanium plate - Surface area of electrodes exposed is 7 cm^2 with a distance of 2 cm	8–10	- Ammonium and total nitrogen removal rate is 80%and 75%
[101]	Synthetic wastewater	- Anode: pure magnesium foil or AZ31 magnesium alloy foil - Cathode: stainless steel plate	5.9–6.1	- 38.8 wt.% of P and 16 wt.% of N for pure Mg anode - 31 wt.% of P and 7.7% of N for AZ31 - High purity struvite which is elongated and - Have a needle-shaped pattern with smooth, sharp edges
[108]	Synthetic wastewater	- Anode: magnesite - Cathode: titanium - Electrolyte: $NaSO_4$	9.0–10.8	- 86.6%–93.3% of Phosphate removal efficiency
[110]	Synthetic wastewater	- Anode: magnesium - Cathode: air - Electrolyte: NaCl	8.5–9.3	- 80%–98% of phosphate recovery
[103]	Fermented waste activated sludge supernatant	- Anode: magnesium alloy - Cathode: magnesium	8.5	- 98% of phosphorus
[111]	Synthetic and authentic water	- Anode: magnesium - Cathode: magnesium	7.6–9	- 93.6%, 74.5%, 71.6% of phosphate recovery in synthetic wastewater using batch electrocoagulation, continuous electrocoagulation, and chemical precipitation - 79.5%, 51.6% and 62.4% of ammonium in SWT using BEC, CEC, and CP.
[107]	Aqueous solution	- Anode: titanium plate coated with Ir oxide and Ru oxide - Cathode: stainless steel mesh - Catholyte: solution of $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ - Anolyte: Na_2SO_4	8.0–10.0	- 96.7% of phosphate recovery

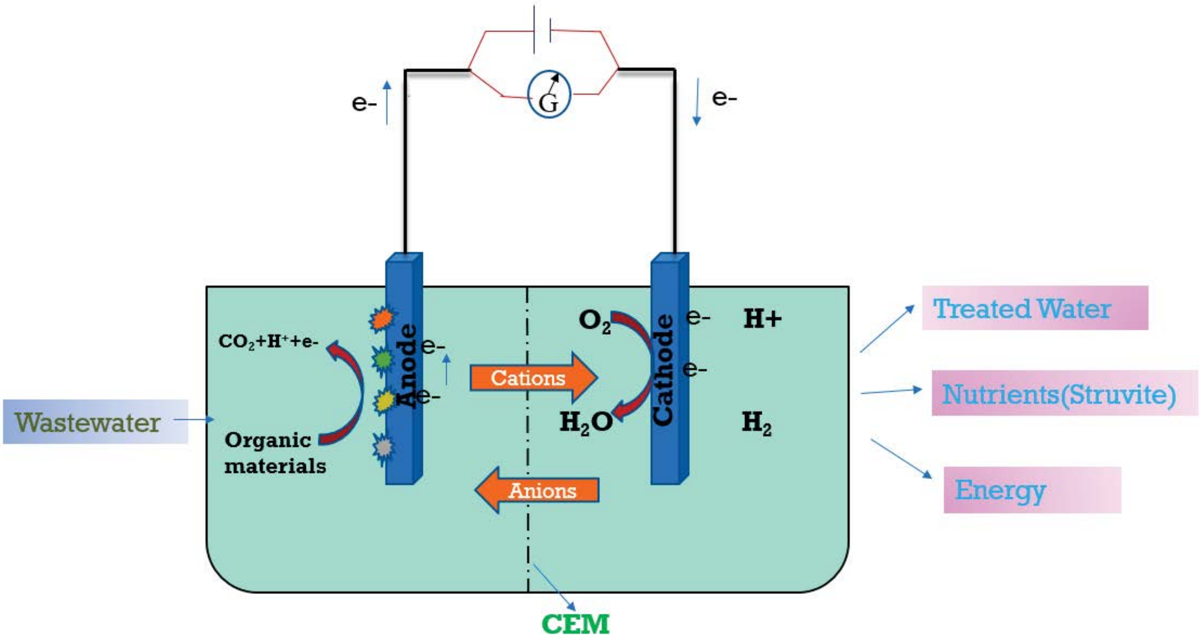

Fig. 8. General scheme of bioelectrochemical system.

[119]. The catalytic activity of microorganisms promotes the redox reaction in the system effected by several available microorganisms such as *Geobacter sulfurreducens* and *Shewanella oneidensis*. They are some of the metal-reducing bacteria that can catalyze the transfer of electrons to an anode effectively [120]. While these electrons flow through the external circuit, the electricity produced in a fuel cell will be utilized for bacterial respiration and the growth of biofilm [121].

4.1. Microbial fuel cell

In the MFC, the electrogenic bacteria break the organic substrate and the chemical energy is converted to electrical energy [122,123]. MFCs are designed either as a single chamber or dual chamber. In a single-chamber MFC, the anodic and cathodic parts will be arranged together with or without a membrane. But in a double chamber, both electrodes will be kept in separate compartments with a cation exchange membrane in between them. Electrons and protons are created in the anode compartment as a result of oxidation of organic substrates by microorganisms and these electrons are transferred through the external circuit to a terminal electron acceptor (TEA) and subjected to reduction. Simultaneously, protons are also transferred to the cathode through a membrane or the electrolyte. Exoelectrogenic bacteria, on the other hand, can transmit electrons to the TEA from outside the cell (exogenously) and generate electricity [124]. By incorporating MFC technology for struvite synthesis, enhanced phosphate recovery can be achieved [125]. Here the phosphorus can be recovered from wastewater by adding ammonium (NH_4) and Mg. In this approach, chemicals for pH modification need not be added. Thus it offers a major cost benefit over traditional struvite crystallization processes, which require the expensive alkali chemicals to modify the pH [126].

Zang et al. [127] used the integrated process by adopting MFC and MAP precipitation together to enhance the phosphate removal efficiency. They used a single-chamber microbial fuel cell with air cathode for urine treatment by using carbon electrodes. The phosphate recovery is up to 94.6% with the recovered ammonium being 28.6%. Using this technique, a power output of around 2.7 Wm^3 can be obtained. Ye et al. [128] built a double chamber microbial fuel cell that could function constantly at varied ammonium–nitrogen concentrations (6–41 mg/L). The effects of ammonium on the elimination of organics, energy output, and nutrient recovery were studied and reported. It was found that reduction in chemical oxygen demand (COD) is very effective as it is greater than 85%. Furthermore, an excess of ammonium in the feed solution jeopardizes the generation of energy. Simultaneously, the phosphate recovery rate attained in the MFC was unaffected by the higher influent ammonium content.

A hybrid reactor model designed by Kim et al. (2021) demonstrated the I_{max} and P_{max} to be 6.439 ± 0.481 mA and 2.084 ± 0.310 mW, respectively, at 2 g/L of COD. The removal efficiency of the C source was above 70% and the removal efficiency of the N and P sources was around 95% [88]. With an alternative source, Fischer et al. (2011) developed a system to recover phosphate from digested sewage sludge instead of wastewater by reducing $FePO_4$ using electrons from the metabolic activity of *Escherichia coli*. The yield achieved was about 82% with the addition of ammonium and magnesium sources [129].

A few research works attempted different types of cell systems. Hirooka and Ichihashi [130] constructed a microbial fuel cell with a single chamber for the removal of phosphorus from synthetic wastewater by adding NH_4^+ and Mg^{2+}. Phosphorus was removed as cattiite ($Mg_3(PO_4)_2 \cdot 22H_2O$) when only Mg was supplied, but the removal rate was lower than struvite. As more NH_4 and Mg were added,

Table 5
Summary of bioelectrochemical methods adopted for N&P recovery

Reference	Type of fuel cell	Source of wastewater	Microbes	Components and conditions	Observations and inferences
[88]	Single chamber fuel cell	Synthetic mineral rich water	Sewage sludge	- Anode: carbon cloth - Cathode: carbon cloth coated with Pt - Ceramic membrane	- Current generation of about 6.5 mA - About 95% of N and P removal
[127]	Single chamber fuel cell	Human urine	Anaerobic sludge	- Anode: carbon felt - Cathode: Pt coated carbon paper - GEFC-10N-Proton Exchange Membrane	- Recovery efficiency of P and N of about 95% and 29%, respectively. - Power generation of about 2.5 W/m^3
[128]	Dual chamber fuel cell	Artificial municipal wastewater	Anaerobic sludge	- Anode: cylinder shaped graphite felt - Cathode: carbon fibre brush - CMI7000 CEM membrane	- Average recovery rate of ammonium decreased as ammonium concentration increased - Phosphate recovery rate was found to be about 80%
[129]	Single chamber fuel cell	Digested sewage sludge	E. Coli (Strain K12 DSM498)	- Anode: six carbon felt electrodes - Cathode: carbon felt - Nafion membrane - $MgCl_2$ is added and pH is maintained at 10	- Orthophosphate mobilization has been done using MFC - Resultant phosphate containing supernatant is utilized for struvite precipitation - Phosphate content in the struvite crystals have ~90% accuracy
[130]	Single chamber fuel cell	Artificial wastewater		- Anode: carbon felt disc - Cathode: Pt coated wet proofed porous carbon paper - Nonwoven polyester cloth separator	- Phosphorus was recovered in the form of struvite when ammonium and magnesium added - When only magnesium was added, cattiite was formed
[131]	Single chamber fuel cell	Swine wastewater	Paddy field soil	- Anode: carbon felt - Cathode: Pt coated wet proofed carbon paper - 20 mL/min flow rate of influent - pH = 8	- COD removal rate of about 90% - Phosphorus removal rate of about 80% of which 27% was on the cathode - Performance of cathode get affected by the precipitation of phosphorus
[132]	Single chamber fuel cell	Raw human urine		- Anode: carbon brush - Cathode: Pt coated carbon cloth	- Precipitation on the cathode decreased the power generation - COD removal efficiency of about 70% - Both Ca and Mg precipitated
[133]	Single chamber and dual chamber fuel cell	Synthetic wastewater	Mixed anaerobic and aerobic sludge	- Anode: plain carbon paper - Cathode: carbon cloth coated with Pt - Nafion 117 as proton exchange membrane	- Phosphorus removal in double chamber cell was in the cathodic compartment - Nitrogen removal rate in dual chamber MFC was found to be low - Maximum power density in single chamber cell was about 559 mW/m^2 and in dual chamber of about 527 mW/m^2
[134]	Single chamber fuel cell	Human urine	Activated sewage sludge	- Anode: plain carbon fibre veil - Cathode: hot pressed activated carbon onto carbon veil - CMI-7000 membrane	- 20% NH_4^+ recovery and 82% PO_4^{3-} recovery - Power of about 15 W/m^3 was produced

(Continued)

Table 5

Reference	Type of fuel cell	Source of wastewater	Microbes	Components and conditions	Observations and inferences
[135]	Dual chamber fuel cell	Urine	Anaerobic digestate	- Anode: stainless steel mesh - Cathode: stainless steel mesh - CMI-7000 ultrex membrane	- Phosphate recovery of about 90% - Ammonium recovery efficiency was about 45% - Average COD removal of about 75% was achieved
[136]	Single chamber fuel cell	Urine	Activated sewage sludge	- Anode: carbon veil - Cathode: activated carbon with 20% PTFE hot pressed to a carbon veil	- Addition of SeaMix increased the amount of struvite from 21% to 95% - Maximum power performance was increased by about 11% by the addition of SeaMix
[137]	Algae biofilm assisted microbial fuel cell	Domestic wastewater	*Scenedesmus quadricauda* SDEC-8	- Anode: carbon cloth - Cathode: carbon cloth	- ABMFC was found to be effective for real, complex and variable wastewater - Removal efficiencies was found to be about 95%, 96% and 81%, respectively for total nitrogen, total phosphorus and COD
[140]	Single chamber electrolysis cell	Synthetic domestic wastewater	Effluent from working microbial fuel cell	- Anode: heat treated graphite fiber brushes - Cathode: stainless steel 304 mesh	- Phosphate precipitation in the form of struvite with about 40% removal rate - Overall energy efficiency of about 73% - Hydrogen production rate of about 1.5 m^3-H_2/m^3-d

the quantum of precipitate was higher. But the recovered phosphorus affected the performance of the cathode leading to the need of dissolving and removing the precipitate formed on the surface of the cathode. Similarly, using air cathode single-chamber microbial fuel cell, 70%–82% of the phosphorus from swine wastewater was eliminated with a power density of 1–2.3 W/m^2 with a reduction of 70%–90% of COD. The amount of phosphorus in the precipitates formed near cathode was calculated to be between 4.5% and 27% of the influent. The quality of the crystal was tested and found to have uneven morphology without the usual needle shape [131]. Santoro et al. [132] used single-chamber MFCs for the treatment of raw human urine. Though in earlier stages using Pt-coated cathode was efficient compared to platinum-free cathodes, there was not much difference in the later stages. The precipitation occurred at high pH, the calcium and magnesium concentrations plummeted, while phosphorous concentrations dropped to about 50% because of the formation of struvite on the cathode.

Interestingly, Tao et al. (2015) compared the performance of single-chamber MFC vs. dual-chamber MFC. Although both systems are capable of removing phosphorus effectively, the efficiency with which nitrogen is removed varies greatly. In a single-chamber MFC, nitrogen removal on the cathode is effective, but a considerable fraction of ammonium was transformed into nitrites in a dual-chamber MFC. Similarly, the single chamber had a higher proportion of electrochemically inactive bacteria than the dual-chamber MFC. Because of the differences in configuration, the performance of the MFC systems in terms of electricity output varies substantially through COD elimination is comparable [133]. A three-stage MFC was also constructed combining with struvite extraction process and electricity generation from urine. Urea hydrolysis in the first stage provides the electrical energy, which was advantageous for struvite precipitation process in the second stage. After collecting struvite by adding magnesium to the original effluent, the supernatant was used in the last step for higher power and more efficient COD reduction. Undiluted human urine was found to be free of 82% of PO_4^{3-}–P and 22% of COD using their three-stage technique. It was found that during operation, the first and third stages of the system produced power of around 14.4 and 11.8 W/m^3, respectively [134].

Sharma et al. [135] demonstrated a stacked MFC for the recovery of nutrients from urine and continued the run for three months with a volume of the reactor as 1.2 L, stainless-steel mesh was used as the electrodes with a proton exchange membrane. The recovery efficiency of PO_4^{3-} and NH_4^+–N in the form of struvite is 90.5% and 46.2%, respectively. The average open-circuit voltage of the stacked MFC was about 3.29 V, with a power density of 14.6 mW/m^2. Focusing on a more economical way of struvite production, SeaMix was found to be a feasible alternative to $MgCl_2$. Merino-Jimenez et al. [136] developed low-cost MFCs with activated carbon as cathode and carbon veil (in the form of fiber) as the anode. The membrane used was made of terracotta clay. The inclusion of SeaMix resulted in a 94% improvement in struvite recovery and a more than 10% increase in power output due to the increase in pH and conductivity.

Table 6
Pros and cons of chemical, electrochemical, and bioelectrochemical methods of MAP production/recovery

Method	Critical factors	Advantages	Disadvantages
Chemical precipitation	- pH - Mg:P ratio - Supersaturation ratio - Stirring speed - Precipitation time	- Easy to operate process - Struvite can be recovered from wastewater by adding an Mg source and maintaining pH	- Requires addition of chemicals for pH adjustment - Excess sludge production and costs for its handling - Technical shortcomings of reactors like fluidized bed reactors
Electrochemical precipitation	- pH - Applied voltage - Electrode - Distance between anode and cathode - Electrolyte	- No need for pH adjustments with chemicals, as OH– is formed at the cathode - Produced H_2 gas can be utilized as a potential fuel - Economical compared to chemical precipitation - When compared to one-time chemical addition, continuous cation dosing allows for improved process control	- Energy consumption depends on the conductivity of the wastewater - External voltage should be applied for the process - Energy consumption
Bioelectrochemical system (MFC &MEC)	- pH - Electrode material - Surface area of the electrode - Distance between electrodes - High ohmic resistance - Higher over potential	- Direct electricity generation - Low sludge disposal - Simultaneous energy and valuable product recovery - No need of pH adjustments with chemicals, as OH– is formed at the cathode - Low operation cost - Water reclamation - Low carbon emission - Efficient nutrient recovery	- Low power density - Electricity production is limited due to the activity of microbes at the anode - Sensitive to pH and substrate loading - Scaling up with efficiency is difficult

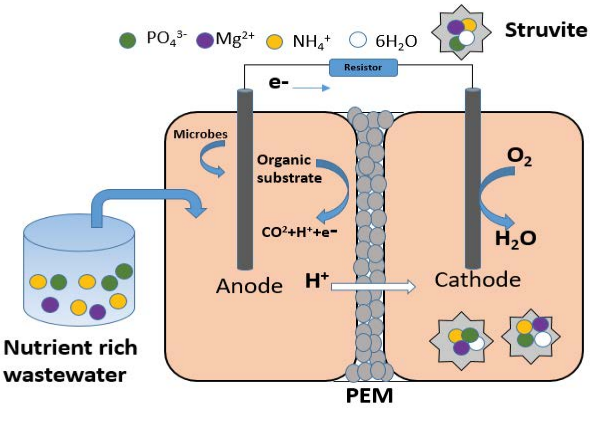

Fig. 9. Schematic diagram of MFC for struvite production.

By taking advantage of an algae biofilm, a microbial fuel cell known as ABMFC was developed by Yang et al. [137]. The nutrient recovery and bioelectricity production by a combination of algal biofilm (AB) and microbial fuel cell (MFC) was implemented. The removal efficiency of total nitrogen was 96% and total phosphorus was 91.5%, which cannot be obtained from a single MFC or single AB with additional power density. According to high-throughput sequencing, *Chlorobia* and *Deltaproteobacteria* flourished well in the symbiotic ABMFC system. Algal biofilm suppressed *Betaproteobacteria*, a diverse organic pollutant degrading bacteria; this could be due to nutrient competition between algae and Betaproteobacteria. In continuous-flow trials, the ABMFC system was shown to be capable of handling real, complicated, and fluctuating effluent, yielding total energy of around 0.1 kWh per m^3 of wastewater.

Recently, a different type of fuel cell, called sediment microbial fuel cell (SMFC), which is considered to be a cost-effective sediment remediation technology for surface water and sediment, was reported. SMFC is a bioelectrochemical system that can transform the chemical energy in organic matter-rich sediment in wastewater into continuous electric current through the metabolic activity of electrochemically active bacteria (EAB). In addition, it will be coupled with aquatic plant, namely AP-MFC, which found to be more efficient in removing N, P and other contaminants through the release of radial O_2 to cathode and depositing organic matter on anode [138].

4.2. Microbial electrolysis cell

MECs are part of the bioelectrochemical system that uses electrohydrogenesis to produce bio hydrogen from acetate and other fermentation end products. In MEC, the bacteria called exoelectrogens oxidize the substrate because of which electrons are released to the anode. In contrast to MFC, in MEC, the cathode is anaerobic so that spontaneous electricity generation is not possible. Therefore, a small external voltage should be applied to generate hydrogen in the cathode [139]. Like MFC, MEC can be used for the recovery of nutrients from wastewater. Cusick and Logan [140] used a single-chamber microbial electrolysis cell to bio-electrochemically crystallize the struvite.

It was found that the rate of struvite crystallization and hydrogen production depends on the cathode material and the applied voltage [140]. Phosphate removal was about 40%, with mesh cathodes achieving a higher removal rate than flat plates. In addition, the same researcher constructed a two-chamber MEC with a fluidized bed combination to greatly minimize the scaling at the cathodic surface. Here the continuous flow increases the cathodic pH and therefore reduces energy consumption. It is also possible to remove the soluble phosphorus from the solution and the corresponding precipitation of struvite. The current generation in the anode chamber led to COD reduction and ammonium elimination [141].

Wang et al. [142] reported a unique struvite crystallization process driven by the bioelectrochemical acidolysis of magnesia (MgO). Due to the migration of Mg^{2+} ions from the anode to the cathode area, struvite is formed in the catholyte by reaction with ammonium (NH_4^+) and phosphate (PO_4^{3-}). Depending on the molar ratios of N and P in catholyte, recovery efficiency ranged from 17.8% to 60.2%. The addition of MgO resulted in struvite crystallization using the liberated magnesium. In the anode chamber, current density was increased by about 11%, and COD removal efficiency was increased from around 78.5% to 92%.

Further advancement in these studies with MEC has been reported. Cerrillo et al. [143] proved the benefits of MEC with three chambers to recover N and P from digested pig slurry. There was a removal efficiency of 20% for phosphate and 36% for ammonium. In addition, the COD was lowered by 34% ± 12%. Unlike other MEC designs, these three chambers avoid struvite precipitation inside the reactor, making it easy to collect. In the two-chamber cell, a maximum P precipitation efficiency of around 94% and a maximum H_2 generation rate of about 0.30 m^3-H_2/m^3-d were attained. It was found that the application of voltage had a considerable impact on H_2 production and P recovery, but influent COD concentration had a large impact on P recovery exclusively.

From the reported literature, it can be inferred that the overall energy recovery in the MEC was found to be in the range of 25.1%–37.7% [144]. But there was a good scope for implementing this in field conditions. According to a case study conducted in the Kingdom of Saudi Arabia, it was proposed to increase the power generation between 611 and 768 MW might be generated from domestic and industrial wastewater between 2025 and 2035. Before MEC is put in force, critical issues like ohmic and concentration losses, saturation kinetics, and competing reactions, all of which reduce H_2 generation can be addressed [145]. Table 5 gives Summary of bioelectrochemical methods adopted for N&P recovery [88,127–146].

5. Conclusion

This comprehensive review discussed the feasible and efficient processes of recovery of nutrients (N and P) as struvite, which are economical in sustainable wastewater treatment and fertilizer management. Struvite (magnesium ammonium phosphate hexahydrate) is an environmentally friendly, slow-releasing nutrient fertilizer that can be partially replaced by synthetic phosphate fertilizer. Although struvite precipitation technology has been known for many years, the design of the units is crucial while they are in operation. Initially, scientists used simple chemical precipitation in conventional reactors such as stirred tank reactors and fluidized bed reactors, which also have many limitations. Subsequently, in order to economically recover struvite, electrochemical reactors were designed and utilized for phosphorus recovery. In terms of energy-saving and environmentally friendly wastewater treatment, bioelectrochemical techniques such as microbial fuel cells proved to be more favorable in terms of simultaneous nutrient recovery, COD removal, and energy production.

Abbreviation

ABMFC — Algae biofilm microbial fuel cell
BBM — Black box model
BEC — Batch electrocoagulation
BES — Bioelectrochemical system
CDI — Capacitive deionization
CEC — Continuous electrocoagulation
CEM — Cation exchange membrane
COD — Chemical oxygen demand
CP — Chemical precipitation
EBPR — Enhanced biological phosphor removal
EC — Electrocoagulation
FBR — Fluidized bed reactor
IAP — Ionic activity product
MAP — Magnesium ammonium phosphate
MEC — Microbial electrolysis cell
MFC — Microbial fuel cell
Mg — Magnesium
N — Nitrogen
NPK — Nitrogen, phosphorus, potassium
P — Phosphorus
PAO — Phosphate accumulating organism
PEM — Proton exchange membrane
SBR — Sequencing batch reactor
SMM — Semi-mechanistic model
TEA — Terminal electron acceptor

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