Advances in Struvite Precipitation Technologies for Nutrients Removal and Recovery from Aqueous Waste and Wastewater

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Abstract: The abatement of nutrient compounds from aqueous waste and wastewater is currently a priority issue. Indeed, the uncontrolled discharge of high levels of nutrients into water bodies causes serious deteriorations of environmental quality. On the other hand, the increasing request of nutrient compounds for agronomic utilizations makes it strictly necessary to identify technologies able to recover the nutrients from wastewater streams so as to avoid the consumption of natural resources. In this regard, the removal and recovery of nitrogen and phosphorus from aqueous waste and wastewater as struvite (MgNH4PO4·6H2O) represents an attractive approach. Indeed, through the struvite precipitation it is possible to effectively remove the ammonium and phosphate content of many types of wastewater and to produce a solid compound, with only a trace of impurities. This precipitate, due to its chemical characteristics, represents a valuable multi-nutrients slow release fertilizer for vegetables and plants growth. For these reasons, the struvite precipitation technology constantly progresses on several aspects of the process. This manuscript provides a comprehensive review on the recent developments in this technology for the removal and recovery of nutrients from aqueous waste and wastewater. The theoretical background, the parameters, and the operating conditions affecting the process evolution are initially presented. After that, the paper focuses on the reagents exploitable to promote the process performance, with particular regard to unconventional low-cost compounds. In addition, the development of reactors configurations, the main technologies implemented on field scale, as well as the recent works on the use of struvite in agronomic practices are presented.

Keywords: ammonium; magnesium; MAP; nutrients recovery; phosphorus; struvite

1. Introduction

The definition of proper processes for the management and the treatment of waste and wastewater is a crucial environmental and social topic. The uncontrolled discharge can induce serious deteriorations of soil and water bodies quality. In particular, the release in the environment of aqueous waste with high amounts of nutrients (nitrogen and phosphorus compounds) is of great concern [1–4]. In fact, this practice induces eutrophication phenomena in superficial water bodies and, consequently, the exhaustion of O2 content [5]. As a consequence of eutrophication phenomena, episodes of harmful algal blooms (HAB) could occur. HAB can release harmful toxins which pose a notable risk for human health and environmental ecosystems [6]. Additional drawbacks take place as some nitrogen compounds (NH3, NO2−, NO3−) are harmful to aquatic life or may cause disease if drinking water is
polluted with these elements [7]. The accumulation of nutrient compounds in aquatic environments is mostly attributable to the use in agricultural activities of chemical fertilizers, animal manures and digestates, as well as to the discharge of urban and industrial wastewater [4,8–15].

Numerous biological and physical-chemical treatments for the abatement of nutrients have been developed. The nitrogen compounds can be removed through typical biological nitrification–denitrification processes [5,15,16]. These processes are widely used and effective for NH₄+ removal in municipal treatment plants, but they are not very suitable for treating high concentrated wastewaters [17]. Indeed, a high ammonium content has toxic effects on microorganisms, which may cause a significant reduction in the process efficiency [1]. Shortcut nitrification/denitrification and anaerobic ammonium oxidation, showed potential to overcome the drawbacks above mentioned and they could be applied in the treatment of high polluting matrix such as leachates, digestates, etc. Nevertheless, these techniques are still under development and they are quite difficult to control and manage [17].

In the context of chemical-physical treatments, ammonium stripping is one of most widely employed treatments for the abatement of NH₄+ from highly polluted wastewater. In this process, typically, the NH₃, transferred from the wastewater stream to the air flow, is absorbed into acid solutions and recovered as ammoniacal salts. In spite of its benefits, this technology has some limitations, such as the need of pH adjustment to values close to 11–12 and the requirement of high air flow rates [18].

Breakpoint chlorination can also be applied to oxidize ammonium to nitrogen gas. However, because the process has a number of disadvantages, including the buildup of HCl and of total dissolved solids, and the formation of unwanted chloro-organic compounds, ammonia oxidation is seldom used today [18].

The abatement of phosphorus from municipal wastewater can be obtained in biological treatment plants which promote the growth of P-accumulating microorganisms. Many different processes have been developed (photoredox A/O, A²/O, Bardenpho, etc.) that assure good efficiencies [18]. A limitation of many of these processes is the occurrence of a decline in phosphorus removal when the nitrogen abatement is contextually applied [18]. In wastewater treatment plants the P abatement and recovery is also conducted through the precipitation of phosphates with the addition of coagulants which generally consist of inorganic salts of multivalent metal ions, such as calcium, aluminum, and iron. These processes are widely applied due to the easy management and simplicity of the required equipment. Moreover, they can be exploited also in the treatment of concentrated aqueous waste and wastewater. On the other hand, the use of coagulants generates high amounts of voluminous sludge which incorporates the organic solids resulting in a heterogeneous matrix which is difficult to manage.

Additional techniques, such as adsorption, ion exchange, reverse osmosis, etc., could be potentially applicable to remove nutrient compounds [3,18]. However, these techniques are not selective and generate concentrated streams, of which disposal is very expensive.

Among the many alternatives, a solution based on nutrients recovery and reuse is very advantageous as it promotes the development of sustainable technologies. In effect, the definition of a virtuous cycle of nutrients to reduce the use of natural resources and, at the same time, avoid pollution phenomena is, currently, a key challenge. The recovery of nutrients is a strict necessity especially in the case of phosphorus. In fact, nowadays phosphorus is mainly obtained by extractive activity [19,20].

The extractive peak of phosphatic rocks will be reached in the next decades and the phosphorus reserves can decrease drastically in the next century [20]. When phosphate rocks drop, extraction and marketing prices will also rise, and industry will be forced to seek alternative sources due to higher demand of phosphorus in the agricultural world. Therefore, the attention of the international scientific community is directed towards the search for sustainable sources of phosphorus and more generally of nutrients. In this regard, the European Commission recently revised the EU Fertilizer Regulation ((EC) 2003/2003) and published the new EU Regulation ((EU) 2019/1009), which includes the fertilizing compounds based on secondary raw materials [10].

Many raw materials recoverable from the treatment of aqueous waste and wastewater could potentially become component materials in the new Regulation ((EU) 2019/1009) [10]. In this regard, the recovery of ammonium and phosphates from wastewater as struvite has gained great interest in
recent years. Struvite is a white orthorhombic crystalline compound, which is composed of Mg\(^{2+}\), NH\(_4^+\), and PO\(_4^{3-}\) (MgNH\(_4\)PO\(_4\).6H\(_2\)O) in equal molar amounts [21,22]. Struvite precipitation takes place when the combination of ammonium, magnesium, and phosphates concentrations overcomes the solubility product under an alkaline environment [23]. In general, struvite precipitation can be aimed to remove and recover the amount of NH\(_4^+\) or PO\(_4^{3-}\) from wastewater [8,24–26]. The recovery of the phosphates content alone is much more sustainable because lower amounts of reagents are necessary. In fact, at most, the chemicals for magnesium supplying and pH setting are required. In the case of nitrogen removal, often, due to the limited contents of Mg\(^{2+}\) and PO\(_4^{3-}\) with respect to the NH\(_4^+\) concentration, higher dosages of the reagents are needed for the treatment of high concentrated wastewater [1].

Anyway, struvite is widely recovered for nutrients recycling from wastewater because it can be produced a relatively pure precipitate with a great amount of both phosphorus and nitrogen, with only trace amounts of impurities [10]. Indeed, unlike other precipitation processes that exploit coagulant agents, the struvite is formed as a mineral salt that incorporates only low quantities of solids and that can be easily recovered by sedimentation [27,28]. Therefore, the formation of voluminous flocculant sludge, containing great quantities of unwanted compounds is avoided. Furthermore, because of its chemical composition, struvite has a demonstrated value as a fertilizer (pure struvite is included in the Regulation EC No 1907/2006 (REACH) as a commercial fertilizer) [29–35]. For these reasons, at present, struvite is the most common recovered compound in pilot and operational facilities in Europe [10]. It was estimated that approximately 15,000 tons are produced in Europe annually [10]. The existing facilities mainly treat urban wastewater to produce struvite, but industrial wastewater, manure, and livestock slurries are also exploited as input aqueous waste [10]. Furthermore, significant struvite quantities are produced outside Europe (USA, Japan, China) [10].

Despite several applications in industrial facilities, the struvite precipitation process is under continuous development. Indeed, a lot of research has been recently carried out to solve some crucial aspects and to improve the process globally.

The aim of this manuscript is to provide a review on the recent progresses on the application of the struvite precipitation processes for the nutrients recovery and recycling from aqueous waste and wastewater. Initially, the basic principles, the parameters, and the operating conditions that affect the process are examined. Afterwards, attention is paid to the reagents that can be used to promote the process, with particular regard to the unconventional ones that can reduce the management costs. The development of reactors for precipitation and recovery, the main technologies implemented at industrial scale, recent studies on the application of recovered struvite as slow release fertilizer, and some economic considerations are also exposed.

2. Chemical Bases on the Struvite Precipitation Process

2.1. Generality on the Struvite Precipitation

Struvite type crystals consist of orthophosphate (PO\(_4^{3-}\)), magnesium (Mg\(^{2+}\)), and mono or bi-valent ions such as ammonia (NH\(_4^+\)), potassium (K\(^+\)), sodium (Na\(^+\)), copper (Cu\(^{2+}\)), nickel (Ni\(^{2+}\)), lead (Pb\(^{2+}\)), manganese (Mn\(^{2+}\)) [9,36]. Magnesium ammonium phosphate (MgNH\(_4\)PO\(_4\).6H\(_2\)O) (acronym MAP), is the most common and stable form which is characterized by a crystalline white orthorhombic prismatic structure (Figure 1). The struvite can be identified through X-ray diffraction (XRD) analysis by comparing the diffractionogram of the solid under examination with that of pure compound (Figure 2). The formation occurs when the concentrations of constituents exceed the solubility product. Precipitation takes place according to the following equation [12]:

\[
\text{Mg}^{2+} + \text{NH}_4^+ + \text{H}_3\text{PO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{MgNH}_2\text{PO}_4 \cdot 6\text{H}_2\text{O} + n\text{H}^+ \quad \text{where} \quad n = 0, 1, \text{or} \ 2
\]  

(1)

Anyway, this reaction is a simplification of the chemistry of struvite formation. In effect, the process involves different chemical-physical parameters and it can be divided into two main steps: nucleation and growth. In particular, nucleation takes place when the ions combine, generating crystals in their embryonic form [37]. The nucleation process can be homogeneous when it occurs spontaneously, or heterogeneous if it occurs in the presence of foreign particles or impurities, and it
is controlled by diffusive mechanisms and by the degree of saturation of the elements in the solution [12]. Struvite crystals growth, instead, is a process controlled by mass transfer mechanisms from the solute to the crystals’ surface and by surface integration mechanisms, through which the material is incorporated into the crystals [38]. These mechanisms depend on several physical-chemical parameters such as pH, supersaturation ratio, temperature, and presence of competitive ions [39]. Furthermore, the reaction kinetics of struvite crystals formation is influenced by thermodynamic equilibrium and by liquid-solid transport phenomena [40]. In the following paragraphs the effects of the main parameters on MAP formation are analyzed.

![Figure 1. Struvite crystals obtained from the treatment of landfill leachate [41].](image)

**Figure 1.** Struvite crystals obtained from the treatment of landfill leachate [41].

![Figure 2. Diffractogram of pure struvite.](image)

**Figure 2.** Diffractogram of pure struvite.

### 2.2. Effects of pH on Struvite Formation

As mentioned above, struvite formation happens when the concentrations of Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ exceed the solubility product (Ksp). The availability of the three components is controlled by the pH and by the overall amounts of magnesium, ammonium, and phosphorus species [42]. The speciation of MAP components is also pH dependent, therefore, the formation and precipitation of struvite is mainly affected by pH [32]. Many studies investigated the optimal pH range for MAP precipitation. Buchanan et al. [43], through a mathematical modeling, found that struvite precipitation in anaerobic lagoons could take place in the pH range 7–11, with the minimum solubility at pH 9. In agreement with this statement, Siciliano et al. [44] observed that the positive effect of alkaline conditions is not relevant for pH greater than 9, for struvite formation in anaerobic digestate. Tünay et al. [45] identified pH values between 8.5 and 9.3 as the optimal. Hao et al. [46] reported a range pH 9–9.5 as the most favorable, with a degree of purity above 90% of recovered precipitate. Huang et al. [47] stated a rapid raise in the reaction rate of struvite formation in response to pH growth from 8.6 to 9.08. In addition to the results above mentioned, further studies identified pH values around 9 as the most favorable for struvite precipitation [48], as summarized in Tables 1 and 2. Such a condition can be justified by considering that, as pH continues to grow above pH 9, the MAP precipitation can be hindered since the availability of ammonium ion will decrease, due to its conversion into ammonia gas, while the permanence of phosphate ions in the solution notably increase [32,49].
Table 1. Operating conditions and nutrients recovery efficiencies identified in some works that used stirred tank reactors (STR) for struvite precipitation.

| Reference | Wastewater Influent | Reactor Type | Reactor Volume | Hydraulic Retention Time (HRT) | Reactor Volume | Mixing | pH Control | pH | Mg Source | Mg Source | P Source | N:Mg:P | P-Removal | N-Removal |
|-----------|---------------------|--------------|----------------|------------------------------|----------------|--------|------------|----|------------|------------|----------|--------|-----------|-----------|
| L         | min                 | rpm          | NaOH           | MgO                          | H₂PO₄         | %      | %          |    |            |            |          |        |           |           |
| [1]       | Landfill leachate   | Batch        | 1              | 30                           | NaOH          | 9      | MgO        | H₂PO₄ | 1:2:1       | =100       | 95       |
| [28]      | Synthetic wastewater| Batch        | 21             | 300                          | NaOH          | 8.7    | MgCl₂:6H₂O | NH₄H₂PO₄ | 2.40:9:1    | 81.40     |          |
| [33]      | Sewage sludge       | Batch        | 0.25           | 30                           | NaOH          | 9      | MgCl₂:6H₂O | H₂PO₄ | 1.5:1:1     | 95         | 89.35    |
| [41]      | Landfill leachate   | Batch        | 4.8            | 30                           | NaOH          | 9      | Seawater bittern | Bone meal | 1:1.1:1.1   | 99         | 95       |
| [44]      | Anaerobic digestion | Batch        | 0.25           | 30                           | NaOH          | 9      | Seawater bittern | Bone meal | 1:1.3:1.3   | 99         | 91       |
| [50]      | Pretreated landfill leachate | Batch | 0.4           | 1                            | NaOH          | 9      | Seawater bittern | Bone meal | 1:1.3:1.3   | 99         | 90       |
| [51]      | Landfill leachate   | Batch        | 0.5            | 30                           | NaOH          | 9      | MgCl₂:6H₂O | NaHPO₄ | 1:1:1       | >92        |          |
| [52]      | Landfill leachate   | Batch        | 1              | 200                          | NaOH          | 9      | MgCl₂:6H₂O | KH₂PO₄ | 1:1.2:1.2   | ≈99        |          |
| [53]      | Synthetic swine wastewater | Continuous | 5              | 10                           | NaOH          | 9      | MgCl₂:6H₂O | KH₂PO₄ | 1:1.2:1.1   | ≈98.9      | ≈85      |
| [54]      | Wastewater treatment liquors | Batch | 1             | 120                          | Aeration      | 8.5    | MgO        | -2.5:1 | ≈90        |           |          |
| [55]      | Anaerobic digestion supernatant | Batch | 1             | 60                           | NaOH          | 10     | MgCl₂:6H₂O | NaHPO₄ | 7.7:1:1     | >90        | 29       |
| [56]      | Synthetic urine     | Continuous   | 20.55          | 261                          | NaOH          | 8.8    | MgCl₂:6H₂O | KH₂PO₄ | 4.3:1:1     | 90         |          |
| [57]      | Synthetic wastewater| Continuous   | 2.4            | 125                          | NaOH          | 8.5    | MgSO₄      | NaHPO₄ | 9.4:1:1     | 88         |          |
| [58]      | Raw swine slurry    | Batch        | 0.35           | 240                          | NaOH          | 10     | MgO        | H₂PO₄ | 1:1:1       | 80         | 77       |
| [59]      | Anaerobically digested manure | Batch | 1             | 60                           | NaOH          | 8.7    | MgCl₂:6H₂O | -1.5:1 | 80         |           |          |
| [60]      | Anaerobically digested centrate | Batch | 1             | 30                           | NaOH          | 9      | MgO        | 30.7:1:1:1 | >90        |           |          |
| [61]      | Landfill leachate   | Batch        | 1              | 125                          | NaOH          | 8.5    | MgCl₂:6H₂O | H₂PO₄ | 1:1:1       | 72         |          |
| [62]      | Synthetic urine     | Batch        | 0.4            | 200                          | NaOH          | 9      | MgO        | 1:1:4:1 | 96.70      |            |          |
| [63]      | Synthetic solution  | Batch        | 1              | 150                          | Aeration      | 9–10   | Seawater bittern | KH₂PO₄ | 1:1:1       | >96        | >88      |
Table 2. Operating conditions and nutrients recovery efficiencies identified in some works that used fluidized bed reactors (FBR) for struvite precipitation.

| Reference | Wastewater Influent               | Seed Material | Reactor Volume | Flowrate | HRT   | pH Control | Mg:P | Mg Source | pH | Airflow Rate | P Removal | Recovered Struvite | Grain Size | Grain Retention Time | Upflow Velocity |
|-----------|----------------------------------|---------------|----------------|-----------|-------|------------|-------|-----------|----|--------------|-----------|-------------------|-----------|---------------------|-----------------|
| [25]      | Synthetic wastewater             | Struvite      | 1.35           | 0.72      | 1.4   | NaOH       | 1:3:1 | MgCl₂:6H₂O | 9.5| 95.8         |           |                   |           |                     |                 |
| [30]      | Anaerobic digester centrate      | Struvite      | 90             | 180       | 0.075 | 1:3:1      | MgCl₂:6H₂O | 8.2 | 80%         | 0.5–3.5    |                   |           |                     |                 |
| [64]      | Anaerobic digester supernatant   | Struvite      | 24.5/28.3      | 18–36     | 0.75–1.5 | 3:3:1 | MgCl₂:6H₂O | 7.6–8.4 | >85%        | 0.5–4.75    | 10               |           |                     |                 |
| [65]      | Synthetic wastewater             | Struvite      | 24.5/28.3      | 18–36     | 0.75–1.5 | 3:3:1 | MgCl₂:6H₂O | 7.6–8.4 | >85%        | 0.5–4.75    | 10               |           |                     |                 |
| [66]      | Urine                            | Struvite      | 2.6            | 2         | 2     | Aeration   | 1:3:1 | Seawater | 0.06 | >98.7%       | 0.036–0.136 | 4–5              |           |                     |                 |
| [67]      | Anaerobic digester centrate      | Struvite      | 24.5/28.3      | 0.074     | 1:3:1 | NaOH       | 1:3:1 | MgCl₂:6H₂O | 8.2 | 85%         | 0.5–3.5    | 10               |           |                     |                 |
| [68]      | Synthetic wastewater             | Quartz sand   | 18000          | 18–36     | 0.75–1.5 | 3:3:1 | MgCl₂:6H₂O | 8.2 | 85%         | 0.5–3.5    | 10               |           |                     |                 |
| [69]      | Synthetic wastewater             | Struvite      | 9.5            | 1.8       | 10    | NaOH       | 1:3:1 | MgCl₂:6H₂O | 9.5  | >90%        |           |                   |           |                     |                 |
| [70]      | Synthetic wastewater             | Struvite      | 2              | 4         | 4.1   | NaOH       | 1:3:1 | MgCl₂:6H₂O | 8.5  | 83%         |           |                   |           |                     |                 |
| [71]      | Raw water                        | Struvite      | 12             | 6         | 2     | Aeration   | 1:1  | MgCl₂:6H₂O | 8   | 0.042       | 0.025      | 0.4–2           |           |                     |                 |
| [72]      | Swine lagoon liquid              | Struvite      | 279.17         | 0.05      | 568   | Aeration/NaOH | 1:9:1 | MgCl₂:6H₂O | 8.4  | 92%         | 0.55–1.18 | 3–4              |           |                     |                 |
| [73]      | Raw water                        | Struvite      | 30.15          | 568       | 0.05  | NaOH       | 1:3:1 | MgCl₂:6H₂O | 8   | 70%         | 0.25–1.19 |                 |           |                     |                 |
| [74]      | Synthetic wastewater             | Struvite      | 30.15          | 568       | 0.05  | MgOH₂      | 1:3:1 | MgO      | 8   | 70%         | 0.25–1.19 |                 |           |                     |                 |
On the other hand, other works identified higher pH values as optimal for struvite precipitation. In particular, Ohlinger et al. [42] found the minimum solubility at pH 10.3 including the presence of magnesium phosphate complex to predict the struvite precipitation in wastewater. Shin and Lee [75] detected a continuous decrease in PO₄³⁻ and NH₄⁺ concentration due to struvite precipitation as the pH was raised to 10.5. Siciliano et al. [50] determined that a pH value of 10 was the best condition for the struvite precipitation in pretreated landfill leachate. The differences in the literature reports may be related to the composition of treated wastewater which was different from one work to another. Indeed, any modification in wastewater chemistry results in differences in ionic strength and activity which, in addition to the other factors, affect the struvite precipitation potential [49]. Furthermore, the type of ionic species in the wastewater also influence the formation of MAP crystals. Indeed, as better discussed in Section 2.5, the presence of competitive ions (Ca²⁺, Na⁺, K⁺, Al³⁺, Fe⁺⁺, etc.), in connection with the pH values, has a great influence on the precipitation process. For example, in the presence of high concentrations of calcium (Ca²⁺), a pH value higher than 10 could cause the formation of a metastable form of hydroxypatite and only a small part of struvite [76].

Therefore, on the basis of these considerations, it can be stated that a unique pH for struvite precipitation cannot be assumed. This means that the pH value to optimize the removal and recovery of nutrients in the form of MAP should be identified through direct investigations on wastewater to be treated.

2.3. Effects of Molar Ratios on Struvite Formation

According to reaction 1, struvite nucleation occurs when Mg²⁺, NH₄⁺, and PO₄³⁻ are present in equimolar concentration in solution [12,37]. Therefore, the availability of the three components is a key factor in the formation of struvite crystals. Generally, there is a significant difference in the molar concentrations of Mg²⁺, PO₄³⁻, and NH₄⁺ ions in real effluents. In particular, many wastewaters are characterized by higher molar amounts of ammonium with respect to the other struvite constituents. This difference is very marked in aqueous waste, such as leachate and digestate, derived from anaerobic biological processes. Only in rare cases, such as the liquid phases of supercritical gasification processes, there is a nitrogen deficit compared to the content of PO₄³⁻ and Mg²⁺ [8]. Clearly, the struvite precipitation aimed at the contextual removal of phosphorus and ammonium is more expensive because, to reach the stoichiometric molar ratios, the addition of reagents, both of magnesium and phosphorus, is required. In this case the process efficiency is directly linked to the molar ratios among the three elements N:Mg:P. On the contrary, the struvite precipitation aimed at the exclusive removal and recovery of phosphorus is a more sustainable process. In fact, due to the excess of ammonium, only the addition of magnesium is, eventually, required and the process depends mainly on the Mg:P molar ratio.

Despite equal molar amounts required for struvite precipitation, the reagents should be overdosed regarding the theoretical value, since in real wastewater there are competitive ions such as, Ca²⁺, Na⁺, K⁺, Al³⁺, Fe⁺⁺, etc., which can react with Mg²⁺ and PO₄³⁻ ions reducing their availability for MAP formation [2,12,77–79].

The optimal molar ratios must be assessed case-by-case as it depends heavily on the chemical-physical characteristics of wastewater. The dosages also depend on the type of chemicals used as sources of magnesium and phosphorus in the treatment. For these reasons, regarding the most favorable molar ratios, a great divergence among the literature reports can be found (Tables 1 and 2). In particular, in the treatment of landfill leachate, NH₄⁺ removals of about 90% were obtained with soluble analytical-grade reagents (MgCl₂·6H₂O, Na₂HPO₄·12H₂O) that were dosed at the theoretical stoichiometric amounts [51]. Also Kabdaşlı et al. [2] obtained a very high NH₄⁺ removal yield, around to 94%, by using pure reagents at dosages (N:Mg:P = 1:1:1.05) close to the stoichiometric values. On the contrary, other works, in which unconventional reagents were exploited, found that greater dosages are necessary. Specifically, Di Iaconi et al. [1] using MgO as source of magnesium observed an increase of ammonia removal, from 67% up to 95%, by doubling the amount of magnesium from the stoichiometric value (1:1:1) to a molar ratios N:Mg:P of 1:2:1. Siciliano et al. [44,50] detected efficiencies near to 90% exploiting seawater bittern and bone meal, as sources of Mg²⁺ and PO₄³⁻,
respectively, dosed at N: Mg: P = 1:1.3:1.3, in the treatment both of pretreated landfill leachate and cattle manure digestate. On the other hand, in another work conducted using the same reagents, Siciliano [41] found that molar ratios of N: Mg: P = 1:1.1:1.1 were sufficient to reach the best efficiency for ammonium abatement in methanogenic landfill leachate. Kim et al. [52] proved that the MAP formation is also influenced by the sequence of chemicals addition. In particular, with amounts of N: Mg: P = 1:1.2:1.2, the best performance for ammonium removal and high struvite deposits were reached by dosing the magnesium and phosphate reagents prior to pH setting [52]. Siciliano et al. [44] confirmed these statements and observed that the pH correction after the Mg2+ and PO43- dosage reduces the precipitation of compounds different from struvite, such as calcium phosphates. Anyhow, the formation of some additional compounds, generally phosphates insoluble salts, cannot be avoided. For these reasons, higher abatements of phosphorus, with respect to the ammonium removals, were often observed [4,52].

In the treatment aimed at phosphorus removal and recovery, many works claimed the importance to apply a Mg: P molar ratio higher than the stoichiometric value [53,80–82]. Quintana et al. [54] found a strong influence of Mg: P ratio on the abatement of phosphates amount and the major removal was detected when pure MgO was dosed at a molar ratio of 1.5. Moreover, the authors observed that the increase of the molar ratio promoted the removal rate growth [80]. Nelson et al. [81] detected a positive effect on phosphorus removal by increasing the Mg: P dose from 1 to 1.6. Furthermore, according to the authors, with the increase of Mg: P ratio the PO43- abatement can be obtained with a smaller increase in pH [81]. This could permit satisfactory phosphorus removals with limited addition of alkali avoiding potentially adverse effects of high pH or ammonia volatilization [81]. Marti et al. [82] argued that the increase of Mg2+ availability decreases the Ca: Mg molar ratio, which favors the precipitation of struvite rather than calcium phosphates. In agreement with this consideration, Jaffer et al. [83] affirmed that with Mg: P addition lower than 1.05:1 the precipitate resulted in a mixture of struvite and hydroxyapatite and a Mg2+ dosage of 1.3:1 was suggested for full scale applications. However, an excess of Mg2+ can cause the formation of magnesium phosphates, reducing the precipitation of struvite. In particular, Korchef et al. [21] observed the phosphate removal caused by MAP precipitation for Mg: P molar ratio ≤4 and by newberyite (MgHPO4·3H2O) and cattiite (Mg6(PO4)2·22H2O) formation for Mg: P = 5.

2.4. Temperature and Struvite Solubility

Temperature considerably affects the solubility, the morphology of struvite crystals, as well as their formation and dissolution. Many studies considered the range between 25 °C and 35 °C as optimal for struvite precipitation. Crutchik and Garrido [84] showed that the temperature growth from 25 °C to 30 °C and 35 °C caused the increase of struvite solubility product and promoted both the presence of crystals with a lesser degree of purity and their dissolution [85]. According to Moussa et al. [86], as the temperature increases from 14 °C to 35 °C the ionic activities and the supersaturation coefficient increase, thus reducing the efficiency of crystals formation by more than 30%. Other studies stated that, as the temperature increased from 25 °C to 37 °C, crystals changed from a prismatic rectangular shape at 25 °C to a dendritic structure [79,87]. The struvite solubility, in combination with the temperature, is largely affected by the chemical composition of the solution. In effect, several studies assessed how the solubility product of struvite undergoes variations with the characteristics of wastewater in which the precipitation occurs. Aage et al. [88] stated that in synthetic aqueous solution the struvite solubility tends to grow in response to the temperature increase up to 50 °C, and then it decreases assuming a value equal to 2.5 × 10-13 at 65 °C. A lower value, of 5.49 × 10-14, was calculated by Ohlinger et al. [42] at pH 10.3 and 25 °C by predicting the struvite formation in digestion. On the other hand, Loewenthal et al. [89], studying the solubility of struvite in a digestate, determined a Ksp value equal to 2.5 × 10-13. Studies conducted by Gunay et al. [90] showed that the solubility of struvite in landfill leachate decreased by 80% in response to pH increase from 6.5 to 8.5. Furthermore, the solubility of struvite can be also influenced by the presence of other ions such as Ca2+, CO32- [91]. The presence of competitive ions is a main problem in digestates where the conspicuous amount of calcium can interfere with the struvite formation processes by subtracting phosphate ions [92]. The level of oversaturation also affects the crystallization process as it causes a decrease of the nucleation time and growth [93]. The
extreme variability of the $K_{sp}$ values reported in literature is shown in the following Table 3 [79,84,88,94,95].

| Reference | Temperature (°C) |
|-----------|-----------------|
|           | 10   | 15   | 20   | 25   | 30   | 35   | 40   | 45   | 50   | 55   | 60   | 65   |
| [79]      | $4.31 \times 10^{-14}$ | $5.14 \times 10^{-14}$ |
| [84]      | $5.51 \times 10^{-14}$ | $7.12 \times 10^{-14}$ | $7.90 \times 10^{-14}$ |
| [88]      | $5.42 \times 10^{-14}$ | $6.90 \times 10^{-14}$ | $1.17 \times 10^{-13}$ | $1.58 \times 10^{-13}$ | $3.02 \times 10^{-13}$ | $3.73 \times 10^{-13}$ | $2.50 \times 10^{-13}$ |
| [94]      | $4.36 \times 10^{-15}$ | $9.16 \times 10^{-15}$ | $2.05 \times 10^{-14}$ | $4.33 \times 10^{-14}$ | $6.84 \times 10^{-14}$ | $5.92 \times 10^{-14}$ | $4.00 \times 10^{-13}$ | $2.53 \times 10^{-13}$ | $2.11 \times 10^{-13}$ | $1.46 \times 10^{-13}$ | $9.73 \times 10^{-13}$ |
| [95]      | $5.13 \times 10^{-14}$ | $6.03 \times 10^{-14}$ | $6.76 \times 10^{-14}$ | $1.00 \times 10^{-13}$ | $8.32 \times 10^{-14}$ |

2.5. Presence of Competitive Ions

The presence in solution of competitive ions, such as Ca$^{2+}$, Na$^+$, K$^+$, CO$_3^{2-}$, HCO$_3^-$, etc., can strongly influence the struvite crystals nucleation and growth [12]. Kabdaš et al. [2] highlighted the negative impact of the presence of these ions both on the induction time and on the morphology and size of the struvite crystals. Mono-valent ions such as Na$^+$ and K$^+$ could compete with ammonium in the formation of struvite compounds promoting the formation of MgNaPO$_4$ and MgKPO$_4$ instead of MAP. In some works, the presence of potassium salts, such as MgKPO$_4$, into the recovered solid of MAP precipitation process was detected [1,64]. However, according to other studies the production of MgKPO$_4$ can take place only in the case of low NH$_4^+$ amounts [29,82]. Na salts were recovered in presence of a high concentration of sodium in the treating mixture [41]. Struvite formation can also be hindered by high alkalinity values. In particular, HCO$_3^-$ and CO$_3^{2-}$ are able to bond Mg$^{2+}$ and NH$_4^+$ ions, which leads to the formation of stable aqueous phases of MgCO$_3$, Mg(HCO$_3$)$_2$, and NH$_4$HCO$_3$ and, therefore, reduces the availability of two constituents for struvite nucleation [47]. In addition to the effects mentioned above, the main adverse impact on MAP precipitation is linked to presence of Ca$^{2+}$ ions. Indeed, high levels of calcium in the solution can completely obstruct struvite nucleation [91]. Furthermore, when calcium ions interact with the orthophosphate, the production of apatite and hydroxyapatite can take place. These mechanisms subtract the phosphate ions from the solution and, therefore, reduce the struvite formation [85,96,97]. The relationship through which the calcium binds to the phosphate in the form of hydroxyapatite is shown below:

$$5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{H}^+$$

(2)

Since calcium represents an ion that competes with magnesium, several studies were carried out to evaluate the influence of calcium concentration on struvite formation [77,92,98]. In particular, according to some works, a Ca:Mg molar ratio lower than 0.2 does not affect the struvite production and it allows to recover a solid with high standards of purity, while values greater than 0.2 reduce struvite quality and slow down the nucleation process [77]. In particular, a Ca:Mg ratio between 0.5 and 0.75 considerably influences struvite formation and its purity degree, while values greater than 1 prevent struvite nucleation [76]. Le Corre et al. [92] also observed that wastewaters with a molar ratio Ca:Mg higher than 1 avoided the struvite formation causing the production of amorphous calcium phosphates. The inhibitory effects of Ca$^{2+}$ ions can be mitigated by dosing excess Mg$^{2+}$ to force out the precipitation of struvite [98]. However, a Mg$^{2+}$ overdose itself can induce the precipitation of magnesium phosphates and, moreover, it increases the treatment costs. Chelation treatments, to form complexes with Ca$^{2+}$, improved the MAP purity in anaerobically digested dairy manure [98]. Indeed, chelating agents such as EDTA, whose stability constant for Ca$^{2+}$ is greater than two orders of magnitude compared to that for Mg$^{2+}$, allow reducing the concentration of calcium in the wastewater without affecting the concentration of phosphorus [97]. Nevertheless, struvite crystals
morphology in the chelation process was inconsistent compared to other recovered precipitates [98]. Furthermore, chelating chemicals addition results in a significant cost increase and their discharge with the wastewater produces additional environmental impacts [98]. As an alternative to the use of chelating agents, CaCO₃ precipitation could be a suitable pretreatment to limit Ca²⁺ interference and keep phosphates in solution for MAP precipitation [98]. In this process, the pH is set to values between 9.5 and 10 in order to promote the formation of insoluble CaCO₃. The precipitation of this salt reduces the calcium content and, by subtracting CO₃²⁻ ions, also reduces the wastewater alkalinity, which itself could hinder the struvite formation [99,100]. In this treatment, supplemental magnesium ions should be dosed after CaCO₃ precipitation. Studies conducted on digestates by Huchzermeier and Tao et al. [98] proved that calcium can be recovered beforehand as calcium carbonate, keeping the content of orthophosphates in solution. Precipitation of CaCO₃ can be also promoted by setting the pH to the required values through insufflation of atmospheric air into the solution, so as to induce the degasification of dissolved CO₂ [22,99,100]. This application limits the consumption of chemicals for pH correction.

2.6. Reagents Used for Struvite Precipitation

As previously discussed, the struvite precipitation processes, in general, require the addition of a proper amount of magnesium and, if ammonium must be removed, phosphorus chemicals. The quantities of these reagents must be evaluated according to the wastewater chemical-physical characteristics. Moreover, the supplementation of alkaline compounds is often necessary to set the pH to the values able to minimize the struvite solubility [52,90,101]. Also in this case, the dosage depends on the wastewater properties and, furthermore, on the quantity of magnesium and phosphorus reagents to be added. Indeed, many compounds of magnesium and phosphorus have an acidic behavior once dissolved in an aqueous solution and, therefore, their dosages increase the consumption of alkaline compounds for pH setting [44]. Obviously, the choice of reagents type has a great impact on process effectiveness. Indeed, the reagents must be effective, simple to use and must not contain elements able to inhibit the struvite nucleation process. Furthermore, to limit the economic burden of the treatment, it is essential to identify and to evaluate the applicability of low-cost unconventional reagents [54,102,103]. Some studies verified the effectiveness of low-cost magnesium-based compounds [90], while few were focused on the application of unconventional phosphorus-based reagents; but these ones are more expensive and their consumption generally represents the main cost of the whole process [1]. As an alternative to the use of external reagents of magnesium and phosphorus, a research topic concerns the reuse of struvite as a reactant in sequential treatments [104–106]. Some works also experimented with the use of alternative reagents and methods for pH setting [47,107]. In the following sections, an overview on the main chemicals and techniques that were investigated and applied for struvite precipitation processes is reported.

2.6.1. Magnesium Sources

In the treatment for MAP precipitation, pure reagents such as MgSO₄, MgCl₂, Mg(OH)₂, and MgO are commonly used [65,99,103]. Some of these salts, such as MgSO₄ and MgCl₂, have the advantage of being very soluble allowing to recover a precipitate with a high purity degree [3]. Due to their easy management, they were used in many studies through which the kinetics of the nucleation process have been assessed [79,94,108]. They are also exploited in full-scale applications such as the Ostara Pearl®, the Phospaq, the Seaborne, and the AirPrex processes. However, despite their benefits, the dosage of MgSO₄ and MgCl₂ causes a marked increase in Cl⁻ and SO₄²⁻ concentrations, with consequent deterioration of the effluent quality [3,109].

The use of MgO, instead, does not produce any increase in solution salinity. However, magnesium oxide has low solubility in water. Therefore, to effectively feed the right quantity of Mg²⁺ ions in solution, it is necessary to pre-treat MgO by means of acid dissolution which complicates the precipitation process [106]. If phosphorus addition is required, MgO is, generally, dissolved through the supplementation of phosphoric acid [1,3,51,110]. However, for given N:Mg:P ratios, the addition of MgO and 85% H₃PO₄ showed the poorest performance among other combinations of soluble
chemicals, in the treatment of effluent of upflow anaerobic sludge blanket (UASB) reactors treating poultry manure wastewater [110]. Li and Zhao [51] detected analogous findings by comparing some chemical combinations in the removal of NH₄⁺ from landfill leachate. These results can be attributed to the low MgO solubility which results in a low global efficiency [110]. In effect, in some studies it was necessary to double the dosage of MgO, with respect to the stoichiometric ratio, to achieve ammonium removal efficiency of about 95% [1,54,80]. This overdose, clearly, notably affects the total cost for struvite production. Similar to the findings obtained with magnesium oxide, Mg(OH)₂ proved to be a less efficient Mg²⁺ source, in terms of NH₄⁺ removal, compared to soluble magnesium reagents [32]. Moreover, by using Mg(OH)₂, the pH value and the Mg:P molar ratio cannot be controlled independently of each other [111].

Over the past years, struvite crystallization by exploiting a magnesium sacrificial anode as the source of Mg²⁺ has attained interest as a possible way for phosphorus removal and recovery. Kruk et al. [112] found that a high-purity magnesium alloy cast anode was very efficient in the recovery of struvite with high purity from water solutions, by using an electric current density of 45 A/m². Hug and Udert [113] obtained a P removal of 3.7 mgPcm⁻¹h⁻¹ exploiting a sacrificial magnesium anode and applying a current density of 55A/m². Song et al. [114] demonstrated that the presence of Cl⁻ in the solution accelerates the Mg⁰ corrosion and facilitates the release of Mg²⁺.

Recently, Huang et al. [106] defined a novel approach for crystallization and precipitation of phosphate as MAP from swine wastewater using metal magnesium as Mg²⁺ source. The study was based on the reactions that the metallic magnesium undergoes in aqueous solutions. As a consequence of these reactions, the metallic Mg⁰ is oxidized to Mg²⁺ with production of OH⁻ and H₂. Therefore, the Mg⁰ corrosion plays two functions for struvite, formation by providing Mg²⁺ and raising the mixture pH. The authors demonstrated that the process efficiency depends mainly on the magnesium metal dosage. With a Mg⁰ dose of 10 g/L and a reaction time of 15 min, phosphorus recovery efficiency of 96.3% was obtained [106]. The reaction system performance was further improved by coupling metallic Mg⁰ with graphite pellets and air bubbling [106]. In fact, the presence of graphite significantly accelerates the Mg⁰ corrosion and the air insufflation reduces the passivation of the metal’s surface. An economic analysis indicated that the cost for dosing the Mg²⁺ through the corrosion of Mg⁰ metal was greater than that of using the MgO, but was similar to those of using MgCl₂ and MgSO₄. The use of metal Mg⁰ was successfully applied very recently in the recovery of P content from livestock wastewater obtaining efficiency close to 98% [107].

In recent years, the scientific community has turned its attention to the use of low-cost magnesium sources. In particular, magnesite [90,115], bittern [77,103,116], seawater [66,117], and wood-ash [118], have been tested.

- **Magnesite** (MgCO₃) is a mineral rock particularly abundant in nature but its low solubility in aqueous solutions makes it necessary to apply adequate pretreatments. Gunay et al. [90] used magnesite (MgCO₃) to evaluate ammonium removal from landfill leachate. In particular, the magnesite was pretreated with HCl to obtain a sufficient quantity of magnesium in solution. Ammonium removal yields in the form of struvite were 91%. The authors evaluated a reduction in the process costs of about 18.3% by using MgCO₃ instead of MgCl₂. However, a notable HCl addition was required to dissolve all the magnesium content of magnesite. In other studies, magnesite was calcined at high temperatures to produce a by-product (BMP), containing MgO, exploitable as a magnesium source in the MAP precipitation processes [54,80,105,115]. Quintana et al. [54,80] observed significantly lower performances in the struvite precipitation process using BMP produced from magnesite calcination compared to pure MgO. This can be justified by considering that BMP has an available Mg²⁺ amount lower than of pure MgO [54,80,105,115]. Moreover, BMP is generally characterized by greater particle sizes which slow down the reactivity [54,80,105].

- **Seawater** has a magnesium content of about 146 kgMg/m³ and represents a low-cost source of magnesium exploitable for struvite precipitation [66]. Rubio-Rincón et al. [117] evaluated the use of seawater as a source of magnesium for phosphorus recovery through MAP formation from separate human urine. In particular, the seawater was mixed with non-hydrolyzed urine and
hydrolyzed urine obtaining a 99% phosphorus removal after 10 min with a Mg:P molar ratio equal to 3.5:1 [117]. Struvite formation was favored with a urine/seawater ratio of 1:1.7 [117]. However, problems linked to the use of seawater were the formation of fine crystals [66] and the co-precipitation of calcite in addition to struvite [119].

- **Seawater bittern** is a by-product obtained from sea salt manufacturing which contains mainly MgCl₂ with small amounts of other inorganic compounds. Its Mg²⁺ content is notably higher than seawater and, therefore, it could represent a suitable low-cost source of magnesium [103]. The addition of bittern to a synthetic solution of swine wastewater was comparable to MgCl₂ and seawater, as a magnesium ions source, in terms of phosphorus abatements [105]. The effectiveness of seawater bittern was also proved for the phosphate recovery in real swine wastewater [105]. Moreover, Siciliano et al. [41,44,50] found that seawater bittern can be efficiently used as a source of magnesium in the removal of NH₄⁺ through MAP precipitation from landfill leachates and digestate of calf manure.

- **Combustion ashes.** Sakthivel et al. [118] investigated the possible application of wood combustion ashes as an alternative source of magnesium to favor struvite precipitation. By applying the wood ashes to the urine, 87% of the incoming phosphorus was removed after a 0.5 h treatment, but the production of hydroxyapatite was mainly observed [118]. Other studies detected mostly the presence of calcium insoluble compounds in the precipitate obtained using fly ashes and calcined paper mill sludge in the treatment of anaerobic digestion reject water [120]. Moreover, due to the high presence of metal compounds in combustion ashes [3], the recovered precipitate is generally incompatible with the legislation for fertilizers.

### 2.6.2. Phosphorus Sources

For treatments aimed at the removal and recovery of NH₄⁺ from high polluting wastewater (leachates, digestates, urine, etc.), because of the great surplus of ammonium relative to the concentrations both of magnesium and phosphorus, the supplementation of phosphorus sources must be also provided [41,44,50,121].

Generally, H₃PO₄ and phosphate salts such as Na₃PO₄, Na₂HPO₄ or NaH₂PO₄ are exploited as P-based compounds [3]. These compounds allow very high ammonium removal yields and the production of struvite with high purity degree. However, the use of pure reagents results in the consumption of natural P resources and makes the process very expensive. Indeed, the addition of phosphorus reagents generally results in the main cost of the entire treatment [1,44,122]. Therefore, it is necessary to identify unconventional and low-cost phosphorus sources effective in the struvite precipitation process. Currently, few studies have focused on the use of P by-products [41,44,50,121,122].

Huang et al. [121] conducted a study using waste phosphoric acid as a source of phosphorus for NH₄⁺ removal from landfill leachate. This work demonstrated that an ammonium removal similar to those achievable with pure phosphate salts could be obtained at pH 9 and N:Mg:P ratio of 1:1.2:1. By coupling the H₃PO₄ waste with low-cost MgO, as the magnesium source and as the alkali compound for pH correction, the NH₄⁺ removal yield was found to be 83% by dosing the MgO with M:Mg:P equal to 1:3:1 [121]. An economic analysis proved that the use of waste H₃PO₄ with the low-cost MgO can reduce the chemical costs by 68%. However, the presence of Al³⁺ in the phosphoric acid waste can significantly hamper the struvite formation by competing for the phosphate ions [121].

Siciliano et al. [41,44,50] used for the first time the bone meal, a by-product obtained from the thermal treatment of meat waste, as a low-cost source of phosphates for MAP precipitation. In Europe, the use of this by-product as a fertilizer is limited [123] and, as it is only suitable for a few alternative uses, it is usually landfilled [124,125]. Therefore, the utilization of bone meal for the struvite precipitation process is very profitable as it allows the recovery of its P content with the production of a more valuable compound which contains both PO₄³⁻ and NH₄⁺. The bone meal was coupled with the seawater bittern, as a Mg²⁺ source, for the ammonium recovery from methanogenic landfill leachates and calf manure digestates [41,44,50].
To dissolve its phosphorus content, the bone meal was properly mixed in sulfuric acid solutions, which resulted in phosphorus concentrations between 68–80 gPO₄³⁻-P/L [41,44,50]. H₂SO₄ was used to limit the dissolution calcium content of bone meal, which remained mostly in the insoluble form as CaSO₄. By coupling bone meal with seawater bittern, about 95% of NH₄⁺ content of raw landfill leachate and about 99% of P, added for the treatment, were removed and recovered by applying molar ratios N:Mg:P equal to 1:1.1:1 [41]. With the same reactants, by treating digestates of calf manure, an NH₄⁺ abatement of about 90% and a P recovery of about 99% were reached at pH 9 and with N:Mg:P = 1:1.3:1.3 [44].

Several bones’ ashes were characterized by Darwish et al. who found that the ash derived from waste fish bones has the highest phosphorus level [122]. The phosphorus content of these ashes was extracted by means of H₂SO₄ and, thereafter, it was effectively applied for MAP precipitation. In particular, by treating wastewater more than 90% ammonium abatement and high purity MAP were obtained [122].

2.6.3. Reactants for pH Correction

Because struvite precipitation occurs in moderate basic conditions, alkaline reagents such as NaOH, MgO, Mg(OH)₂, KOH are generally used to increase the pH to the optimum value [67,126–128]. Soluble compounds (NaOH, KOH) allow an easy and effective correction but they increase the salinity of solution and supply sodium and potassium that could interfere with struvite formation. On the other hand, magnesium oxide and hydroxide permit to increase the pH and, at the same time, they provide Mg⁺₂ ions required for MAP nucleation. However, due to their low solubility, these compounds must be dissolved in acids. Moreover, the pH setting and the addition of magnesium ions cannot be controlled separately. To reduce the cost connected to the consumption of alkaline compounds, recent studies showed that it is possible to raise the solution pH by using alternative reagents such as plant combustion ashes [40,103]. The experiments conducted by Huang et al. [48] stated the possibility of using plant ash as the alkali reactant obtaining that, under optimal conditions, >96% of phosphate was recovered from swine wastewater. Wang et al. [107] coupled the use of plant ash, for pH setting, and magnesium pellet, as Mg⁺₂ sources, to remove and recover the phosphorus content from livestock wastewater. With the addition of plant ash and magnesium metal of 11.66 and 3.33 g/L, respectively, the PO₄³⁻ abatement was 97.69% in 60 min [107]. The pH increase can also be achieved through the wastewater aeration. In this way, in fact, the CO₂ is stripped from the aqueous solution which, by varying the carbonate balance of the wastewater, results in the pH growth. Using CO₂ degasification technique, Korchef et al. [21] obtained an efficient phosphorus recovery from synthetic wastewater. A study conducted by Fattah et al. [23] at the Lulu Wastewater Treatment Plant (Richmond, BC), using a struvite crystallizer and a CO₂ cascade stripper, reached a P abatement of 90%, saving 86% of caustic soda usage. Nevertheless, the efficiency of this technology depends on different parameters, i.e., the influent characteristics, temperature, aeration flowrate, etc. The results of the experiments conducted by Siciliano et al. [44] showed that the CO₂ degasification technology has low effectiveness in the ammonium removal from high concentrated wastewater. In fact, the addition of acidic reactants of phosphorus and magnesium, required to compensate the ammonium surplus, causes a pH drop that cannot be balanced by air insufflation. These results agree with the statements of Sàidou et al. [22] who did not detect struvite formation when aeration was applied in the treatment of synthetic solutions with a pH lower than 6.5. Other studies highlight the application of processes involving the combination of aeration and the use of alkaline reactants to increase the pH value [99].

2.6.4. Struvite Reuse as a Reactant

As an alternative to the use of unconventional reagents, the recycling of struvite decomposition products could be a suitable option to limit the consumption of reactants and the treatment costs in the removal of ammonium. Indeed, during struvite decomposition NH₄⁺ ions are released, and the residues can be used as phosphorus and magnesium source for the treatment of raw wastewater. Different decomposition techniques including struvite pyrogenation, distillation, acidolysis, chlorination, and electrolysis were developed [4,17,104,105,129,130]. The pyrogenation in alkali
solutions has largely demonstrated its efficiency in ammonium release. The pyrogenation of MAP in NaOH solutions takes place according to the following reaction [104]:

$$\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}(s) + \text{NaOH} \rightarrow \text{MgNaPO}_4(s) + \text{NH}_3(g) + 7\text{H}_2\text{O}$$  \hspace{1cm} (3)

He et al. [17] found an ammonium-release higher than 96% when struvite was pyrolyzed with an OH:\text{NH}_4^+\text{molar ratio equal to 1:1, a temperature of 90 °C, and a heating time of 2 h. Zhang et al. [131} observed that the optimal conditions for pyrolysis production from struvite of coking wastewater were: OH:\text{NH}_4^+ = 1:1, heating temperature of 110 °C, and heating time of 3 h. With the same reaction time and temperature, in a very recent work, it was confirmed that the best molar ratio of NaOH to \text{NH}_4^+ was 1:1 for the pyrolysis of struvite from composting leachate [132]. Comparable findings were reported by Yu et al. [133]. Türker et al. [134] stated that distillation combined with NaOH addition at OH:\text{NH}_4^+ = 1:1 induced the complete NH$_3$ stripping in half-an-hour. The amorphous magnesium sodium phosphate (MgNaPO$_4$), produced from reaction 3, makes it possible for the NH$_4^+$ to replace Na$^+$ in a basic solution, forming again MgNH$_4$PO$_4\cdot6$H$_2$O. Therefore, the struvite pyrolysate can be used to remove and recover the ammonium amount from wastewater. Successful NH$_4^+$ abatements were obtained by exploiting the MAP decomposition residues as the unique source of phosphate and magnesium [17]. The NH$_4^+$ abatement decreased progressively with the increase of struvite reuse cycles, and in the sixth cycle, NH$_4^+$ removals of 84% and 62% were obtained for synthetic wastewater and landfill leachate, respectively [17]. In a five-cycle treatment of anaerobic digester effluents, NH$_4^+$ recovery was initially 92% and then it gradually decreased to 77% in the fifth stage [134]. The authors argued that the NH$_4^+$ abatement decreased as a fraction of recycled struvite residues remained in the supernatant during each cycle by reducing, in this way, the molar ratio required for the complete ammonium abatement. Moreover, during the subsequent treatments, the recycled magnesium phosphate became less active because the Mg$_3$(PO$_4$)$_2$ or Mg$_3$P$_2$O$_7$ content increased [134]. The NH$_4^+$ removal efficiency did not decrease, and stably remained around 90%, if the pyrolysate was supplemented with soluble salts of magnesium and phosphorus during the treatment cycles [134].

The main disadvantage of pyrogenation is the high temperatures required (≥90 °C) to obtain the struvite decomposition [17]. Huang et al. [128] proposed a process based on the air stripping technique which was able to reduce the decomposition temperature and stop the formation of less active compounds (Mg$_3$P$_2$O$_7$). The authors found that the gas/liquid ratio of 3600, the temperature of 60 °C, and the OH:\text{NH}_4^+ molar ratio of 2:1 were the optimal operating conditions for struvite decomposition, reaching an ammonium release higher than 92% [128]. The NH$_4^+$ removal from synthetic wastewater was stably higher than 80% by reusing the MAP decomposition products six times. In a continuous process, approximately 91% NH$_4^+$ and 97% PO$_4^{3-}$ was removed and recovered from swine wastewater with the supplementation of bittern [128]. Anyhow, the decomposition of struvite in basic environment could cause the dispersion of NH$_3$ in the atmosphere, making the process hardly applicable in field conditions [129].

Struvite decomposition in acidic solutions can be effectively applied at moderate operating temperature and it avoids the dispersion of ammonia gas [129]. In fact, in adequate acidic conditions, MAP is transformed in hydrated magnesium phosphates (newberryite) with the release of NH$_4^+$ in the solution, according to the following reaction:

$$\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}(s) + \text{H}^+ \rightarrow \text{MgHPO}_4\cdot3\text{H}_2\text{O}(s) + \text{NH}_4^+ + 3\text{H}_2\text{O}$$  \hspace{1cm} (4)

The ammonium ions remain in the acidic solution and could be potentially reused as a fertilizer source [4,129]. The newberryite resulting from reaction 4 can react in a basic environment with NH$_4^+$ ions forming again MgNH$_4$PO$_4\cdot6$H$_2$O. Zhang et al. [129] found that ammonium was efficiently released from MAP in a HCl solution at pH 5.0 and temperature 60 °C. With a dose ratio of MgHPO$_4$·3H$_2$O to NH$_4^+$ of 2, the MAP precipitates were repeatedly used five times reaching ammonium removal higher than 98% [129]. Siciliano et al. [4] tested various organic and inorganic acids such as H$_2$SO$_4$ (95%), HCl (32%), HNO$_3$ (60%), and CH$_3$COOH (80%) and, at the same time, the effects of pH and temperature were analyzed. The detected results demonstrated the high effectiveness of hydrochloridric and acetic
acids, which permitted a high and selective release of ammonium at T = 50 °C and pH = 5.5. The multiple recycling of struvite decomposition products, combined with the addition of a low quantities of PO₄³⁻ and Mg²⁺ at molar ratios of N:Mg:P = 1:0.05:0.05, permitted steady ammonium abatements of about 82%.

Huang et al. [105] investigated the chlorination process with the dosage of NaClO to the struvite produced from swine wastewater. In this treatment, the overall reactions in the system can be expressed as follows [105]:

\[
\text{ClO}^- + H^+ \rightarrow \text{HClO}
\]

\[
\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{MgHPO}_4 \cdot 3\text{H}_2\text{O} + \text{NH}_4^+ + 3\text{H}_2\text{O}
\]

\[
2\text{NH}_4^+ + 3\text{HClO} \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^-
\]

As the chlorination reactions proceed, the amounts of Mg²⁺ and HPO₄²⁻ rapidly increase and, in oversaturation conditions, they may form insoluble MgHPO₄⋅H₂O and Mg₃(PO₄)₂[105]. The study of Huang et al. [104] demonstrated that the struvite decomposition efficiency is affected by the pH and Cl/N ratio obtaining the better performance at pH 6 and Cl/N = 8.5. The multiple recycling of MAP decomposition products proved that the ammonium removal did not decrease as the number of reuses increased [105]. According to the authors, this may be attributable to the fact that the amounts of active Mg²⁺ and PO₄³⁻ remained unchanged during the multiple-reuses. In this treatment, however, the ammonium amount is not recovered but, instead, it is oxidized to N₂.

Liu et al. [135] used electrolysis, supported by the addition of NaCl as an electrolyte, to induce the struvite decomposition. With the addition of NaCl, chlorine forms at the anode and it is then transformed to HClO and ClO⁻ in the electrolytic reactor. Therefore, the overall reactions occurring in such a system are similar to those of the chlorination process. Optimum conditions for the electric voltage, NaCl, reaction time, and initial struvite amount of 7 V, 0.06%, 1.5 h, and 1.25 g/L were found by the authors [135]. The use of dissolved struvite allowed abatements of phosphorus and ammonium from swine wastewater up to 79% and 53%, respectively [135].

3. Reactors Configurations

3.1. Stirred Tank Reactors—STR

Stirred tank reactors (STR) represent the most used reactors in laboratory studies [28,53,55–57,59–62,136,137]. From a structural point of view, they are very simple units equipped with a mixing system that allows for the homogenization of the wastewater with the reactants, as well as auxiliary devices for the introduction of reagents and wastewater, the extraction of precipitate and of surmatant, and for the control of the operating parameters [28,56,58].

The mixing condition inside the reactor represents a fundamental aspect because it affects the struvite formation [57]. An effective mixing promotes the crystals nucleation and growth by improving the mass transfer of ions from the solution to the solid phase. Liu et al. [66], in a study conducted on synthetic and real urine samples, reported that by increasing the mixing energy from 160 rpm to 240 rpm, the precipitation efficiency of struvite crystals increased by 33%. The experiments conducted by Ohlinger et al. [138] showed that the struvite crystals morphology was more dendritic in the reactor’s areas affected by low turbulence, while the crystals had more regular shapes in areas with greater turbulence. In effect, a too low stirring speed favors the formation of fouling on the blades of the mixer producing a reduction of the stirring efficiency and, consequently, a reduction of the quality of the struvite crystals [28]. Furthermore, insufficient stirring energy increases locally the oversaturation in the solution and, therefore, promotes the local nucleation of new struvite crystals without promoting their growth. Consequently, the crystals growth rate increases with the turbulence conditions in the reactor [12]. However, the improvements on crystals growth and morphology disappear beyond a certain
mixing speed [66]. In effect, limited growth of struvite crystals was observed with stirring speed greater than 500 rpm [57,95].

Generally, completely mixed reactors can operate continuously or in batch mode. A batch reactor works according to a series of phases and the struvite production and precipitation occur in the same unit. On the contrary, in a continuous reactor only the struvite formation takes place, while the precipitation phase occurs in a separate unit.

In some studies, a single unit was developed and used in which both the struvite formation and sedimentation occurred, and which operated continuously. This unit consisted of two parts. The bottom part was the reaction zone, while the top part was a settling zone designed to avoid the discharge of fine particles with the effluent [28,56,82]. The reaction zone operated as a perfectly mixed reactor [139]. The settling zone was equipped with a baffle to guide the flow. The effluent flowed out at the top of the settling zone over a weir. The mixer was an axial flow propeller. A second mixer was placed at the end of the axis to avoid solids deposition at the bottom flow gate. In the experimental set-up used by Aguado et al. [56], the reactor was provided with a solids trap put at the bottom part of the reaction zone. This purge system allowed the harvesting of the larger precipitate particles, while the smaller solids remained growing within the reactor [56]. The phosphorus recovery efficiency achieved with this configuration was greater than 87% in the treatment of separate urine. The average dimension of the recovered solids was between 110 μm and 320 μm.

Kim et al. [53] developed a lab-scale airlift reactor able to operate in continuous mode and that was effectively used for struvite crystallization. The reactor worked with a hydraulic retention time of 10 min for the mixing zone, and 3 h for the entire reactor, obtaining NH₄⁺ and PO₄³⁻ removal of 95% and 98%, respectively.

As previously described, struvite precipitation can also be induced by the dissolving CO₂ degasification technique. In these processes, the air bubbling through the solution is exploited to promote the pH increase but, at the same time, it allows to mix and homogenize the mixture in the reaction zone. Therefore, the air insufflation replaces the mechanical mixer in the stirred tank reactors. Clearly, the airflow rate notably influences the process efficiency as it affects the reaction pH and the mixing conditions. Phosphorus removal efficiency of about 78% was observed by Saidou et al. [22] for experiments conducted with air flowrates between 10 and 25 L min⁻¹. For higher air flowrates, the phosphorus removal decreased [22]. The authors argued that with excessive air flowrates the liquid shear stress increased. This affected the transfer of struvite constituent ions from the liquid to the solid phase and inhibited their reaction with the crystal surface, hence limiting the particles growth. Therefore, it is not suitable to operate with too high flowrates as they would not improve the process performance and, on the other hand, would increase the operational costs.

In general, in stirred tank reactors the control of the struvite formation process is simpler and manageable compared to the other technologies, which justifies their large utilization. In particular, STR are not affected by the problems related to the flow control, typical of fluidized bed reactors (FBR) [30] and they do not present plant complexities. Moreover, STR can be easily used both in batch and continuous mode. Furthermore, the hydraulic reaction time can be reduced to a few minutes, obtaining high process performances (Table 1). On the other hand, the high stirring velocity (Table 1), necessary to mix the solid particles, causes great energy consumptions and makes it difficult to control the dimension of MAP crystals [39]. In fact, fine struvite particles are generally produced in stirred tank reactors. These disadvantages can be only partially limited by exploiting the air insufflation.

### 3.2. Fluidized Bed Reactors—FBR

The FBR, in the classical configuration, consist of a central body with a predominantly longitudinal development in which crystals nucleation and growth take place [140]. The waste stream is, generally, introduced at the bottom together with the reagents necessary for struvite nucleation. From the top of the reactor, the liquid falls into an external clarifier from which part of the flow is recirculated to the bottom of the crystallization reactor [65,68]. In some configurations, the recirculation of the effluent and suspended struvite crystals is carried out directly from the top to the bottom of the reaction tank. The recirculation flowrate can vary considerably depending on the type of
wastewater and on the characteristics of the reactor. Struvite crystals nucleation begins in the FBR central body, through mechanisms of interaction with the other struvite particles or with seeding inert materials that constitutes the fluidized bed [12,69]. The fluidization of the particles in the reactor can be guaranteed either by an appropriate upward speed of the recirculation flow or by aeration [67,69–71]. The air insufflation, in addition to the bed fluidization, promotes the pH increase and, consequently, it reduces the dosage of alkaline compounds to reach the pH conditions suitable for struvite nucleation [66,69,72].

Le Corre et al. [108] obtained phosphorus removal up to 80% in a study conducted on a batch FBR laboratory pilot plant by applying recirculation flow rate between 1.35 and 1.5 L/min, directly from the top of the reactor, and an airflow rate between 5 and 10 mL/min. However, the process showed an overproduction of small particles. The authors found a motivation in the actual negative surface charge of struvite crystals and proposed as possible solutions the coagulation of fine particles or the use of seed inert material, which could help to improve the growth step.

In this regard, Battistoni et al. [69] effectively used inert sand as a seed material to promote struvite crystallization and growth. In particular, the authors studied the auto-nucleation and crystal growth of struvite in a demonstrative reactor for the treatment of supernatant of anaerobic digester. By treating an influent flow rate up to 2 m³/h, operating in metastable conditions, phosphorus removals between 69.4% and 86% were detected [69]. The minimum recycling flow rate, necessary to fluidize the bed, was 17 m³/h and it allowed the growth of rounded-shaped crystals with dimensions of about 0.7 mm [69].

On the other hand, Shimamura et al. [73] affirmed that in the conventional FBR, as the crystallization progresses, the particle sizes of MAP become large and it is difficult to keep them constant. The excessive growth of struvite particles could cause operational difficulties in the system. Therefore, the authors developed a two-tank type unit consisting of a main reaction tank and a sub reaction tank that allowed them to produce particles with uniform dimensions. In particular, fine particles (mean size 0.05 to 0.25 mm), floating in the upper part of the main reaction tank, were transferred, at a frequency of once in three to four days, into the sub reaction tank where they grew up to about 0.3 mm [73]. These particles were returned totally into the main reactor where they acted as a seed material. With this operating mode, the average particle dimension in the main reactor remained stable. Dimensions of MAP granules around of 1 mm were maintained depending on wastewater characteristics, recirculation ratio, influent flow rate, and magnesium additions [73].

Several other studies aimed to verify different plant configurations for fluidized bed reactors. Bowers and Westerman [74] developed a FBR unit with conical walls for the treatment of swine lagoon liquid. The cone-shaped fluidized bed crystallizer offers significant advantages for precipitating the struvite particles because its range in upflow velocity (high velocity at the bottom, diminishing to a low velocity at the top) retains a wide range of particle sizes in a dense bed [74]. With this type of reactor orthophosphate removals up to 82% were reached in field conditions [74].

Other authors used a fluidized bed reactor made by different zones with an increasing diameter [24]. The diameter change causes turbulent eddies above each transition zone, ensuring adequate mixing conditions and helps to classify the fluidized particles by size [27,68]. The larger particles accumulate at the bottom and are harvested periodically. In the experiments of Bhuivan et al. [68], phosphate removals of about 75–85% were detected with an upflow velocity of about 400–410 cm/min. The results detected by Fattah et al. [23] showed that the reactor with an increasing diameter was able to remove over 90% of phosphate at pH 7.5. Guadie et al. [70] designed a cone-inserted fluidized bed reactor which had three distinct parts, with the diameter that gradually increased toward the top, and cone-shape structures at an angle of 45° between each part. The strategy of inserting of cones aimed at reducing unwanted particles loss at each junction. The authors found that with the same operating conditions, the reactor with cones obtained phosphorus removal yields between 93% and 98%, while a reactor without cones reached lower removal yields between 78% and 81% [70].

In other studies, pilot scale reactors with a dual function, crystallization by aeration and struvite separation by settling were designed [55,71,111,141,142]. This type of reactor has an internal reaction zone, which consists of an aeration column for struvite formation, and an external settling zone for
precipitate separation. Such a configuration can be easily created with only minor modifications to an existing settling tank in a wastewater treatment plant [141]. In the experiments conducted by Liu et al. [143], MAP formation was directly proportional to the aeration rate and reached a plateau at a specific flowrate of around 0.73 L/(L·min), with a phosphorus removal of about 92.5%.

Some authors included an internal recycle of precipitate through air lift [142]. In the internal recycle seeding reactor (IRSR), seeds are lifted constantly by air from the settling zone to the reaction zone to contact with wastewater to form new struvite particles. The crystals concentration can be controlled by adjusting the circulation flowrate and the amount of solids at the bottom. This type-unit, with respect to a non-seeded reactor, permitted to increase the phosphorus recovery by 19% in the case of low P concentrations in wastewater, but showed comparable efficiencies in the case of high P influent concentrations [142].

The fluidized bed reactors have the main advantages in the rapid growth of struvite crystals [12]. Furthermore, in FBR the dimensions of MAP particles increase over time and several modalities (use of seed inert material, use of metallic meshes, use of internal seeds recycle, etc.) can be exploited to limit the fine particles production [39]. In effect, in FBR large crystals were obtained (Table 2). However, the fluidized reactors are characterized by a management complexity higher than stirred tank reactors. This is attributable to the difficulty in controlling the flows for the bed fluidization and for the eventual recycle of fine produced particles. Furthermore, the high flowrates cause, in general, high energy consumption [12,70]. In addition, the fluidization of solids in the reactor produces the erosion of internal walls and devices [39]. Therefore, a frequent maintenance may be required which increases the process expense [39].

3.3. Bioelectrochemical Systems—BES

Bioelectrochemical systems (BES) represent promising technologies for recovering energy, biofuels, or chemicals from wastewater treatment. BES utilize living microorganisms to drive oxidation and reduction reactions at solid electrodes [144]. With respect to conventional fuel cells, BES operate in relatively mild conditions and do not exploit costly precious metals as catalysts [145]. BES can be divided into two main categories: Microbial fuel cells (MFC) and microbial electrolysis cells (MEC). The first one, thanks to the action of microorganisms, produces electricity, while the second one exploits electricity to produce biofuels [144]. In addition to the conventional applications, BES could play a role in the recovery of nutrients in the form of struvite in the wastewater treatment plants [146–150].

3.3.1. Microbial Fuel Cells—MFC

MFC are bio-electrochemical systems that generate electricity by reproducing the natural bacterial interactions in which microorganisms catalyze organic compounds such as glucose, acetate, butyrate, or wastewater [151,152]. By oxidizing the organic substance, the electrons from the anode migrate, through an electric circuit, to the cathode to be transferred to an electron acceptor such as oxygen [153]. *Shewanella putrefaciens* [154], *Aeromonas hydrophila* [155], *Escherichia coli* [156], and other microorganisms, are used for the catalytic activities through which an electromotive force is generating.

Fischer et al. [156] proved that MFC could be applied for phosphate recovery from digestate of sewage sludge. In this application, a MFC system was exploited exclusively to release orthophosphate from iron phosphate contained in the digestate. A successive addition of Mg²⁺ and NH₄⁺, as well as pH setting, were executed outside MFC for phosphorus recovery as struvite crystals [156]. You et al. [148] developed a three-stage MFC/struvite extraction system to maximize urine utilization in terms of electricity generation and struvite recovery. This system consists of a stirred reactor for struvite precipitation put between two MFC units. The authors observed that placing MFC before the struvite precipitation process helped struvite collection by accelerating urea hydrolysis, and furthermore, removing struvite from urine before the MFC helped minimize system blockages without hindering MFC performance. With this system 82% of phosphate was removed [148].

Ichihashi and Hirooka [157] found that phosphorus can be removed and recovered directly through MFC because of the struvite crystals deposition on the surface of the liquid side of the cathodes. Indeed, a local pH growth occurs near the cathode, where water is being consumed and
hydroxide is generated as a byproduct [157]. This pH increase, in presence of sufficient amounts of Mg\(^{2+}\) and NH\(_4^+\), creates favorable conditions for struvite crystallization. In a study conducted in a single chamber MFC reactor, phosphorus recovery efficiencies, in the form of struvite, of up to 40% were observed [58,157–159]. Tao et al. [160] compared the removal efficiencies of phosphorus and ammonium in a single-chamber MFC reactor and a two-chamber system. The work proved that the two systems can both efficiently remove phosphorus with efficiencies close to 90% [160]. However, phosphorus was removed by the mutual effect of chemical precipitation and microbial absorption. Exclusively on the cathode of the single chamber, crystals with prismatic morphology typical of struvite were observed [160]. Santoro et al. [159] treated human urine in a single chamber MFC reactor demonstrating the possibility of phosphorus recovery in the form of struvite and hydroxyapatite. Furthermore, the high concentrations of ammonium generated by the hydrolysis of urea are potentially recoverable in the form of struvite by adding Mg\(^{2+}\) and PO\(_4^{3-}\) based reagents until reaching the equimolar conditions [148,159].

Hirooka and Ichihashi [150] evaluated the effect of NH\(_4^+\) and Mg\(^{2+}\) additions on the precipitation of phosphorus in artificial wastewater by an air-cathode single-chamber microbial fuel cell. The experimental results proved that when both NH\(_4^+\) and Mg\(^{2+}\) were dosed the phosphorus was removed through struvite precipitation at the cathode.

However, the fouling on the cathode, reducing the electrical performance of the cell, is one of the main problems related to the MFC operations. Indeed, the accumulation of solids blocks mass transfer near the cathode, therefore, to restore the system efficiency, the deposited solids must be frequently removed [150,159].

3.3.2. Microbial Electrolysis Cells—MEC

In a Microbial Electrolysis Cells (MEC) the electrons migrate from the anode, where the organic substrate is oxidized, to the cathode where, through the addition of electricity from the outside and in the presence of a suitable catalyst, it is possible to obtain valuable products such as H\(_2\), CH\(_4\), and chemicals as struvite [144,146,147,161].

Cusick and Logan [146] investigated the phosphorus recovery as struvite in a single chamber MEC unit. The MEC cathodes were either stainless steel 304 mesh or flat plates. Phosphorus removal was between 20% and 40%, with higher removal reached with mesh cathodes than using flat plates. Cathode accumulated solid were verified as struvite crystals. In a subsequent study by Cusick et al. [147], a two-chamber MEC reactor with a fluidized bed cathode chamber was developed to ameliorate phosphorus abatement and limit cathode scaling. In this system, the particles scour the cathode and help to reduce scale accumulation.

The authors observed phosphate reductions in digestate supernatant between 70% and 85%, with an energy consumption of 0.2–0.3 Wh/L, notably less than that needed in other methods for struvite formation [147]. The collected solids showed an equimolar composition of Mg and P supporting phosphorus removal through struvite formation [147].

In the study conducted by Almatouq and Babatunde [161] on synthetic wastewater with a chemical oxygen demand (COD) of 500 mg/L, using a double-chamber electrolytic microbial cell, a phosphorus removal of 95%, in the form of struvite, was found. Furthermore, H\(_2\) was produced with a maximum production rate of 0.28 m\(^3\)H\(_2\)/m\(^2\)/d, by applying a voltage of 1.1 V. The produced hydrogen could be used as an energy source to reduce the operating costs of struvite production [147,162]. This study highlighted the problem of fouling due to the accumulation of struvite on the cathode which causes a reduction in the efficiency of the MEC reactors. In effect, although MFC and MEC are promising technologies, the actual applicability at an industrial level still seems very far away, therefore, further studies are needed for their development.

3.4. Ion Exchange Technologies

Adsorption/ion exchange are promising methods for nutrients removal as they are simple, economical, and result in less sludge production [163]. Ion exchange process is suitable for reducing nutrient amounts provided that the ion exchange resins are selective, low cost, and effectively
regenerable and reusable [164]. Ion exchange resins are, typically, used as filter media in filter-based systems and after a period of utilization they become exhausted, causing a deterioration in the removal efficiency. The exhausted resins can be regenerated using proper regenerating chemicals or a mixture of them [164]. The nutrient removed during the regeneration of resin can be subsequently recovered by precipitation as struvite [164]. In particular, the REM NUT process is based on two commercial exchangers, a natural zeolite and a strong base anion resin removing NH₄⁺, K⁺, and PO₄³⁻ respectively, from biologically oxidized urban wastewater. Nutrients are then recovered by precipitation from the exchangers spent regeneration effluents in the form of NH₄⁺ and/or K⁺ struvite [163]. According to Petruzelli et al. [163], one of the main limitations of this process is the low availability of effective PO₄³⁻ selective sorbents, which prevents its application on a full scale. The authors investigated a “P-driven” version of the REM NUT® scheme using a PO₄³⁻ selective sorbent developed at Lehigh University, PA, USA [163]. P removals stably higher than 80% were reached in subsequent cycle runs [163]. Other types of resins were tested for phosphorus recovery [164]. Nur et al. [164] used the Dowex 21K-XLT resin for P adsorption from a membrane bioreactor effluent. The resin showed a maximum PO₄³⁻ absorbing capacity of 38.6 mg/g [164]. The adsorbed phosphate was desorbed by leaching the column with 0.1 M NaCl solution and, afterwards, it was recovered as struvite through the addition of NH₄⁺ and Mg²⁺ at the stoichiometric molar ratios and pH 9.5 [164].

Contrary to the conventional applications in which ion exchange processes are used to catch nutrient ions from wastewater, Mijangos et al. [165,166] exploited the ion exchange isothermal supersaturation (IXSS) to recover struvite with spontaneous precipitation reactions. In the IXSS process Mg²⁺ is stripped from a weak cationic resin and replaced with the excess of NH₄⁺ in the wastewater [165,166]. The highly supersaturated solution, containing Mg²⁺, PO₄³⁻, and the residual NH₄⁺, remains stable while it is flowing alongside the fixed bed, therefore avoiding clogging problems. After leaving the column, the chemical environment destabilizes the supersaturated solution, and this promotes reagentless struvite precipitation. The authors obtained stable supersaturated MAP solutions by stripping magnesium from Lewatit CNP80 cation exchange resin in Mg-form, under batch and dynamic conditions [165,166]. The pH of MAP formation was about 8.0 and X-ray diffractograms of the produced precipitates confirmed the presence of MAP crystals [167]. Ortueta et al. [167] studied three different ion exchangers: Lewatit CNP80 macroporous carboxylic resin, Lewatit S100 microporous sulphonic resin, and Amberlite IRC86 macroporous sulphonic resin, for production of MAP. In the case of the carboxylic microporous resin, Amberlite IRC86, was proved the presence of struvite in the produced precipitate through XRD analysis.

However, the applicability of ion exchange processes can be notably limited by the characteristics of wastewater. Indeed, by treating wastewater with high suspended solids, such as anaerobic mud or swine waste, fouling phenomena can make the exchange columns ineffective [168]. Therefore, strong pretreatments are necessary before ion exchange processes.

3.5. Membrane Technologies for Nutrients Recovery

Membrane separation technologies separate the incoming wastewater stream into two fractions, the aqueous flow that passes through the membrane, called permeate, and the phase rich in solids, called retentate [169]. The membranes selectively separate the different components of the wastewater mainly based on the size and without phase transformation. Membranes can be built with organic or inorganic materials [169]. The membrane operations of interest in this area include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and forward Osmosis (FO), electrodialysis (ED) [170].

In particular, the nutrients in particulate form can be recovered by UF and NF, while the nutrients present in soluble form can be recovered by RO or FO.

Generally, the use of these technologies for the struvite precipitation processes aim to obtain a permeate or a retentate rich in N and P so as to be subsequently recovered by precipitation [171–175].

Bu et al. [172] evaluated the possibility of ammonium and phosphorus recovery in the permeate of an anaerobic membrane bioreactor (AnMBR) treating swine manure. At pH 9 a phosphorus removal of about 70.5% was reached, obtaining struvite crystals with a purity of 98% [172].
Hakimi et al. [176] studied the struvite precipitation process on the permeate of AnMBR reactor treating abattoir effluent. In this study 82% and 66% removal of phosphate and ammonium, respectively, were reached at pH 9.5. Kumar and Pal [173] applied a membrane-integrated hybrid system for the removal and recovery of ammonium from wastewater of a coke-making plant. After a nanofiltration process the permeate side had high concentrations of NH₄⁺ in the uncontaminated form, as impurities were rejected. Ammonium was recovered through MAP precipitation in a separate STR reactor by dosing external sources of Mg²⁺ and PO₄³⁻. Over 97% of ammoniacal nitrogen precipitated out as struvite at stoichiometric molar ratios and pH 9 [173].

Other studies evaluated the possibility of recovering phosphorus and nitrogen via forward osmosis [175]. In this technology water passes from a solution with lower osmotic pressure into a solution with higher osmotic pressure that is known as the draw solution (DS) [171]. The process can concentrate PO₄³⁻, Mg²⁺, and NH₄⁺ in the feed side to allow MAP recovery [172]. The forward osmosis has several advantages such as high pollutants rejection and lower fouling tendency in comparison to conventional pressure-driven membrane processes [171]. Studies were conducted testing different types of draw solute for the nutrients concentration. Zhang et al. [177] and Xue et al. [178] exploited seawater brine as a draw solution for mining nutrients from urban wastewater and urine. Xie et al. [179] used MgCl₂ as a draw solution for nutrients removal from anaerobically digested sludge centrate. Volpin et al. [175] used a commercial fertilizer blend as DS to concentrate real diluted urine. During the concentration, the urea in the urine was recovered because it diffused to the fertilizer. The mixture of concentrated PO₄³⁻, reverse Mg²⁺ flux from the DS, and the magnesium ions present in the flushing water permitted to recover about 93% phosphate, in the form of MAP, in a separate crystallization unit [175]. Pramanik et al. [171] studied the effects of different draw solutions (MgCl₂, EDTA-2Na, and NaCl) on the FO performance for the treatment of digested dairy manure, followed by phosphorus recovery through struvite precipitation. MgCl₂ gave the best results because the reverse flux of Mg²⁺ to the concentrated inlet flow provided favorable conditions for struvite crystallization.

Despite the encouraging results in experimental works, the membrane technologies are hardly applicable in field conditions due to some unfavorable aspects. The main disadvantages of using membrane technologies include the high energy costs and the fouling phenomena.

4. Full-Scale Struvite Recovery Technologies

In addition to the numberless applications at laboratory and pilot scale plants, currently, due to its profitable aspects, the struvite recovery processes are applied at industrial scale for the treatment of municipal and industrial wastewater and agro-industrial waste [19]. The most used industrial-scale technologies include:

- OSTARÁ (Pearl®). Ostara technology uses a FBR for struvite crystals recovery consisting of three zones with an increasing diameter from the bottom to the top. In the lower area, there is reagents feeding and recovery of struvite crystals; in the central one the nucleation and growth of the crystals take place; while in the upper part, the discharge of the treated wastewater occurs. The effluent is recirculated with a flow rate of about 20 times the inlet flow [180]. MgCl₂ is added to guarantee the molar ratio Mg:N:P equal to 1:1:1, while NaOH is added as an alkaline reagent [19]. This technology has been developed since 2005 by the University of British Columbia. Currently, 22 plants that use this technology are installed all over the world, most of which are located in the USA and Canada. Ostara technology allows up to 22% of total phosphorus to be recovered in an urban sidestream wastewater treatment plant, and up to 95% of phosphorus and 15% of ammonia nitrogen in the treatment of digestion supernatants [181]. Furthermore, the process allows daily productions of about 500 kg/d of struvite particles with sizes between 1.5 and 4.5 mm [20].
- SEABORNE. The Seaborne process was developed in 2006 in Germany and it involves nutrients recovery from digested sludge pretreated with sulfuric acid [181]. The technology consists of a first acidification phase with H₂SO₄ to extract nutrients and metals. The remaining solid phase is incinerated while the liquid phase undergoes a process for the recovery of the heavy metals by gas-liquid precipitation using H₂S-rich biogas [181]. Subsequently, nutrients recovery as struvite takes place in a completely mixed reactor after the addition of Mg(OH)₂, as a
magnesium source, and NaOH to reach the pH 9. Finally, the residual dissolved ammonium is recovered through a scrubber in the form of ammonium sulfate [19,20].

- **PHOSPAQ™.** This process, developed in Holland, aims at the removal both of phosphorus and ammonium present in the wastewater. The process takes place in a completely mixed aerated reactor to obtain the simultaneous degradation of COD and nutrients recovery in the form of struvite. Aeration permits the biological COD oxidation and, at the same time, the CO₂-stripping which favors the establishment of pH values around to 8.2, suitable for the struvite precipitation [19]. MgO is dosed as a source of Mg²⁺ to reach the stoichiometric N:Mg:P molar ratios. With this technology it is possible to produce MAP particles with dimensions of about 0.7 mm [19,20]. Phosphorus removals between 75% and 81% were obtained in an industrial-scale application conducted on potato processing wastewater.

- **ANPHOS®.** This technology for phosphorus recovery was developed in the Netherlands and operates in batch conditions. In particular, in a first aerated reactor the waste alkalization takes place by CO₂-stripping, while in a second reactor, Mg(OH)₂ is introduced as a source of Mg²⁺ to promote the MAP formation. This process can recover 80–90% of the phosphorus contained in the influent. Once dried, the produced struvite can be directly used as a fertilizer [20]. With this treatment, a reduction in the influent COD also occurs, which leads to a lower oxygen consumption in the subsequent treatments [20].

- **PHOSNIX.** The process involves the phosphorus recovery as struvite from supernatants of digested sludge in a fluidized bed reactor [67]. This process was developed by the Japanese company Unitika Ltd. Environmental and Engineering Division. Mg(OH)₂: is dosed as a source of magnesium, until the molar ratio of Mg:P of 1:1 is reached to allow struvite crystals nucleation and growth. pH values between 8.2 and 8.8 are guaranteed by an aeration system and the addition of NaOH, which also promote the ammonium stripping. The process allows recovering struvite crystals directly usable as fertilizers between 0.5–1 mm in size [67].

- **NuReSYS.** The NuReSYS (Nutrients Recovery System) process was developed in Belgium for struvite recovery from digested sludges and dewatering effluents. This process allows the continuous recovery of the phosphorus using a completely mixed reactor [67]. The pH suitable for struvite crystallization is guaranteed by an aeration system which induces the CO₂-stripping. The process can operate in two different modes. Specifically, it can be applied to favor the spontaneous precipitation of struvite, without adding magnesium, to avoid the scale formation on the sludge management equipment. The other configuration, instead, exploits the introduction of Mg(Cl)₂, as a source of magnesium, to allow better efficiency in phosphorus removal. Phosphorus abatement about 96% and a production of struvite particles of variable sizes between 2 and 6 mm, were obtained with NuReSYS process [126].

- **AirPrex®.** AirPrex technology was developed in Germany to solve the struvite incrustation problems downstream of the anaerobic digestion processes [182]. This technology uses two reactors for struvite precipitation and recovery from digestates before dehydration treatment. In the first reactor, the nucleation and growth of struvite crystals take place. This unit is aerated to promote the pH increase around 8 and to keep the struvite crystals in agitation. Two vertical partitions further promote an effective circulation. The second conical bottom reactor allows the sedimentation of struvite crystals and the discharge of the purified effluent [20].

- **MULTIFORM™.** Multiform technology was developed in the United States for nutrients recovery from agro-industrial wastewater. The plant unit consists of a cone-shaped fluidized bed reactor that allows to remove about 80% of the phosphorus from wastewater with a struvite crystals retention time equal to three days [74]. Crystallization is favored by adding Mg(Cl)₂, as a source of magnesium, and NaOH as an alkaline reagent. Although the struvite crystals are produced quickly, the crystals obtained have a low degree of purity [74].

### 5. Use of Struvite as a Fertilizer

Struvite has some characteristics very favorable for the use in agronomic applications. First of all, struvite contains essential nutrients such as nitrogen and phosphorus for plant growth [39].
Furthermore, its low solubility in environmental conditions induces a slow release of ammonium and phosphorus in the soil, which allows optimal plant growth over the time, avoiding potentially harmful overdose phenomena [183]. Finally, the struvite precipitation from waste and wastewater recovers nutrients that would be otherwise dispersed in the environment, saving environmental and economic damages [184]. Zhang et al. [183] calculated that for every 100 m$^3$ of treated livestock wastewater, up to 1 kg of struvite can be recovered, allowing to avoid the dispersion of nutrients in surface water bodies.

Anyhow, the potential reuse in agronomic practices should satisfy specific legal requirements. Clearly, the recovered compounds must not contain hazardous elements able to produce environmental impacts or human health damage. The EU Fertilizing Products Regulation ([EU] 2019/1009) [185], in the case of inorganic macronutrient fertilizers, establishes threshold values for the following elements: Cd (60 mg/kg\text{dry matter}), Cr$^6+$ (2 mg/kg\text{dry matter}), Hg (1 mg/kg\text{dry matter}), Ni (100 mg/kg\text{dry matter}), Pb (120 mg/kg\text{dry matter}), As (40 mg/kg\text{dry matter}), Cu (600 mg/kg\text{dry matter}) and (1500 mg/kg\text{dry matter}). In addition to these limits, a fertilizer containing more than 1% by mass of organic carbon shall meet requirements for pathogens [185]. Similarly, the legal regulations in other countries fix limits for heavy metals and organic micropollutants [33,111]. Therefore, it is essential to recover a precipitate characterized by limited amounts of hazardous elements. In this regard, struvite has been shown to be characterized by a low content of heavy metals and dangerous micropollutants, such as PCBs [33,186].

Several studies were carried out to evaluate the effects on plant growth using struvite recovered from wastewater as a fertilizer [34,41,128,186]. Struvite was tested as a slow-release fertilizer in pot plants, vegetable crops, ornamental plants, turf grass, and field crops [51]. El-Diwani et al. [63] conducted a comparative study on broad bean growth rate using a commercial fertilizer and struvite recovered from the treatment of industrial wastewater. In particular, the study compared the broad bean growth in absence of fertilizers with struvite and using a mixture of pure fertilizing compounds. The struvite was dose at a rate of 2%, whereas, in the sample with pure compounds, nitrogen, phosphorus, and potassium were applied at a rate of 20, 50, and 40 mg/Kg\text{soil} as ammonium nitrate, superphosphate, and potassium sulphate, respectively. The results of plant growth tests showed that the application of struvite increased the fresh and dry weight of broad bean plants at different stages of growth.

Li and Zhao [51], to assess the fertilizing power of the struvite, recovered from landfill leachate, executed a set of pot tests using four species of vegetables including Chinese flowering cabbage, Chinese chard, water spinach, and water convolvolus. Each plant was growing without added fertilizer, with struvite supplementation, and with the feeding of a model fertilizer. The germination and growth of the vegetables in the pots with struvite showed notably higher rates compared to those in control tests [51]. The experiments also proved that, due to its poor solubility in water, the struvite overdosing did not cause any problems. Furthermore, the authors observed that the MAP utilization did not result in more heavy metals in the vegetables than those from control and model fertilizer [51]. Yetilmesoy and Zengin [110] also studied the potential use of struvite, recovered from UASB treated poultry manure wastewater, through a series of tests with fast-growing plants such as portulaca (\textit{Portulaca oleracea}), garden cress (\textit{Lepidium sativum}), and grass (\textit{Lolium perenne}). In particular, a comparison was made using garden soil as control; garden soil with addition of struvite; sand with addition of KCl as control; sand with addition of KCl and MAP precipitate.

The experiments showed that the plants that were treated with struvite grew much faster than the garden soils and the samples with only KCl. Moreover, the application of struvite notably increased both fresh and dry weights of the plants up to 257% and 402%, respectively [110].

Liu et al. [130] conducted a study using MAP recovered from swine waste as a slow-release fertilizer for corn growth. In this study, plant growth was evaluated on an unfertilized soil (control), on a soil fertilized with struvite, and on a soil fertilized with a generic chemical fertilizer, consisting of a superphosphate (20% of P$\text{O}_3$) and urea (46% of N) [130]. The results showed that struvite can be successfully applied to the cultivation of corn in pots as the plants’ heights and circumferences,
as well as the nutritional components, were similar in plants fertilized with MAP and with generic chemical fertilizers [130].

Ryu et al. [186] compared the fertilizing power of struvite recovered from a semiconductor wastewater treatment plant with those of complex commercial fertilizers and organic compost for Chinese cabbage cultivation. The tests showed different growth rates in relation to the type of used fertilizer. In particular, the tests carried out with struvite showed the second-best growth rate, second only to the samples treated with the complex fertilizer [186]. The best performances of the complex fertilizer have been identified in the greater supply of potassium (K). The lowest accumulation of Cu and no detection of Cd, As, Pb, and Ni was observed in the struvite-treated samples. Overall, a dosage of 1.6 gstruvite/kgsoil was identified to effectively grow Chinese cabbage [186].

Uysal et al. [34] conducted a study on tomato and corn plant growth using struvite recovered from the anaerobic effluent of the baking yeast industry. Four different sets of experiments were performed to evaluate struvite effect on crops: a set without the use of any fertilizer, a set with NH4NO3, a set with the addition of fertilizer based on NH4NO3 and KH2PO4, and finally, a set in which the recovered struvite was added with four different dosages (2.85, 5.71, 8.58, 11.42 gstruvite/kgsoil) [34]. The results showed that with the minimum dosage of struvite (2.85 gstruvite/kgsoil) the same quantitative results were obtained as commercial fertilizer, while the best result in terms of dosage was equal to a quantity of struvite of 5.71 gstruvite/kgsoil [34].

Siciliano [41] carried out agronomic tests to analyze the fertilizing potential of struvite precipitate recovered from the treatment of methanogenic landfill leachate. The fertilizing effects of MAP in cultivating Spinacia oleracea were compared with those of vegetable soil and of a commercial fertilizer [41]. The growth of vegetables in the pots with MAP was notably higher than those in the pots with only garden soil and in the pots with the fertilizer. Moreover, the struvite utilization as fertilizer did not result in an increase of metals absorption by vegetables [41].

These studies confirmed the effectiveness of MAP recovered from aqueous waste and wastewater as a slow release fertilizer. In effect, as previously discussed, struvite is produced at industrial scale and, among the different processes, the struvite products Pearl and NuReSYS are certified as fertilizers in the United States, United Kingdom, and Belgium, respectively. In addition, the struvite obtained by the Seaborne process is used locally.

6. Economic Considerations

The actual applicability of struvite precipitation for the removal and recovery of nutrients from waste and wastewater process is, obviously, strictly related to economic evaluations. For this analysis, the construction costs, the operational costs, and the potential benefits detectable by the struvite reusing and selling should be considered [86]. The struvite precipitation process generally exploits common reactors and separation units whose construction costs are quite restricted. Therefore, in the evaluation of the economic sustainability, the operational costs have a major impact which largely depend on the characteristics of wastewater subjected to the treatment. In particular, the addition of reactants, required to create the chemical conditions for struvite formation, and the consumption of energy, for the agitation systems, represents the main expense items [69,187]. In the literature there is a variety of processes for the recovery of struvite from wastewater. The cost of these processes cannot be well compared due to the differences in the operational conditions.

In general, the use of the air insufflation could permit a significant reduction in the overall process costs. In effect, as previously discussed, the air flux guarantees the mixing conditions and, moreover, it allows to set the pH to the required values for struvite precipitation, saving the consumption of the alkaline reagents. However, this approach is effective only when the treatment is aimed at the removal and recovery of phosphorus content.

The use of pure reagents generally results in a very expensive treatment. For this reason, the use of unconventional low-cost reactants is currently a key topic in the development of sustainable struvite precipitation processes. For the recovery of the phosphorus, the consumption of magnesium reactants can affect up to 75% of the total costs [54,66,90,103]. Etter et al. [116], in a study conducted on separate urine using a 500 L reactor with a struvite recovery efficiency of 90%, estimated the treatment
costs using three different magnesium sources: MgSO₄, bittern, and magnesite. Assuming an average selling price of struvite of about 0.41 €/kgמימ, the use of MgSO₄ was found to be very expensive to generate profits, while using magnesite, the estimated gain was three times higher than that determined using bittern [116]. Clearly, such an analysis is affected by the assumed price of the struvite, of which real market value is very difficult to define. In effect, Ueno and Fujii [67] reported that it is possible to sell the struvite obtained from the sewage dewatering sludge treatment at 245 €/Ton.

Dockhorn [188] calculated the cost for phosphorus recovery from digested sludges assuming P concentrations between 50 mg/L and 800 mg/L. According to the author, the expense per ton of produced struvite varies from 2800 €/Ton, by treating effluent with a P concentration of 50 mg/L, to 520 €/Ton in the case of wastewater with a phosphorus level of 800 mg/L [188]. Moreover, it was estimated that the overhead costs can be decreased by 30% using a low-cost magnesium source.

Huang et al. [106], using Mg metal a Mg⁰ source for P recovery from swine wastewater, estimated that the chemical costs in a continuous-flow reactor could amount at 0.25 $/kg of recovered struvite or 0.21 $/m³ of treated wastewater. The authors observed that the cost for providing the Mg⁰ by the corrosion of magnesium metal was greater than that of using the MgO, but it was in line with those of using MgCl₂ and MgSO₄ [106].

Gunay et al. [90] found that, in the removal of NH₃ from landfill leachate, when magnesite was used instead of MgCl₂, the contribution of magnesium cost to the total operation costs decreased from 40.2% to 4.4%. However, when the treatment aims at the removal of ammonium, the consumption of phosphorus reagents represents the primary cost of the whole process [1,41,44,187]. Indeed, Di Iaconi et al. [1] calculated a cost of about 24 €/m³ in the treatment of leachate using MgO and H₃PO₄ as magnesium and phosphorus sources. Considering the quantity of ammonium removed in the process (i.e., about 2.5 kg NH₃-N per m³ of leachate), a specific cost of 9.6 €/kgNH₃-N removed was calculated [1]. The authors’ estimations indicate that the cost of H₃PO₄ represents approximately 50% of the entire costs [1].

Huang et al. [121] conducted an economic evaluation by comparing the utilization of waste H₃PO₄ and low-cost MgO respect to other chemicals combinations. The overall expense for chemicals consumption was found to be 19 $/m³ in the case of using MgCl₂·6H₂O, Na₂HPO₄·12H₂O, and NaOH. The total cost decreased to 5.99 $/m³ when waste phosphoric acid and MgO were used as reactants [121].

Siciliano and De Rosa estimated a total cost of about 5.4 €/m³ by using bone meal as phosphorus source, and bittern as magnesium source, in the ammonium removal from digestate [44]. Instead, the outlay resulted in about 10.2 €/m³ using pure reagents (MgCl₂·6H₂O and H₃PO₄) [44]. Therefore, these results indicate that the use of bone meal and seawater bittern allows at least halving the overall chemical expense. In another study, Siciliano [41] found an overall cost of about 7.98 €/m³ by using the abovementioned low-cost reagents (bone meal and bittern) for the treatment of landfill leachate. By taking into account that the recovered struvite was around 63 kg/m³ of treated leachate, the production cost was 127 €/ton of produced struvite. This cost is about half the price of commercial fertilizers composed both of ammonium and phosphorus such as (NH₄)₂PO₄ [41].

Other works proved the possibility to notably reduce the operational costs for ammonium removal from high concentrated wastewater by reusing the by-products obtained from struvite decomposition, as magnesium and phosphorus source [4,77,104]. This approach, however, does not allow recovering and reusing the struvite as a slow release fertilizer.

7. Conclusions

The present review aims to assess the progress in struvite precipitation processes. The theoretical background, the operational conditions, the type of reactants, the reactors configurations, and the industrial applications are examined. Great attention was placed on the identification of unconventional low-cost reagents exploitable for struvite precipitation. Moreover, the applications of struvite as a slow release fertilizer and some economic considerations are reported. The analysis of the numberless scientific papers examined clearly showed that struvite precipitation is a well-defined technology applicable under different modalities for the treatment of various types of wastewater. Indeed, the process proved its effectiveness both in the treatment of urban wastewater
and high concentrated aqueous waste such as landfill leachate, digestates, etc. The struvite formation is mainly affected by the temperature, pH, the type of reagents and their dosages, and the presence of competitive ions. As the struvite solubility increases with the temperature, values below 25 °C were, generally, considered as preferable. Regarding the other parameters, quite a large variability of values considered as optimal to reach the best performance can be found in the literature reports. In particular, pH values in the range 7.6–10.5 were reported as suitable to promote MAP formation. Regarding the N:Mg:P molar ratio, the stoichiometric value (1:1:1) must be guaranteed to allow the struvite crystals nucleation. However, overdoses of magnesium as well as of phosphorus, if the treatment aims at N removal, are necessary to ensure satisfactory performance. Depending on the type of reagents used, overdoses of magnesium up to 4, with respect to the theoretical dosage, were reported in the literature. Instead, dosages of phosphorus up to 1.3 were applied. Calcium was identified as the most competitive ion and Ca:Mg ratios lower than 0.2 were suggested to prevent the slowdown of struvite nucleation process. The parameters variability is in part attributable to the different characteristics of treated wastewater which, obviously, influence the struvite formation. Moreover, the difference in the system configurations and in the applied process modalities can also justify the variability of reported values. In general, very high performances were obtained using pure reagents. However, the consumption of chemicals represents a main cost item. Therefore, currently, there is great attention on the use of low-cost reagents to reduce the overall process expense. Many studies proved the possibility of exploiting several unconventional magnesium reagents and alkaline compounds to promote the struvite formation. Recently, some by-products exploitable as phosphorus reactants have been identified and effectively applied. This represents a main aspect because it makes more sustainable the struvite precipitation in the removal of ammonium nitrogen. The reuse of struvite decomposition residues, as possible reactants for the treatment of raw wastewater, has been also explored. This approach can reduce the overall process cost, but it does not allow to exploit the produced struvite in agronomic practices. The research activity is currently focused also on the optimization of reactors configurations for struvite formation and precipitation. The STR and FBR have largely proved their effectiveness and are the most applied reactors. Nevertheless, many studies are constantly in progress to further optimize these types of units. Other types of reactors, such as BES, ion exchange reactors, membrane reactors, have been investigated. However, their applicability in field conditions still appears far away. Various papers demonstrated the great value of struvite produced from the treatment of waste and wastewater as a fertilizer for the growth of many types of plants and vegetables. In effect, the struvite produced in some industrial processes is currently used as a commercial fertilizer. Therefore, it can be concluded that the struvite precipitation technology is a profitable approach for the removal and the recovery of nutrients from wastewater streams. However, further research needs to be conducted to identify other types of low-cost unconventional phosphorus sources, which could reduce process costs in wastewater treatment with high ammonium concentrations. Furthermore, the processes based on the reuse of struvite decomposition residues must be tested on a larger scale to verify their actual applicability. Finally, in the aim to exploit the struvite precipitate as slow release fertilizer, technology improvements are required to produce larger crystals that could be more easily recovered and reused.

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