

Review

Recovery of Phosphorus from Waste Water Profiting from Biological Nitrogen Treatment: Upstream, Concomitant or Downstream Precipitation Alternatives

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Received: 19 June 2020; Accepted: 14 July 2020; Published: 18 July 2020



Abstract: Mined phosphate rock is the largest source of phosphorus (P) for use in agriculture and agro-industry, but it also is a finite resource irregularly distributed around the world. Alternatively, waste water is a renewable source of P, available at the local scale. In waste water treatment, biological nitrogen (N) removal is applied according to a wide range of variants targeting the abatement of the ammonium content. Ammonium oxidation to nitrate can also be considered to mitigate ammonia emission, while enabling N recovery. This review focuses on the analysis of alternatives for coupling biological N treatment and phosphate precipitation when treating waste water in view of producing P-rich materials easily usable as fertilisers. Phosphate precipitation can be applied before (upstream configuration), together with (concomitant configuration), and after (downstream configuration) N treatment; i.e., chemically induced as a conditioning pre-treatment, biologically induced inside the reactor, and chemically induced as a refining post-treatment. Characteristics of the recovered products differ significantly depending on the case studied. Currently, precipitated phosphate salts are not typified in the European fertiliser regulation, and this fact limits marketability. Nonetheless, this topic is in progress. The potential requirements to be complied by these materials to be covered by the regulation are overviewed. The insights given will help in identifying enhanced integrated approaches for waste water treatment, pointing out significant needs for subsequent agronomic valorisation of the recovered phosphate salts, according to the paradigms of the circular economy, sustainability, and environmental protection.

Keywords: precipitated phosphate salts; calcium phosphate; magnesium phosphate; struvite; waste water treatment; nitrification; denitrification; anammox; resource recovery; circular economy

1. Introduction

Phosphorus (P) is an essential element for all living organisms as a constituent of nucleic acids, energy-transfer molecules in metabolism, cell membranes, and body building blocks. Phosphorus is also an irreplaceable nutrient, non-manufacturable nor destroyable. Its shortage limits crop growth and agri-food production [1]. Yet, when P is discharged in excess to aquatic and terrestrial ecosystems, it acts as a pollutant, causing eutrophication and nutrient imbalances [2]. Phosphorus has no significant gaseous phase, so it cannot flow freely in the atmosphere. This is in contrast with the nature of the other essential elements supporting life—carbon (C), nitrogen (N), oxygen (O) and hydrogen (H). Nowadays,

mined phosphate rock is the largest source of P for use in both agriculture and industry. However, this is a finite resource irregularly distributed around the world. This means that P availability is linked to geopolitical considerations that may lead to uncertainties about supplies [3,4]. In this regard, the creation of (inter)national strategic P reserves has already been suggested to stabilise commodity prices [5] and the European Union (EU) has identified phosphate rock and P as two of the 27 critical raw materials of high importance to the EU economy and of high risk associated with their supply [6].

As an alternative to mined phosphate rock, organic waste and waste water are renewable sources of P, typically available at the local scale. The P present in these waste streams is chemically or organically bound—i.e., forming complex molecules—or dissolved as orthophosphate. The recovery of P from secondary streams and its subsequent reuse, either directly or after intermediate processing, represent a major opportunity for exploiting new and more sustainable pathways for producing P fertilisers. Phosphorus has no substitute but can be reused continuously, and thus, it is a good example of a critical resource that can be utilised more efficiently in the circular economy framework to support sustainable growth with less pollution [7]. Methods potentially applicable for P recovery from waste water and organic waste have been reviewed elsewhere [8–10].

Among the procedures allowing for P recovery from waste streams, chemically induced crystallisation/precipitation/mineralisation of the already dissolved phosphate in the form of low soluble salts is one of the most common alternatives. Precipitation is achieved by appropriately supplying metal ions to the liquid phase, typically magnesium (Mg^{2+}), to form magnesium phosphate minerals (MgP) [11–13]; calcium (Ca^{2+}) to form calcium phosphate minerals (CaP) [14,15]; or iron (Fe^{2+}) to form iron phosphate minerals (FeP) [16–20]. In waste water treatment plants (WWTPs), this kind of process can be implemented at different locations [9,21] in order to foster resource recovery by producing a specific P-rich stream while meeting water quality standards of the receiving water bodies. Additionally, these processes may also involve additional benefits linked to overall plant performance and energy balance such as: (1) prevention of uncontrolled formation of scale deposits in pipelines and recirculation pumps [22–25]; (2) improvement in sludge dewaterability, allowing for producing a dryer solid product, which is advantageous from the point of view of subsequent transport and thermal processing [26,27]; (3) reduction in P backflows [27,28].

Biological N removal (BNR) is typically applied to reduce the ammonium (NH_4^+) content in waste water through its transference to the atmosphere as dinitrogen gas (N_2). Origin of the waste water—either from municipal, industrial or agricultural sources—will determine its composition, and thus, treatment particularities. In this context, treatment based on the combination of autotrophic nitrification—aerobic oxidation of ammonium to nitrite (NO_2^-) (i.e., nitritation), and subsequently, to nitrate (NO_3^-) (i.e., nitrataion)—, plus heterotrophic denitrification—anoxic reduction of nitrate to nitrite, and finally, to N_2 (NDN)—, has commonly been considered. In recent years, the fully autotrophic treatment, based on the combination of partial nitritation (i.e., 57%) and anaerobic ammonium oxidation (anammox) (PNA), is attracting the interest of the water industry as a more energy-efficient strategy [29,30]. Hence, the number of new PNA facilities operating worldwide is increasing fast [31,32]. Some encouraging reasons are the lower energy demand for aeration in partial nitritation and there being no need for an organic C source in anammox (which favours its integration with the anaerobic digestion process to produce biogas as a renewable energy source). Alternatively, nitrification can be applied individually in view of converting ammonium to nitrate, thereby mitigating ammonia (NH_3) emission from storage facilities and enabling N recovery from high loaded waste water streams [33,34]. Other biological N treatment processes based on its assimilation and immobilisation and aiming at the recovery of N products, such as single cell proteins, amino acids, and protein-rich aquaculture plants (e.g., duckweed and algae), are out of the scope of this work.

Phosphate precipitation can be applied before (upstream configuration), together with (concomitant configuration), and after (downstream configuration) biological N treatment; this is chemically induced as a conditioning pre-treatment, biologically induced inside the reactor, and chemically induced as a refining post-treatment. The aim of this contribution is to perform a detailed

review of the available alternatives for P recovery from waste water flows when biological N treatment is coupled with phosphate precipitation in view of producing materials easily usable as green fertilisers. Particular attention is given to the analysis of the implications of the sequence in which biological treatment and phosphate precipitation are combined. The potential requirements to be complied by the recovered P-rich materials in order to be covered by the EU fertiliser regulation will also be overviewed.

2. Research Framework

The scientific literature has been reviewed on the basis of publications appearing in journals indexed in the database Science Citation Index Expanded (SCIE), which was accessed via the Web of Science Core Collection (Clarivate Analytics, Philadelphia, PA, USA). The trend on research productivity is shown in Figure 1, after defining a multi-term topic search including relevant words for the core element under study (e.g., phosphorus, phosphate), the management strategy to be applied (e.g., recovery, recycling), the technological process to be used (e.g., precipitation, crystallisation), the product formed (e.g., struvite, apatite), and the by-products to be processed (e.g., sewage, digestate, urine). Those publications out of our scope (e.g., medical studies, alternative P management strategies), but accidentally retrieved, were mostly discarded using automatic filters. The full list of words included in the multi-term topic search, or discarded, are provided as Supplementary Material. Clearly, there is an upward trend in the number of publications that appeared, which is in line with the case study previously reported by Magri [35], particularly focusing on phosphate precipitation from anaerobic digestates. Following this procedure, the total number of publications retrieved for the last 50 years (1970–2019) was 3050, with about 68,400 citations and an h-index of 107 (accessed on 10 January 2020). According to the growing interest in P recovery from waste streams, some critical literature reviews and comparative technology assessments were recently published. These papers analyse issues such as the principles of phosphate crystallisation, the by-product sources being processed, laboratory feasibility studies, available technologies at pilot- and full-scale, complementary pre-treatments, related environmental and economic aspects, remaining challenges to be addressed, and fertilising properties of the recovered products [10,12,13,15,36–44]. As a complementary approach, this paper focuses on the analysis of alternatives for coupling biological N treatment and phosphate precipitation when processing waste water, while giving some insights about the potential needs for the subsequent use of the recovered phosphate products as P fertilisers.

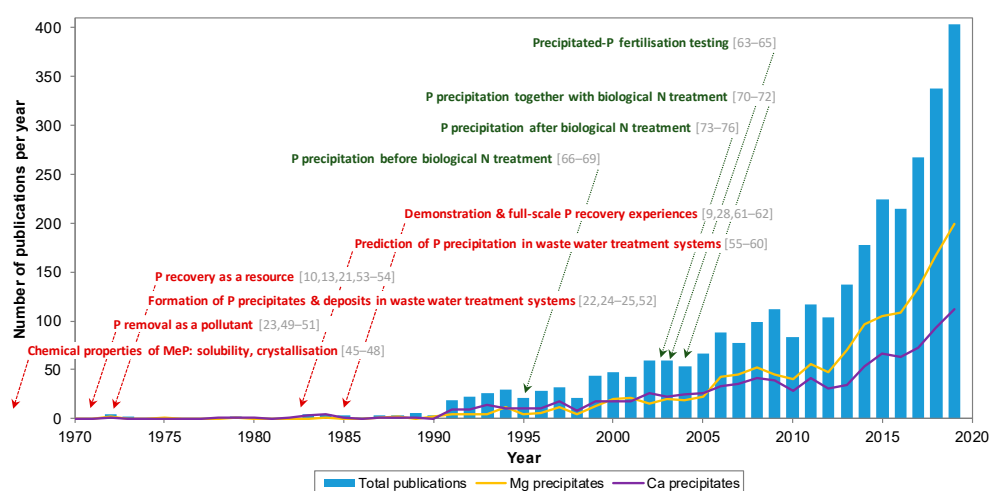


Figure 1. Trend on the number of published papers related to mineral phosphate precipitation from waste water (Source: Web of Science; Accessed: January 10th 2020). Comments indicate meaningful topics and papers [9,10,13,21–25,28,45–76] in this research field (the main topics reviewed in this work are shown in green colour).

3. Forms of Mineral Phosphate Precipitates in Waste Water Treatment

Phosphate recovery from waste water through crystallisation and precipitation is commonly achieved by inducing the formation of MgP or CaP mineral forms (Table 1). Moreover, in recent years, P recovery as FeP (via crystallisation, not flocculation) has also received considerable attention. Phosphate crystal formation follows two consecutive steps—nucleation (crystal birth) and development of the crystals in the bulk liquid until reaching equilibrium (crystal growth). Control of these stages may be complex, as it involves considering a combination of factors, including the crystal state in waste water, thermodynamics of liquid–solid equilibrium, mass transfer between solid and liquid phases, reaction kinetics, and physicochemical parameters such as temperature, pH, mixing energy, supersaturation, and the presence of foreign ions [12]. Particle size is an important characteristic of the end product obtained. If fine particles represent a significant fraction of the solids formed, this may negatively impact on the soluble phosphate uptake efficiency [77] as well as on the quality of the recovered product in view of its subsequent valorisation [78].

Orthophosphates (PO_4) can be ionised in multiple groups, including from acidic to basic conditions, phosphoric acid (H_3PO_4), dihydrogen phosphate ion (H_2PO_4^-), hydrogen phosphate ion (HPO_4^{2-}), and phosphate ion (PO_4^{3-}), depending on the pH as well as on the temperature and ionic strength of the aqueous solution [11] (Figure 2a). In general terms, phosphate precipitation is only possible in supersaturated solutions. Supersaturation causes spontaneous nucleation, and in such circumstances, crystallisation is expected to be fast and abundant, without the need for seeding material addition. It occurs when the saturation index (*SI*), which is typically calculated as shown in Equation (1) [60], reaches positive values. In such equation, *IAP* stands for the ionic activity product and K_{sp} is the solubility product constant at the given temperature ($\text{p}K_{sp} = -\log_{10} K_{sp}$). The ionic activity of the species “*i*”, $\{i\}$, is correlated with its molar concentration, $[i]$, according to the corresponding activity factor ($\{i\} = \gamma_i \cdot [i]$). In turn, this coefficient depends on the ionic charge and the ionic strength of the medium, as described elsewhere [11,48,56,57]. As far as the medium becomes diluted, the γ_i coefficient approaches 1. The *SI* provides a non-linear scale for supersaturation. Yet, $SI > 0$ is not sufficient for precipitation, since an activation energy barrier prevents the ions to aggregate as crystals. The activation energy can be surmounted by a high *SI* and presence of nucleation seeds, such as pre-existing crystals or foreign bodies and surfaces. After nucleation, the crystals further increase in size and form particles by aggregation, coagulation, and crystal growth [79].

$$SI = \log_{10} IAP - \log_{10} K_{sp} \quad (1)$$

The MgP are most frequently precipitated as magnesium-ammonium-phosphate hexahydrate (MAP, struvite) $[\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}]$ at pH above neutrality [37]. Although potassium (K^+) can replace NH_4^+ , leading to the formation of magnesium-potassium-phosphate hexahydrate (MPP, K-struvite) $[\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}]$ [46,47,80], the simultaneous availability of NH_4^+ and K^+ constrains the precipitation of MPP [81]. Magnesium-hydrogen-phosphate trihydrate (newberyite) $[\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}]$ [82,83] and trimagnesium phosphate octahydrate (bobierrite) $[\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$ are also likely to precipitate at some point [58] (Figure 2b). In the case of CaP, the range of possible compounds is even wider [84]. Usual phases involve hydroxyapatite (HAP) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$, tricalcium phosphate (TCP) $[\text{Ca}_3(\text{PO}_4)_2]$, amorphous calcium phosphate (ACP) $[\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}]$ —similar to TCP, but with no structured crystalline order—, octacalcium phosphate (OCP) $[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}]$, dicalcium phosphate anhydrous (DCPA, monenite) $[\text{CaHPO}_4]$, and dicalcium phosphate dihydrate (DCPD, brushite) $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]$ (Figure 2c). In this group, HAP [45,85] is preferentially formed, under neutral or basic conditions, as the most thermodynamically stable and insoluble mineral phase. However, HAP precipitation is a rather slow phenomenon. Thus, transient formation of intermediate phases—i.e., metastable states but exhibiting a faster formation rate such as DCPD (this is the most soluble phase of all those referred above), OCP, and ACP—is also feasible. Subsequently, these precursors may slowly transform into HAP [86,87]. Co-precipitation of different mineral forms involving MgP and CaP is a common issue depending on

waste water composition and the operational conditions applied [88]. Finally, the typical FeP formed in WWTPs is ferrous iron phosphate (vivianite) $[\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}]$, mostly in anaerobic systems with relatively low sulphide concentrations when iron and phosphate are available [17].

Table 1. Main phases of interest regarding magnesium phosphates (MgP), calcium phosphates (CaP), and iron phosphates (FeP) when applying mineral precipitation aimed at phosphorus recovery in waste water treatment. Me, metal—Mg, Ca or Fe.

Name	Empirical Formula	Molecular Weight (g/mol)	P Content (wt %)	Me/P Molar Ratio	pK _{sp} (25 °C)	Requirements
<i>MgP minerals</i>						
Magnesium ammonium phosphate (MAP, struvite)	$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	245.41	12.62	1.00	13.26 ¹	pH > 7; Mg/Ca molar ratio > 0.6
Magnesium potassium phosphate (MPP, K-struvite)	$\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	266.47	11.62	1.00	11.68 ²	NH_4^+ unavailable
Magnesium hydrogen phosphate trihydrate (newberyite)	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	174.33	17.77	1.00	5.51 ³	Acid pH values
Trimagnesium phosphate octahydrate (bobierrite)	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	406.98	15.22	1.50	25.20 ⁴	Basic pH values
<i>CaP minerals</i>						
Hydroxyapatite (HAP)	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1004.6	18.50	1.67	116.8 ⁵	Long timescale (ripening of precursors); Low Mg/Ca ratio
Tricalcium phosphate (α -TCP and β -TCP)	$\text{Ca}_3(\text{PO}_4)_2$	310.18	19.97	1.50	25.5 (α), 28.9 (β) ⁵	-
Amorphous calcium phosphate (ACP)	$\text{Ca}_x(\text{PO}_4)_y \cdot n\text{H}_2\text{O}$	*	*	*	*	Lack of crystallisation nuclei
Octacalcium phosphate (OCP)	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$	982.53	18.91	1.33	96.6 ⁵	-
Dicalcium phosphate (DCPA, monenite)	CaHPO_4	136.06	22.76	1.00	6.90 ⁵	Acid pH values
Dicalcium phosphate dihydrate (DCPD, brushite)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	172.09	18.00	1.00	6.59 ⁵	Acid pH values
<i>FeP minerals</i>						
Ferrous iron phosphate (vivianite)	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	501.61	12.35	1.50	36.0 ⁶	Stimulated by Fe dosage

References: ¹ [48], ² [47], ³ [82], ⁴ [89], ⁵ [84], and ⁶ [90]. * This value cannot be determined precisely.

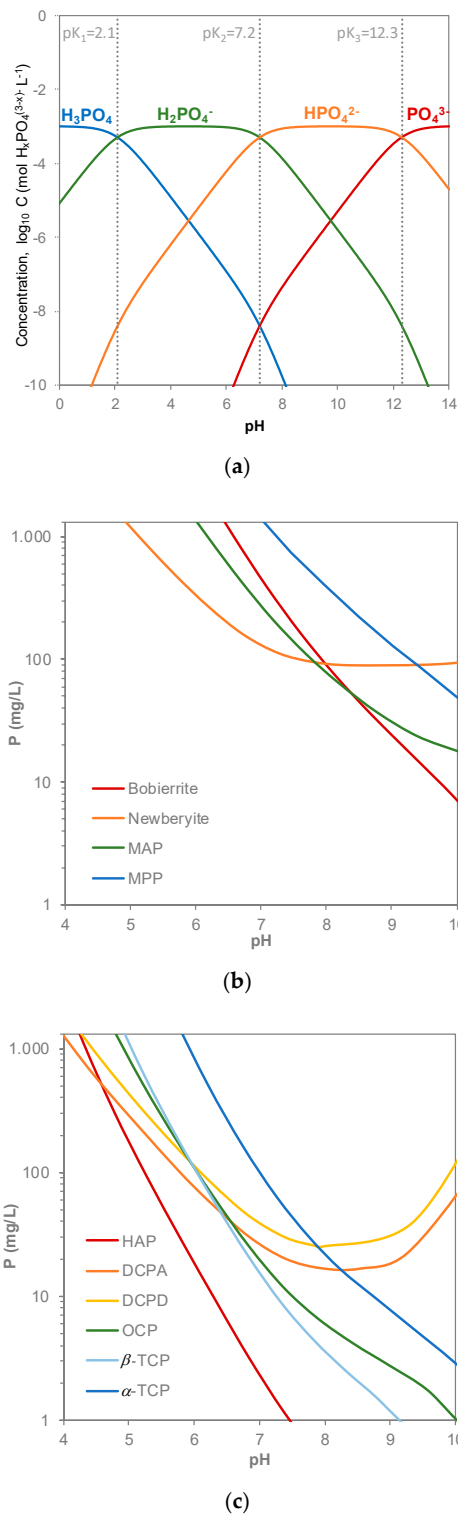


Figure 2. (a) *Top*: Logarithmic concentration diagram for phosphoric acid (1 mM, 25 °C); Soluble orthophosphate concentration in water as a function of pH at the equilibrium, according to the solubility isotherms of: (b) *Middle*: the magnesium phosphate (MgP) phases in the Mg(OH)₂-X-H₃PO₄-H₂O system at 25 °C. The component X is only considered for MAP as NH₃, and for MPP as K(OH), and equimolarly to Mg(OH)₂ in both cases. Values for the X/Mg molar ratio higher than 1 will favour precipitation of the solid phase; (c) *Bottom*: the calcium phosphate (CaP) phases in the Ca(OH)₂-H₃PO₄-H₂O system at 25 °C. At pH values above ~4.5, HAP is the most stable phase. At lower pH values, DCPA is more stable than HAP. Calculations made using Visual MINTEQ [60].

4. Linking Phosphorus Recovery to Biological Nitrogen Treatment

Mineral phosphate precipitation from waste water can be applied before, together with, and after biological N treatment (Figure 3). In engineered systems for BNR (this refers to both NDN and PNA processes), an initial nitrification is typically required [29,91]. This aerobic process (in particular, nitrification, which is the first step of nitrification involving ammonium conversion into nitrite) entails proton release (ca. $2.0 \text{ mol H}^+ \text{ mol}^{-1}$ oxidised- NH_4^+), and consequently, it causes reduction in pH as well as degradation of alkalinity and buffer capacity—mostly due to the decrease in the total inorganic carbon content (TIC; this is the carbonate system: $\text{H}_2\text{CO}_3^* + \text{HCO}_3^- + \text{CO}_3^{2-}$). Air sparging, eventually related to the supply of oxygen for nitrification, will also favour dissolved carbon dioxide (CO_2) stripping [92,93]. Oppositely, both heterotrophic denitrification and anammox imply proton consumption (ca. $1.0 \text{ mol H}^+ \text{ mol}^{-1}$ reduced- NO_3^- and $0.13 \text{ mol H}^+ \text{ mol}^{-1}$ oxidised- NH_4^+ , respectively). Hence, these two processes promote a rise in the pH value and provide alkalinity to the bulk liquid, even though in a lesser extent than has already been consumed in the previous step (final proton release range approximately is $1.0\text{--}1.2 \text{ mol H}^+ \text{ mol}^{-1}$ removed-N as N_2). In addition, the transformation of the ammonium into N_2 will imply a decrease in the ionic strength of the medium—loss of salinity—favouring mineral precipitation due to a higher effective concentration of the ions involved. Since phosphate precipitation typically requires increasing pH, the collateral effects of BNR treatments, such as the reduction in the buffering capacity, ionic strength and soluble CO_2 content, will allow for a reduced dosage of chemicals to the water flow, involving significant cost savings in process operation for concomitant or downstream precipitation layouts.

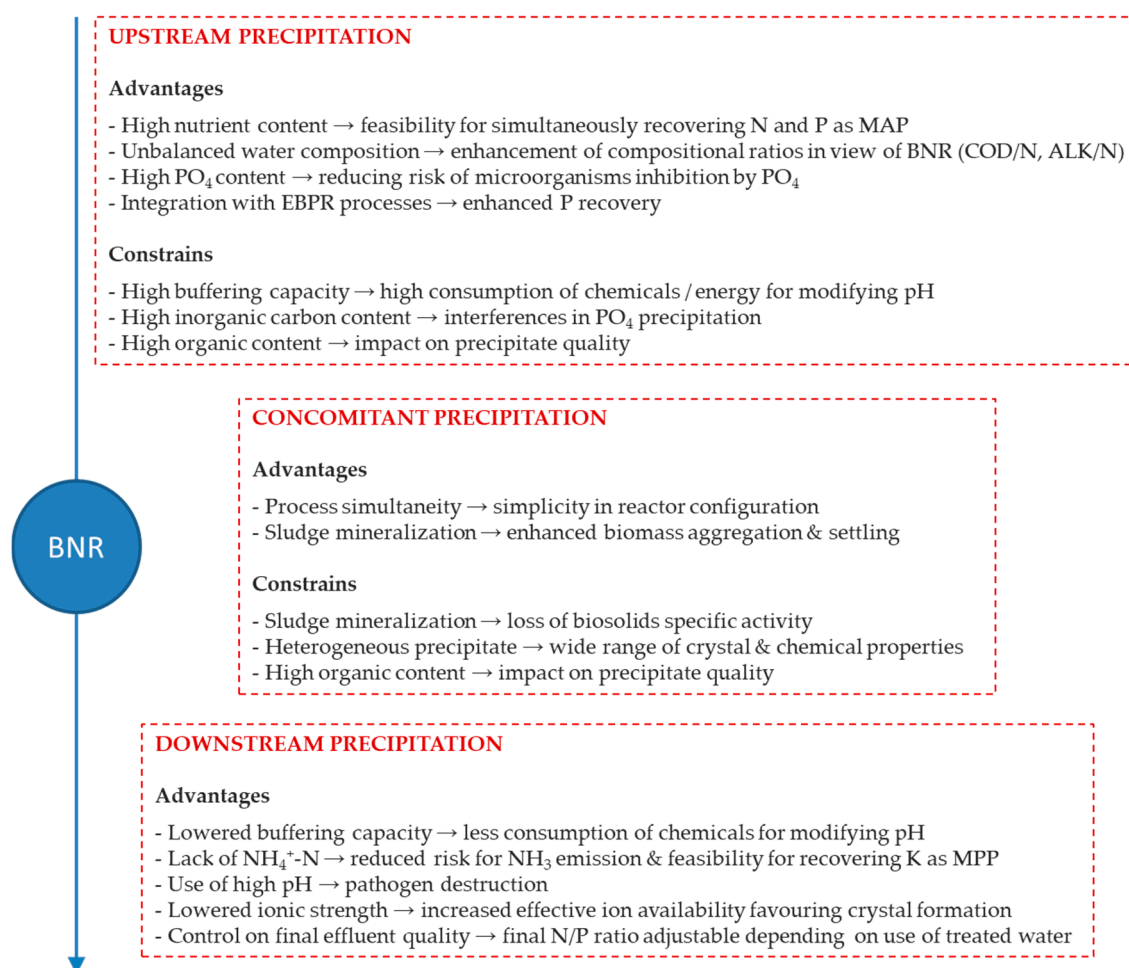


Figure 3. Advantages and constraints for recovering P by precipitation depending on the location of the process in relation to biological N treatment (upstream, concomitant or downstream precipitation).

In municipal WWTPs performing nutrient removal (Figure 4), NDN is typically used in the mainstream (large flow of low loaded waste water), whereas PNA can more robustly be applied in the side-stream following anaerobically digested sludge dewatering (small flow of warm, i.e., 15–35 °C, high loaded waste water). This internal liquid stream—named as centrate when obtained by centrifugation—contributes only about 2% of the total influent flow entering the plant, but contains 10–30% of the total N and P load [27,94,95]. Particular treatment of the centrate rather than its recirculation to the headworks of the treatment plant favours optimised configurations in terms of energy-efficiency, cost-effectiveness, and sustainability [94]. The application of precipitation technologies in facilities equipped for chemical P removal in the mainstream—mostly using Fe and aluminium (Al) salts as flocculants [49,50]—may entail a reduced recovery potential due to limited availability of the salt-forming ions at the equilibrium [16]. Yet, sludge digestion triggers orthophosphate release, especially when running at thermophilic conditions [96]. Hence, the implementation of enhanced biological P removal (EBPR), or chemical P removal using iron, in the mainstream, commonly results in the accumulation of phosphate in the centrate [16]. Chemical P removal is preferred over EBPR when stringent limits are enforced. Phosphorus entering the treatment plant but not recoverable from the centrate will partly be contained in the treated effluent (ca. 20%) and partly in the digested dewatered sludge (ca. 50–70%). According to van der Kooij et al. [97], optimised phosphate precipitation from centrate in WWTPs would result in recovery efficiencies of 3–8% of all P excreted by humans. Otherwise, according to the World Health Organization, only about one-third of the global population is served by sewerage sanitation and could conceivably benefit from the resource recovery options stated here.

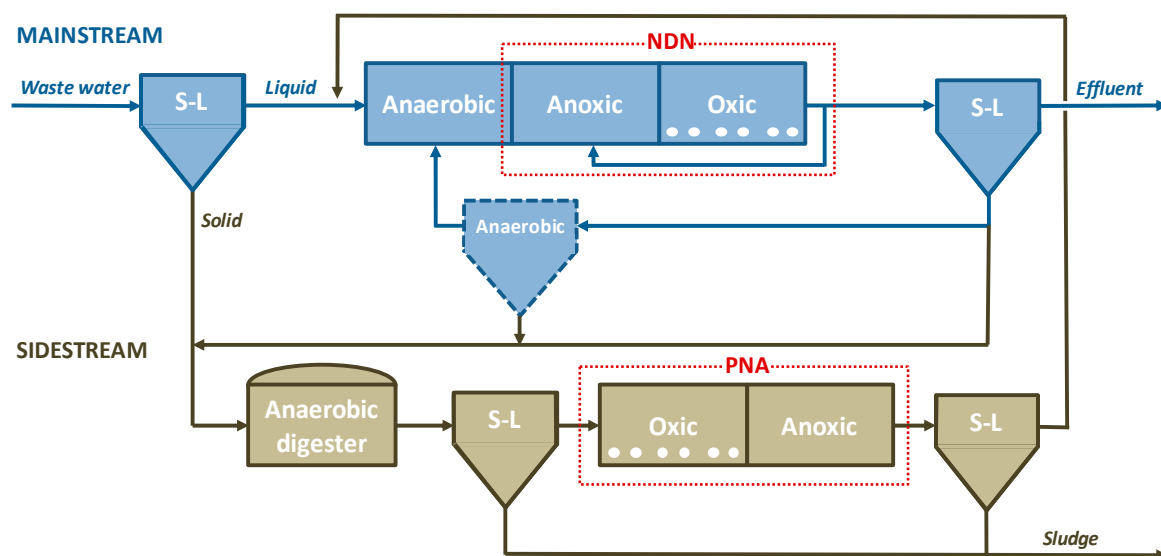


Figure 4. Example of layout for a biological waste water treatment system including the main- and side-stream. Potentially, P recovery by precipitation can be performed before, together with, or after N removal (it concerns bioprocesses such as NDN and PNA). Particular schemes will vary depending on the specificities of the treatment to be applied.

Alternative layouts for biologically treating N from waste water are feasible by modifying the scheme shown in Figure 4. This is particularly applicable when waste water comes from sources other than municipal (e.g., industrial or agricultural).

MgP precipitation as MAP allows for the simultaneous recovery of P and N (struvite theoretically contains 12.6% P, 5.7% N and 9.9% Mg on a dry weight basis—as well as 44% crystal water—which is equivalent to ratios of 0.45 g N g⁻¹ P and 7.9 g MAP g⁻¹ P). Hence, it interestingly involves N recovery rather than its removal. Yet, P is usually present in waste water at lower concentrations than N, so N is recovered at a low efficiency, mostly remaining in the water line entering the bioreactor (e.g., frequently, waste water contains more than 4.5 g N g⁻¹ P, so maximum potential for N recovery as MAP is less

than 10%). Alternatively, CaP precipitation as HAP involves formation of a mineral with a higher P content (HAP theoretically contains 18.5% P and 39.8% Ca on a dry weight basis, which is equivalent to 5.4 g HAP g⁻¹ P). Once formed, phosphate precipitates can be settled, dewatered, and dried in view of favouring transport. A holistic approach is needed when integrating chemical and biological processes for waste water treatment, since the modification of the pH to favour mineral precipitation may result in unappropriated pH and/or lack of alkalinity for the subsequent biological N treatment. Recently, Shaddel et al. [98] suggested that the adaptation of the precipitated product to the physicochemical properties of the targeted waste water would allow improving of the value chain for the recovered P—e.g., CaP and MgP can be precipitated at different locations within the same treatment facility, depending on NH₄⁺ availability.

Overall, the recovery potential when using precipitation technologies is low, typically 10–15% [27,99], and maximum 30–40% [36,100] of the P load in the influent stream, the rest remaining in the biosolids. Economic feasibility for P recovery will depend on its content in the liquid phase, with threshold levels close to 50 mg PO₄-P L⁻¹ [21]. In this regard, final implementation of P recovery by precipitation may include the use of preliminary mobilisation–dissolution procedures [36,101]. Although the modest recovery potential mentioned above seems to offer a limited contribution to resolve global P shortage issues, at the local scale, it may help in creating new opportunities in more sustainable communities and protecting the environment while reducing treatment costs [102].

4.1. Phosphorus Recovery before Biological N Treatment (Upstream Configuration)

Integrative waste water treatment alternatives, considering P-recovery by chemical precipitation before biological N oxidation or removal, have conceptually been analysed under different scenarios [103,104] and also experimentally studied [66–69,105–122], as summarised in Table 2 (an extended version of this table is provided as Supplementary Material).

Table 2. Summary of experiences integrating chemical precipitation aimed at P recovery, followed by biological N oxidation, or removal (upstream precipitation). More details are given as Supplementary Material.

Waste Water Source	Precipitation Performance	Bioprocess Performance	Precipitate Characteristics	Reference
<i>NDN as the bioprocess following chemical P precipitation</i>				
Hydrolysed urine	MgP precipitated in lab tests simultaneously to vacuum thermal stripping at 25–65 °C by adding MgCl ₂	NDN via nitrite; Increased COD/N and ALK/NH ₄ ⁺ -N mass ratios after precipitation favoured NDN	MgP mostly precipitated as MAP; Composition of the precipitate: 13.1% P, 8.2% Mg, 5.3% N	[68]
Anaerobically digested sludge dewatering centrate from a municipal WWTP	MgP precipitated in a lab batch reactor by adding MgCl ₂	Nitrification in a fixed-film reactor, denitrification in a MFC-cathode; MFC-anode fed with raw waste water	No data available for the precipitate	[105]
Anaerobic lagoon digester supernatant in a swine farm	MgP precipitated in lab batch tests; Raw vs. (organically) fermented superphosphate fertiliser used as P source; Fermentation increased water-soluble P and provided bCOD	NDN in a SBR; COD/TN mass ratio raised by adding fermented superphosphate favouring NDN	MgP precipitated mostly as MAP; Effectiveness of the precipitate as fertiliser demonstrated in a pot test (increased crop yield)	[106]

Table 2. Cont.

Waste Water Source	Precipitation Performance	Bioprocess Performance	Precipitate Characteristics	Reference
Side-stream sludge fermenter effluent from an EBPR system treating low-strength synthetic waste water	CaP precipitated in a SBR by adding Ca(OH) ₂	EBPR in a continuous flow-activated sludge system; Fermentation of purged sludge + precipitation of released P lead to improved P uptake and N removal in the mainstream	Composition of the precipitate: 13.8% P	[107]
Urine	PO ₄ precipitated in a lab stirred system using RO brine (from a reclaimed WWTP in a thermal power plant) as metal ions source	NDN via nitrite in a continuous flow-activated sludge system using an internal/external COD source	Precipitates produced at different brine/urine mixture ratios with 10–15% P; The amount of brine added affected Mg or Ca in the solid; No presence of hazardous compounds	[108]
Ultrafiltered permeate from an(aerobically) digested sludge dewatering centrate in a municipal WWTP	MgP precipitated in lab batch tests; Mg/NH ₄ /PO ₄ adjusted with MgCl ₂ + K ₂ HPO ₄ ; Use of seeding material	NDN in a continuous flow-activated sludge system for treating raw sewage plus MgP precipitation effluent; Mixing of precipitation effluent with raw sewage decreased COD and N removal efficiency	MgP precipitated mostly as MAP; Quality of the MgP precipitated potentially compromised by the heavy metals content	[109]
Urine-seawater mixture	PO ₄ precipitated in a lab continuous flow reactor incl. a concentric cylinder differentiating hydrolysis-precipitation zone and settling-separation zone	Nitrification in a continuously aerated SBR (for subsequent in-sewer denitrification); ALK added as NaHCO ₃ based on pH set-point	MgP precipitated mostly as MAP; MAP purity directly correlated with urine content	[110]
Low-strength synthetic waste water	MgP precipitated in a lab FBR	NDN in a MBR intermittently aerated; P-recovery in FBR enhanced SND and COD, NH ₄ ⁺ and PO ₄ removal in MBR	MgP precipitate mostly as MAP	[111]
Low-strength synthetic waste water	CaP precipitated in a lab upflow reactor; CaCl ₂ added after the anaerobic stage of an EBPR system and CO ₂ stripping by aeration; Calcite as seeding material	EBPR in a continuous flow-activated sludge system for N and P removal; Chemical P precipitation favoured EBPR	CaP precipitate mostly as HAP (or precursors); Composition of the precipitate: 8–13% P; Carbonate co-precipitation	[112,113]
Side-stream sludge fermenter effluent from an EBPR system treating low-strength synthetic waste water	MgP precipitated in batch by adding MgO	EBPR in an SBR also involved partial N removal through NDN; Fermentation of purged sludge followed by precipitation of the released N and P lead to higher P separation efficiency and complete nitrification	MgP precipitate mostly as MAP	[114]

Table 2. Cont.

Waste Water Source	Precipitation Performance	Bioprocess Performance	Precipitate Characteristics	Reference
Swine waste water	MgP precipitated in a lab CSTR; Precipitate recovered from an external settler; MgP precipitate partly recycled to the reaction tank as seeding material	NDN in a 2-stage continuous flow activated sludge system (+ settler); COD/TN mass ratio increased favouring NDN, COD/TP mass ratio increased favouring EBPR	MgP precipitate partly as MAP; <i>Anhydrous</i> precipitate with 25.3% P, 18.3% Mg, 7.1% N, 5.4% K, 2.5% Ca; Quality of the precipitate potentially compromised by the organic content	[115]
Anaerobically digested landfill leachate	MgP precipitated in a lab stirred system using MgCl ₂ and PO ₄	NDN in an SBR; BOD ₅ /NH ₄ ⁺ -N mass ratio increased favouring NDN; The higher MgCl ₂ addition the higher NH ₄ ⁺ separation as MAP; High Cl ⁻ could limit nitrification	Composition of the MgP formed not determined analytically	[116]
Rare-earth smelting waste water	MgP precipitated in lab batch tests; Mg/NH ₄ /PO ₄ adjusted with MgSO ₄ + Na ₂ HPO ₄ (among other P-sources)	SND in a batch system using immobilised microorganisms; COD/NH ₄ ⁺ -N mass ratio increased favouring NDN; Rare metal ions removed from the liquid phase favouring biological treatment	MgP precipitate mostly assumed as MAP; Composition: 15.6% P, 9.3% N, 8.3% Mg; Quality of the MgP precipitated compromised by the rare metal content	[117]
Raw swine waste water obtained by centrifugation	MgP precipitated in lab batch tests; Mg/NH ₄ /PO ₄ adjusted with MgCl ₂ + KH ₂ PO ₄	NDN in a fill-and-draw system under intermittent aeration; BOD/TN increased enhancing NDN; Additional PO ₄ precipitated as CaP by adding CaCl ₂ once biotreatment ended	Composition of the MgP not determined analytically	[66,118]
PNA as the bioprocess following chemical P precipitation				
Digester sludge thickening lagoon supernatant in a municipal WWTP	MAP precipitated by the Ostara® process at full-scale	PNA in an IFAS-SBR with intermittent aeration; High PO ₄ inhibited anammox bacteria; Higher tolerance to PO ₄ stress when biomass grew as biofilm rather than forming flocs	No data available for the precipitate	[69]
Anaerobically digested sludge dewatering centrate in a municipal WWTP	MgP precipitated in a lab CSTR with MgO	PNA as 2-step process (PO ₄ precipitated after PN) and also as 1-step process (with intermittent aeration) using SBRs	Composition of the MgP formed not determined analytically	[119]
Anaerobically digested industrial (potato) waste water	MgP precipitated in a lab mixed reactor with MgCl ₂ ; Urea added to the crystallisator as N source	PNA as 2-step process (CSTR w/o sludge retention + UFBR) and also as 1-step process (UFBR)	MgP precipitate mostly as MAP	[120]

Table 2. Cont.

Waste Water Source	Precipitation Performance	Bioprocess Performance	Precipitate Characteristics	Reference
Anaerobically digested industrial (potato) waste water from a UASB reactor + anaerobically digested sludge dewatering centrate in a municipal WWTP	MAP precipitated by the PHOSPAQ™ process at full-scale, aeration supplied for bCOD degradation and CO ₂ stripping; MgO dosed as Mg source	PNA as 1-step process with granular sludge and dynamically controlled continuous aeration at 37 °C	MAP with low heavy metals content with respect to EU standards for fertilisers; Precipitate fertilising effectiveness demonstrated in field tests	[121,122]
Anaerobically co-digested sludge dewatering supernatant in a municipal WWTP	MgP precipitated in a CSTR using MgCl ₂ or MgCO ₃	PNA as 2-step process: MBBR + SBR; PO ₄ -P increase implied specific anammox activity loss	Composition of the MgP formed not determined analytically	[67]

Chemically induced phosphate precipitation before BNR from waste water—and also in the case of not considering BNR—typically requires to increase the pH (preferably above 8.0–8.5) by dosing an alkaline reagent (e.g., sodium hydroxide, NaOH) or by applying CO₂ stripping [93,123], and to adjust the amount of alkaline-earth metal ions (i.e., Mg²⁺ or Ca²⁺) available to effective concentrations according to the accessible phosphate—typically slightly above the theoretically needed ratios. The chemicals commonly used as precipitant agents are oxides (MgO, CaO), hydroxides (Mg(OH)₂, Ca(OH)₂), and soluble salts (e.g., MgCl₂, CaCl₂) [68,107,122]. Alternatively, low grade renewable sources, including secondary raw materials and by-products [108], or seawater [110], can also be used. Feasibility of their use depends on factors, such as metal compound availability, solubility, and reactivity [39].

The composition of the waste water to be treated will determine the particular operational conditions to be applied and the quality of the recovered product. At high pH, availability of TIC may negatively impact on phosphate precipitation efficiency due to undesired competition for formation of non-phosphated compounds [14,60,124]. In this regard, Song et al. [14] reported experimental work showing that at pH 8.0, the phosphate precipitation rate was significantly slowed down (and the phosphate precipitation efficiency decreased) by the presence of carbonates, probably because of the formation of ion pairs between carbonate and Ca, leading to a decrease in free Ca²⁺ ions. In spite of this fact, at pH 9.0–11.0, the effect was not so obvious, and carbonate co-precipitated with phosphate, resulting in a decrease in P content in the precipitate. The presence of solids and organic compounds is expected to negatively affect efficiency of crystallisation and purity of the precipitate [125,126]. This factor may introduce some constraints on the handling of the recovered product. Otherwise, precipitation can help adjusting compositional ratios when aiming at treating raw liquid streams. This is, for instance, the case of the BOD/N ratio (BOD is biochemical oxygen demand) before applying the NDN process. By considering MAP precipitation as pre-treatment, Maekawa et al. [66], treating raw swine waste water, achieved a rise in the BOD/N ratio from 1.6 to 7 g O₂ g⁻¹ N before biological treatment, or similarly, Chen et al. [116], treating digested landfill leachate, increased this ratio from 1.5 to 6.5 g O₂ g⁻¹ N (a minimum value of 5–6 g O₂ g⁻¹ N is needed to ensure complete denitrification, according to Henze et al. [127]). When processing complex industrial waste waters with moderate N load, such as those produced by the leather tanning industry, the appropriate addition of chemicals for precipitating MAP, together with an optimised management of source separated streams, may allow decreasing the concentration of ammonium to typical levels for urban waste water. In such context, and depending on local regulations, MAP precipitation may allow for direct effluent discharge to the public sewer, making unnecessary biological treatment based on nitrification or NDN. If further biological treatment for chemical oxygen demand (COD) removal was still required, then the remaining ammonium would be mostly uptaken by the heterotrophic organisms growing within the reactor (as a high-rate activated sludge system) [128,129]. The high Ca content in this kind of waste water can compromise MAP precipitation, making the dosage of an extra amount of phosphate necessary. The potential valorisation of the precipitate will depend on the content of heavy metals (e.g., chromium),

or sulphide, among other factors [130]. Alternatively, when MAP valorisation as fertiliser is not feasible, it can still be converted thermally to magnesium-hydrogen-phosphate for its further reuse in the precipitation process. In this conversion, NH_3 gas is released [131]. By absorbing this ammonia into a CO_2 aqueous solution, an ammonium bicarbonate stream is obtained, which potentially can be treated by PNA [132], among other options.

When processing organic streams, by introducing an acidification step before precipitation, either abiotic [133] or biotic [101], targeting P mobilisation, it is feasible to increase significantly the availability of soluble orthophosphate in the liquid phase, therefore enhancing the potential for recovering P in the form of mineral precipitate. The presence of suspended particles ($1\text{--}3\text{ g L}^{-1}$) may favour the aggregation/agglomeration of small phosphate crystals, resulting in bigger crystalline structures [134]. The presence of inorganic impurities in the waste water will also affect the quality (i.e., composition), particle size (i.e., mean, homogeneity), and separation capacity of the precipitated products [135,136].

The precipitation process can be operated in a dedicated reactor where particles are suspended by either the liquid flow rate [69,111,137], upflow circulation of air [122,138] or mechanical stirring [67,115,139]. Although this is the conventional scenario for conducting phosphate precipitation, with several technologies commercially available [9] and being increasingly applied, some shortcomings have also been reported, such as recovery of low-value products, high operational costs, unsatisfactory P recovery efficiency, complex operating conditions, high energy consumption, and large footprint [18,43]. Additionally, some negative experiences were also reported in the literature concerning phosphate precipitation. As an example, Karakashev et al. [140] tested MAP precipitation within a complex strategy for treating pig manure, which integrated multiple processes. Precipitation was specifically applied to anaerobically digested manure supernatant (obtained by centrifugation). MgO was added as precipitant agent (30% overdosed) at pH 8.5 and $30\text{ }^\circ\text{C}$. In such conditions, 96% P uptake efficiency was achieved so that some Mg still remained in the water line. Nitrogen loss due to ammonia stripping was also detected. The availability of residual Mg negatively affected the biological activity in a subsequent high-rate anaerobic process—i.e., upflow anaerobic sludge blanket (UASB) reactor. Moreover, it also triggered uncontrolled MAP formation within a downstream aerated bioreactor for partially oxidising ammonium to nitrite before an anammox reactor.

High phosphate levels have been reported as inhibitory for some groups of microorganisms involved in N removal processes, especially for the anammox bacteria. Phosphate limiting concentrations may vary widely [141] depending on factors such as bioreactor configuration, biomass aggregation form, and microbial species involved [142,143]. As an example, total inhibition sometimes has been described above $155\text{ mg PO}_4\text{-P L}^{-1}$ [144], whereas in others cases, concentrations as high as $1665\text{ mg PO}_4\text{-P L}^{-1}$ (which is tenfold higher, much above the range of phosphate concentrations usually found in waste water) only caused 50% inhibition regarding the maximum anammox activity. Thus, the implementation of a phosphate precipitation step prior to a PNA system aiming to decrease phosphate concentration in the water line can help in optimising bioprocess performance [69,119]. Yet, some phosphate should remain available in order to assure biomass growth [145]. Moreover, when culturing anammox granular biomass, phosphate availability can contribute to enhance settleability and other mechanical properties of the granules due to the accumulation of CaP precipitates [146–149].

4.2. Phosphorus Recovery Together with Biological N Treatment (Concomitant Configuration)

4.2.1. Biologically Induced Phosphate Mineralisation

Biomineralisation is a widespread phenomenon in nature that occurs from the formation of rusty proteins in bacteria to macroscopic structures of shells and bones. More in detail, biologically induced mineralisation involves the precipitation of minerals as a collateral consequence of the reaction between extracellular ions and metabolic products released across or into the cell wall. These minerals are expected to have a heterogeneous range of crystal and chemical properties [150]. The active role of microorganisms, mostly bacteria, inducing biomineralisation of soluble phosphate together with Mg^{2+} , Ca^{2+} or Fe^{2+} ,

has already been described amply in natural environments and related laboratory experiments [151–153]. Thus, under appropriate conditions, microbial activity may trigger the formation of extracellular (crystal) aggregates of minerals such as MAP [154–156], bobierrite [157], ACP [158] or HAP [153]. Factors affecting such process include bacterial strain [152,154,158,159], temperature [160], pH [161–163], constituent ion concentration [162–164], salt concentration [159], and agitation [165]. Otherwise, there is still a great potential for improving scientific understanding and developing practical implementations of biologically induced P mineralisation in the field of waste water treatment [70,166,167].

4.2.2. Phosphorus Recovery Experiences in Concomitant Configuration

Previous experiences concerning simultaneous biological N oxidation or removal and biologically induced P precipitation within the same bioreactor in the framework of waste water treatment, aimed at promoting P recovery, are summarised in Table 3 [70–72,168–172] (an extended version of this table is provided as Supplementary Material). This approach allows simplifying the configuration of the treatment system. Promising results have been obtained at lab-scale using different kinds of bioreactors running with suspended, granular or biofilm-type sludge. Operational conditions such as temperature and pH, as well as concentration of constituent ions (e.g., NH_4^+ , Mg^{2+} , and Ca^{2+}), will play a critical role in mineral phosphate formation, mostly as CaP.

Recent works conducted at Tohoku University (Japan) with anammox biomass in expanded bed reactors showed that, using synthetic substrate and under optimised bioreactor operation, simultaneous N removal and P uptake were feasible at rates as high as $16.7 \text{ g N L}_r^{-1} \text{ d}^{-1}$ and $1.2 \text{ g P L}_r^{-1} \text{ d}^{-1}$ at $25 \text{ }^\circ\text{C}$ (by adding CaCl_2 in the internal recirculation) [172], or $44.8 \text{ g N L}_r^{-1} \text{ d}^{-1}$ and $0.4 \text{ g P L}_r^{-1} \text{ d}^{-1}$ at $35 \text{ }^\circ\text{C}$ (using inner mineral cores of granules as biofilm carriers) [170]. A highly mineralised sludge grew within these reactors, with a relative volatile content that could fall down to values below 25% of the dry weight. A composite granule formed by a bacterial biofilm (mostly anammox cells) attached to the inorganic core was observed. Local pH gradients were reported. The increase in pH value in the inner part of the granule facilitated the crystallisation of phosphate. Even though reported N removal efficiencies were high (75–90%), these values might still be enhanced by integrating a pre-denitrification stage (i.e., NO_3^- reduced to NO_2^-) prior to the anammox reactor (an internal recirculation would be needed for such configuration) in order to remove the nitrate formed by the anammox reaction (i.e., anammox reaction involves ca. 10% N conversion to nitrate) [173]. Use of mechanically stirred reactors resulted in much lower activities than those mentioned above [70,71]. As an example, Johansson et al. [70] treated anaerobically digested sludge dewatering centrate in a granular sludge sequencing batch reactor (SBR) operating the PNA process at $25 \text{ }^\circ\text{C}$ according to loading rates of $0.3 \text{ g N L}_r^{-1} \text{ d}^{-1}$ and $0.02 \text{ g P L}_r^{-1} \text{ d}^{-1}$, achieving 66% N removal (no chemicals were added). The accumulation of minerals increased the density of the granules, leading them to settle fast to the bottom of the bioreactor, where they could easily be harvested. Phosphorus content normally is 1–2% dry weight in normal activated sludge and 5–7% in P enriched EBPR sludge [174]. By considering the concomitant configuration discussed in this section, values of 10–16% have typically been reported [70,169,172]. Candidatus *Accumulibacter phosphatis*, which is commonly found in EBPR systems [175], has also been found in granular PNA systems and identified as potentially responsible for inducing HAP precipitation [176]. Biologically induced MAP production from anaerobic sludge dewatering concentrates has also been demonstrated as feasible in preliminary incubation experiments using specifically selected microbial strains (e.g., *Bacillus pumilus*, *Brevibacterium antiquum*, *Myxococcus xanthus*, *Halobacterium salinarum*, and *Idiomarina loihiensis*), opening a completely new route for P recovery via biomineralisation [166,177,178]. On this line, biologically mediated MAP (and other MgP together with calcium carbonate) precipitation was also reported in open, mixed-culture, biofilm bioreactors treating low-strength domestic waste water, while potentially responsible microorganisms were isolated for further characterisation (mostly heterotrophic bacteria growing aerobically) [179,180].

Table 3. Summary of experiences integrating biological N oxidation, or removal, and mineral precipitation aimed at P recovery inside the bioreactor (concomitant precipitation). More details are given as Supplementary Material.

Waste Water Source	Experimental Conditions	Bioprocess Performance	Precipitate Characteristics	Reference
<i>Nitrification as the bioprocess concomitant to P precipitation</i>				
Synthetic urine	Long-term nitrification in trickling filters partially packed with pumice and mussel shells	PO ₄ precipitation induced by Ca released from mussel shells; Mussel shells also provided carbonate needed for buffering the system	Composition of the CaP formed not determined analytically	[168]
Synthetic waste water mimicking anaerobic digester dewatering centrate	PN in aerated SBR vs. SBBR packed with polyethylene particles	SBR: faster start-up; SBBR: more stable facing disturbances in dissolved oxygen conditions	Suspended solids containing 9–10% P; Complementary work [169] in the SBR transforming PN into NDN showed that PO ₄ precipitated in different form depending on pH	[71]
<i>Anammox as the bioprocess concomitant to P precipitation</i>				
Synthetic waste water mimicking effluent from a PN reactor	Anammox process in an EBR with internal recirculation; Reactor at 33 °C and pH 8.6	NLR 5 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 87%; PLR 0.21 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 66%; Granule size 1.3–1.7 mm; Complementary works: [170] attached film EBR (35 °C) reached NLR 50 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 90% + PLR 0.55 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 72%; [171] attached film EBR (35 °C) reached NLR 10 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 77% + PLR 0.15 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 68%; [172] EBR (25 °C) reached NLR 20 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 84% + PLR 1.32 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 94%	CaP recovered as HAP; Granules with 83% mineral content, 28.9% Ca, 13.4% P, 0.9% N, 0.5% Mg	[72]
<i>PNA as the bioprocess concomitant to P precipitation</i>				
Anaerobically digested sludge dewatering centrate in a municipal WWTP	PNA process as 1-stage SBR at 25 °C; No addition of chemicals (w/o pH control)	NLR 0.31 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 66%	CaP recovered as HAP; Granules purged with 71% ashes, 33.5% Ca, 15.8% P; Heavy metals complied with EU standards for P fertilisers and needs from P industry	[70]

4.2.3. Interaction between biological N treatment processes and soluble phosphate availability

Beyond waste water composition, the availability of dissolved phosphate in the N removal bioreactor is highly influenced by the evolution of pH, which drives naturally occurring phosphate precipitation/redissolution phenomena. Dissolved phosphate availability is favoured by acidification (nitrification) [181–183], which may be interesting for promoting its subsequent precipitation as a phosphate salt. Thus, in activated sludge systems, performing BNR with significant co-occurring

mineral phosphate precipitation, a final step under anoxic conditions (e.g., denitrification), will help in maximising P separation efficiency from the water line, while concentrating P in the sludge [184,185]. This phenomenon—CaP precipitation—has also been reported in denitrifying biofilms, where biomass remains attached rather than suspended [52,55]. On the other hand, in the case of co-occurring EBPR within activated sludge bioreactors under alternative anaerobic-anoxic/aerobic conditions due to the metabolism of polyphosphate accumulating organisms (PAOs), microbial phosphate release will be particularly significant during anaerobic periods, eventually leading to co-precipitation events [186–188], or favouring the implementation of alternative configurations aimed at P recovery [54,174,189,190]. This can also be significant for new aerobic granular sludge (AGS) systems mostly operated in batches [191,192] and performing simultaneous nitrification–denitrification (SND). The PAOs—which are associated with the formation of dense and compact granules as well as other facultative anaerobic denitrifying bacteria—may become dominant in the core of the granule, and thus, they can play a role in phosphate release under anaerobic conditions, inducing local P precipitation [193–196]. Yet, the overall contribution of this phenomenon in the removal of P from waste water is conditioned by the re-dissolution of the precipitates under aerobic conditions [175,181] and it may cause instability of the mature granules [197]. Alternatively, anaerobic phosphate release in granular sludge systems may enable the implementation of external P recovery strategies [198]. Metal ions—and particularly, divalent ions such as Ca^{2+} and Mg^{2+} needed for phosphate crystallisation—tend to bind to the negatively charged extracellular polymeric substances (EPS) produced by the cells, favouring biomass adhesion and granulation [199]. The nature of the EPS matrix determines which ion is combined. In the case of alginate-like EPS (which are usually produced by AGS), these substances have high affinity for Ca^{2+} but low affinity for Mg^{2+} , making Ca^{2+} participate in the formation of the gel structure but Mg^{2+} only as a counter ion and, consequently, determining which mineral phase is formed. Moreover, Mg^{2+} and K^+ play a significant role in maintaining the stability of the EBPR process as phosphate counter ions [200]. Thus, temporal increases in the availability of these ions may induce the development of struvite-like structures onto the AGS-MgP precipitation. Since NH_4^+ is mostly removed by SND, MPP is expected as the main struvite type on the aerobic granules. Yet, when NH_4^+ is available, NH_4^+ adsorption may accompany K^+ release due to ion exchange [201]. Finally, CaP precipitation and recovery has also been addressed in anaerobic granular reactors targeting biogas production as a renewable energy source [202,203]. Both, carbon source and bulk pH value (7.0–7.5) were identified as key factors for the formation and growth of ACP granules in UASB reactors [204].

4.3. Phosphorus Recovery after Biological N Treatment (Downstream Configuration)

Previous experiences reporting P precipitation after biological N oxidation or removal are summarised in Table 4 [73–76,99,124,205–210] (an extended version of this table is provided as Supplementary Material). Biological N treatment based on nitrification involves a reduction in the buffering capacity of the liquid effluent. Denitrification and anammox processes counteract this effect, but only partially, as described in Section 4. Thus, downstream precipitation takes advantage of the high decrease in alkalinity commonly achieved through biological treatment [74,76], resulting in a lesser consumption of chemicals to increase the pH value [73,124]. Moreover, the alkaline environment applied during precipitation may favour sanitation of water by enhancing pathogen destruction [99,211].

High-rate activated sludge systems running with short solids retention times allow for significant COD removal from sewage. The high removal of organic compounds that takes place in these bioreactors is mostly attributed to the adsorption of the colloidal particles onto the suspended solids. Subsequently, such biosolids are separated by settling. According to the operational conditions described above, nitrification does not occur, and ammonium is partially adsorbed, or assimilated, by heterotrophic organisms. Downstream, the ammonium remaining in the biologically treated waste water, together with the orthophosphate available, can simultaneously be precipitated as MAP [129].

Alternatively, addition of $\text{Ca}(\text{OH})_2$ following high-rate biological treatment has also been suggested to raise pH, favouring ammonia stripping and CaP precipitation [212].

Table 4. Summary of experiences integrating biological N oxidation, or removal, followed by chemical precipitation aimed at P recovery (downstream precipitation). More details are given as Supplementary Material.

Waste Water Source	Bioprocess Performance	Precipitation Performance	Precipitate Characteristics	Reference
<i>Nitrification as the bioprocess preceding chemical P precipitation</i>				
Anaerobically digested swine waste water from a UASB reactor	Nitrification in a continuous aerated system at pilot-scale; Similar tests also conducted considering NDN and PNA as the bioprocess preceding P precipitation	CaP precipitated in lab batch tests using hydrated lime; Similar results to those previously given by [205]	Field tests were also performed; The sludge formed contained 30% Ca, 5.7% P, 2.5% Mg; The high Ca/P ratio indicates carbonate co-precipitation	[74]
Anaerobically digested industrial (potato) waste water from a UASB reactor	Nitrification in an aerated CSTR	CaP precipitated in a lab CSTR with CaCl_2 ; High pH and Ca/P triggered co-precipitation of carbonates and MgP; Nitrification reduced $\text{Ca}(\text{HCO}_3)_2$ inhibition and carbonate precipitation making Ca available for CaP precipitation	CaP precipitated mostly as HAP; Ca/P/Mg ratio as 1.5/1.0/0.1	[206]
Anaerobically digested industrial (potato) waste water previously processed for urease-induced partial phosphate removal	Nitrification in an aerated MBR; Mg content and pH increased due to preliminary ureolytic phosphate removal	CaP precipitated in lab batch tests; Several chemicals used to raise pH and test effect of TIC; TIC decrease due to nitrification implied shorter dosage of NaOH; NaOH supply w/o nitrification may lead to MgP and CaCO_3 formation; pH increase with $\text{Ca}(\text{OH})_2$ favoured PO_4 precipitation due to extra Ca dosage; pH increase with Na_2CO_3 hampered Ca and PO_4 precipitation	Composition of the precipitate not determined analytically; Similar results than in [207]	[124]
Surface lagoon liquids from swine farms	Nitrification in fluidised bed reactors with sludge immobilised in supporting porous medium; >90% ALK reduction and prevention of NH_3 emission	CaP precipitated in lab batch tests; $\text{Ca}(\text{OH})_2$ added as precipitant; pH increased to ≥ 9.5 for optimum P precipitation; Similar field test in [73]; P in effluent adjustable for on-farm use according to crop needs	Composition of the precipitate: 2.5–10% P; Nitrification favoured P availability in the precipitate; The recovered material can be exported and reused as P-fertiliser; The high pH value applied in the precipitation process destroys pathogens	[208]

Table 4. Cont.

Waste Water Source	Bioprocess Performance	Precipitation Performance	Precipitate Characteristics	Reference
<i>NDN as the bioprocess preceding chemical P precipitation</i>				
Fertiliser industry waste water	NDN in a continuous flow activated sludge system at pilot-scale	MgP precipitated in a continuous pilot-scale unit; Mg/NH ₄ /PO ₄ adjusted with MgCl ₂ + H ₃ PO ₄ ; Mg and PO ₄ recovered from the precipitate by heating allowing the recycling within the process	Composition of the precipitate after drying: 24.0% P, 16.6% Mg, 1.1% N	[209]
Subfloor slurry from a pig farm, liquid separated by a rotary press	NDN in a continuous flow activated sludge system at full-scale	CaP precipitated in a continuous full-scale unit; Hydrated lime injected to pH 9.5	Composition of the precipitate not determined analytically; Total faecal coliforms and enterococci reduced	[99]
Calf manure	NDN running at full-scale	MPP precipitated in: (1) lab experiments at room temperature, (2) pilot plant running as CSTR, and (3) full-scale plant (3 CSTRs + settler); MgO added as Mg source	<i>Lab:</i> Fine-grained elongated crystals with a max. diameter of several tens of microns; <i>Pilot plant:</i> the recovered product contained 12.5% P, 10.7% Mg, 11.4% K, 1.3% Ca, 0.7% N (5.5% organic-C)	[210]
<i>PNA as the bioprocess preceding chemical P precipitation</i>				
Anaerobically digested sludge dewatering centrate from two municipal WWTPs -with chemical vs. biological P removal in the mainstream-	PNA as 1-step process at lab- and pilot-scale	MgP precipitated in lab batch tests; K uptake from water line positively correlated with pH value up to 11	MgP precipitated as MAP and MPP; Precipitate composition (pH 11): 11.4% P, 9.2% Mg, 4.3% K, 3.5% N, 0.9% Ca	[76]
Anaerobically digested manure centrate	After biological treatment, Mg/K/P molar ratio adjusted to ca. 2.0/4.5/1.0	MgP precipitated in lab batch tests targeting MPP recovery; Different dilutions rates tested to decrease interference by TSS	MgP precipitated mostly as MPP with co-precipitation of other salts; Suspended particles favoured aggregation of crystals as star-asterisk forms	[75]

Lack of ammonium in the N treated effluents allows raising of pH for precipitating MgP without the risk of favouring ammonia emission while recovering other minerals rather than MAP, such as newberyite [213] (which has a specific P content higher than MAP, see Table 1) and MPP (K-struvite) [75,76]. Potassium, together with N and P, is a key macronutrient for plants typically obtained by mining soluble K-salts (potash) [214,215]. Yet, there is growing interest in obtaining K from alternative renewable resources, including waste waters. Optimum pH for precipitating MPP is higher than for precipitating MAP, within the range 10.5–11.5 [76,216,217]. Successful attempts for simultaneously precipitating P and K have been reported using raw urine [218,219], digested sewage sludge dewatering centrate [76], digested livestock manure centrate [75], and other waste water streams. In the case of N treated effluents, availability of residual NH₄⁺ will trigger simultaneous MAP and MPP formation, resulting in a (N-P-K) multi-nutrient product [76,210]. Similarly, the availability of other cations such as sodium (Na⁺) will interfere in the precipitation of MPP, thereby reducing K recovery efficiency [220–222]. The crystal size of the MPP formed is a critical aspect in view of its subsequent use. By optimising process operation parameters related to supersaturation, feeding,

and mixing, larger crystals can be obtained [223,224]. Moreover, a downstream dewatering step can be advisable to prevent excess of fines in the water line, while improving the agglomeration of the precipitated material [81]. Concerning the liquid effluent, beyond satisfactory discharge into water bodies, ion precipitation can also help adjusting water quality in terms of the N-P-K content to match specific requirements according to the final use (e.g., reuse for crop fertigation) [73].

5. Use of Recovered Phosphate Products

The use of the recovered phosphate salts as fertilisers must promote plant growth and nutrient uptake without leading to overall adverse environmental or human health impacts [225]. Recovered MgP products (i.e., MAP) have been proven as equivalent to regular mineral P fertilisers and more effective than recovered CaP products [63,64]. Besides, recovered CaP products are very similar in composition to the mined phosphate rock, so they can be mixed with ores at the beginning of an industrial P production process [226]. Currently, precipitated phosphate salts are not typified in the European fertiliser regulation, and this fact limits marketability.

5.1. Quality Criteria for the Precipitated Phosphate Salts to be Covered by the EU Fertiliser Regulation

In the EU, those materials used as fertilisers must comply with the requirements stated by the fertilising products regulation (EU) 2019/1009 [227]. Currently, the precipitated phosphate salts, as well as other derivate products, are not typified as a Component Material Category (CMC) within this regulation. Nonetheless, the topic is in progress. The requirements to be complied by these materials in view of their possible inclusion in an updated version of the rule are overviewed below, according to the criteria fixed by the Joint Research Centre (JRC) of the European Commission [228], who is in charge of establishing a regulatory framework, enabling the production of fertilising products. In this regard, to be accepted as EU fertiliser, the recovered precipitated phosphate salts will have to comply with the requirements laid down for a new CMC “precipitated phosphate salts and derivatives” as well as with those for the already established Product Function Category (PFC) “1C-Inorganic fertilisers”. The newly proposed CMC “precipitated phosphate salts and derivatives” aims to cover a wide range of phosphate-based compounds of high purity produced through a precipitation process with the intention to be used as fertilising materials or as intermediates in the manufacturing processes of P-fertilisers, and which are sufficiently effective at providing P to plants. The technical proposal for the inclusion of precipitated phosphate salts and derivatives in the (EU) fertilising products regulation includes the following items: (1) input materials and reagents; (2) production process conditions; (3) agronomic value; (4) environmental and human health aspects; (5) physicochemical properties; (6) handling and storage. As a fertilising product, the use of this material must not lead to overall adverse environmental or human health impacts and must provide plants/mushrooms with nutrients or improve their nutrition efficiency, either on its own or mixed with another material, among other market aspects.

As input materials to the precipitation process, common waste water flows to be taken into account are main- and side-streams in municipal WWTPs and effluents from food processing. Animal manure liquid fractions have also been considered as promising input materials [229]. Concerning the production process, it has been suggested to differentiate between those facilities specifically designed to produce fertilising materials and those others where the precipitated phosphate salts are recovered as a by-product resulting from a process aimed at producing different primary outputs (e.g., energy and treated water), as long as the material quality criteria are fulfilled. The agronomic value of the precipitated phosphate salts has been proposed not to be assessed on the basis of minimum extractable P content (due to misinformation on agronomic efficiency), which is in line with the criterion used for other CMCs. However, it was suggested to label the ratios water-extractable P to total P, and acid-extractable P to total P. Recommended minimum P solubility values are as follows: 25% in water, 30% in neutral ammonium citrate, and 35% in formic acid.

From the point of view of environmental and human health, and regarding the presence of inorganic, organic, and biological toxic elements, safety must be assured by a combination of requirements in the production process and parameter assessment on the precipitate. Most input materials intended for P recovery through precipitation have high contents of inorganic and organic (micro)pollutants [230], which can be transferred to the precipitate, usually adhered onto organic matter [231,232]. Yet, available data concerning the presence of contaminants in the precipitates, which have often been measured for high-purity precipitated phosphate salts with low organic C content (TOC), tend to indicate safe levels [228,233]. To prevent risks associated with particular organic (micro)pollutants (e.g., flame retardants, pharmaceutical compounds), it has been proposed to limit the organic C content in precipitated phosphate salts to a maximum of 3% of the dry matter content [228,234]. By applying satisfactory operational conditions during the production process and considering a maximum threshold for the organic C content, the risk associated with the accumulation of microbial pathogens in the precipitate will be reduced. In turn, this may help reducing the risk of appearance of microbial resistances in the agrifood chain. Standard microbial testing is proposed, considering as limit values the absence of *Salmonella spp.* in a 25 g sample and 1000 CFU g⁻¹ fresh mass (CFU is colony-forming units) for *Escherichia coli* or *Enterococcus*. Additional tests would be required when manure or municipal waste water were used as input material for the production process, ensuring absence of viable *Ascaris sp.* eggs in a 25 g fresh mass, and concentrations of *Clostridium perfringens* (as a spore-forming bacteria) below 100 CFU g⁻¹ fresh mass. Potentially, the precipitated phosphate salts may contain significant levels of trace elements, including heavy metals and metalloids, when such elements are available in the water flows under processing [235,236]. When managing biosolids in WWTPs, organic C has commonly been shown as an important metal-sorption phase [237]. Thus, low organic contents in the precipitate may also help reducing associated metal/metalloid levels. Since typical levels of these contaminants [238] are one or two orders of magnitude below the limit values fixed by the EU fertiliser regulation for the PFC level “inorganic macronutrient fertiliser” [227]—i.e., cadmium (Cd): 60 mg kg⁻¹ P₂O₅; chromium (Cr) VI: 2 mg kg⁻¹ dry matter; nickel (Ni): 100 mg kg⁻¹ dry matter; lead (Pb): 120 mg kg⁻¹ dry matter; arsenic (As): 40 mg kg⁻¹ dry matter; copper (Cu): 600 mg kg⁻¹ dry matter; zinc (Zn): 1500 mg kg⁻¹ dry matter—it has not been suggested to include additional specific limit values for metals and metalloids, regardless of the input material.

In relation to the physicochemical properties of the precipitated phosphate salts, the regulation proposals for the new CMC have mostly concerned on the total P content, the micronutrients content (Al and Fe), and the presence of physical impurities. Thus, the precipitated salts have been suggested to have a total P content of 16% (P₂O₅ equivalent) or more, on dry weight basis. According to available data from running plants [228], a 20% P₂O₅ limit value seems an achievable target. Moreover, the assessed material should contain less than 10% dry matter of Al plus Fe (elemental forms), assuming a Fe/P molar ratio not compromising plant P-availability [239]. Finally, visually detectable physical impurities (above 2 mm) should be less than 0.3% dry matter and total macroscopic impurities less than 0.5% dry matter, in line with the provisions established for other CMCs [227]. As handling and storage conditions, it is proposed to avoid physical contact between input and output materials in the production plant after the precipitation process and to store the precipitated phosphate salts in dry conditions. All the above referred considerations seek to ensure appropriate material quality and chemical composition for the intended functions of the fertilising materials.

5.2. Expected Characteristics of the Precipitated Phosphate Salts Depending on the Production Process

Overall, the characteristics of the recovered end-products are strongly dependent on the input material and the precipitation process applied [88,240]. Although final decision on the criteria to be fulfilled in order to include precipitated phosphate salts in the EU fertilising products regulation [227] is still pending, characteristics of these materials must be aligned with the abovementioned quality criteria. Thus, the main aspects to be specified will likely be related to the environment, human health, and the physicochemical properties, and focused on features such as the organic C content, toxicity

limit values (concerning both chemical and biological agents), and particular contents of P, Al, Fe, and physical impurities.

When P precipitation is conducted before biological N treatment (upstream configuration), phosphate is frequently crystallised heterogeneously within a wet sludge. Depending on the waste water source, the resulting product may contain a high amount of impurities including solid particles, organic C—easily above the aforementioned 3% dry matter—and heavy metals. The availability of organic C (mostly if biodegradable or not previously digested) will condition the later handling and storage of this P-rich material. Simultaneous phosphate precipitation and biological N treatment (concomitant configuration) is still under development and not applicable at a large scale, but it is known that this frequently leads to the formation of a heterogeneous precipitate mixed with organic C (basically, constituted by the microbial cells catalysing the process). Although the nature of this organic C will be different from the case of the upstream configuration, organic contents will be still high. Washing and drying the recovered solids may help in improving their characteristics in view of fitting the requirements needed for a marketable fertiliser product [238]. When P precipitation is applied after biological N treatment (downstream configuration), the resulting product will have a higher purity and contain less organic C. Risk of chemical and biological toxicity will likely be reduced due to the lower availability of organic matter, potential biodegradation, and adsorption phenomena occurring within the bioreactor and the alkaline environment applied to achieve P precipitation, which will promote pathogens destruction [99,211] (Table 5).

Table 5. Major expected characteristics for the recovered precipitated phosphate salts depending on the production process configuration (upstream, concomitant and downstream alternatives).

Characteristics	Upstream	Concomitant	Downstream
Purity	Presence of solids and other compounds will disturb crystallisation and affect purity of precipitate	Heterogeneous precipitate	Increased effective ion availability favouring crystal formation
Organic content	High	High	Low
Toxicity	Potential presence of metals, organics and pathogens depending on the waste water origin	-	Pathogen destruction depending on process pH
P form (most probable)	MAP and CaP. Carbonate forms may co-precipitate together with phosphates	CaP and MAP	Absence of ammonium will favour formation of alternative MgP salts such as MPP

It is important to ensure that any treatment alternative to be implemented at the full-scale will be able to produce valuable materials according the upcoming definition for the CMC “precipitated phosphate salts and derivates”. The aim of the EU regulation is to cover a wide range of phosphate-based compounds of high purity, sufficiently effective at providing P to plants, while reducing the risk of contamination by the long-term application to agricultural soils [241]. Thus, any material that fulfil the proposed quality criteria should be considered. The data summarised in the previous sections of this review indicate the potential occurrence of a wide range of mineral forms in the end-products of the precipitation processes (Table 1). Most of the time, the precipitated P is in the form of struvite, calcium phosphate or a mixture of Ca- and Mg-salts [240]. The form, in which P is combined with other elements to form the precipitated phosphate salts, has a strong effect on the later accessibility to P for plants.

5.3. Agronomic Efficiency Achieved when Using Precipitated Phosphate Salts

Plants can only absorb P if it occurs in specific chemical forms, the most relevant of which is orthophosphate (H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} as soluble ions). However, in soils, only a small portion of the total P is available as PO_4 dissolved in the soil solution, while the largest amount is bound to

chemical compounds of different solubility. The amount of P dissolved, and thereby accessible for plant roots during the life cycle of a crop, is defined as plant-available P [242]. Typical relative solubilities for different recycled fertilisers can be found in the literature, referring to the most frequently used extractant chemicals and according to the EU fertiliser regulation [227]. However, the highly variable chemical composition and structure of the P-compounds and other components available in the recycled material, together with its inherent characteristics (e.g., granule size), may affect the solubility in a given extractant chemical [240,243], leading to an unsuitable assessment of the plant-available P. Besides dominant chemical form and structure, soil–plant–fertiliser interactions may also affect P release dynamics, and availability for crops, depending on: (1) soil properties (e.g., pH, texture, existence of potential P sorption sites); (2) plant characteristics (e.g., plant species, root traits, strategies for mobilising P from soil, temporary variations in nutrient demand); (3) fertiliser properties (e.g., crystal size, granule size, application method, presence of impurities, occurrence of co-precipitations); (4) type of trial conducted (e.g., properties of the growing substrate, trial duration, pot/field trial, pot size, basic/multi-nutrient supply, weather conditions) [244,245]. Despite such a long list of factors potentially inducing variability when assessing recycled fertilisers' efficiency, there are some common conclusions that can be distilled from the data available in the literature [64,225,240,245]. Otherwise, the agronomic efficiency of a fertiliser can be assessed with respect to a reference (or control)—i.e., relative agronomic efficiency (RAE)—on the basis of plant biomass yield (dry matter increase per unit of nutrient supply), or plant nutrient uptake (dry matter yield*biomass nutrient concentration) [246].

The objective for those materials that could be included in the newly proposed CMC “precipitated phosphate salts and derivatives” is to supply P to plants as a macronutrient. Nowadays, precipitated salts, such as (relatively pure) struvite, several forms of CaP, or a mixture of CaP + MgP, are gaining relevance as a by-product for agronomy. Struvite (MAP) is the most common precipitated phosphate salt, with a high potential to be marketed as a recycled nutrient source since its production is feasible according to a relatively high purity standard (only containing trace amounts of impurities), and also, it has a high P-content and a demonstrated value as a P-fertiliser [63,64,247]. Nonetheless, other CaP and MgP are also registered under the REACH Regulation (Regulation (EC) No 1907/2006) as fertilisers [248]. Constituent molecules and ions, and how they are arranged in the recovered materials, have been proven to influence on the plant-available P. In this regard, P will be unavailable for crops if it is strongly bound to certain bi- and trivalent ions. Beyond plant nutrition, this aspect is also relevant because of the potential accumulation of P in soil at the long-term, and social aspects linked to farmer's confidence and market acceptance of innovative P fertilisers derived from secondary raw materials.

Concerning the agronomic efficiency of the struvite as P fertiliser, published data show variable values for the RAE depending on the origin of the struvite, even when it has been tested under identical growing conditions [249,250]. As it has been mentioned above, this is probably because of the presence of co-precipitates and impurities, or the different sizing of crystals and product granules. Nonetheless, good agronomic performance has been reported for a wide range of soil pH values [225,245,251], even though, in some cases, limited availability of P was found in basic soils [244,252]. It has also been suggested that the high agronomic efficiency of the struvite as P fertiliser is favoured by naturally-occurring local acidifying processes in roots, the uptake of ammonium by the roots, and the nitrification of ammonium to nitrate by the soil microbial community [253–255]. Moreover, several authors did not find significant differences in the RAE for other MgP [63,64,225], showing better P availability than when considering recycled CaP.

The precipitation of CaP may involve the formation of different compounds. While mono- and di-calcium phosphates show the highest P availability for plants, the formation of compounds with an increasing Ca content in the binding forms—i.e., with higher values for the Ca/P molar ratio—generally results in lower values for P availability [256]. In addition, the RAE of the CaP varies widely depending on factors such as the aggregation size, crystalline structure, cation content (e.g., Mg^{2+}), and presence of co-precipitates [257]. In this regard, several authors have obtained lower values for the RAE of the CaP than for the RAE of other conventional fertilisers, as well as of the struvite [63,64,225,245,250]. Generally

speaking, CaP tend to show better P availability for plants under (moderately) acidic conditions than under neutral or alkaline conditions, since acidic environments favour the transformation of P into reactive forms [243,250]. In calcareous soils, the Ca present in the soil solution will tend to precipitate on the surface of the CaP granules [258]. After soil application, CaP can evolve and transform into more stable mineral phases [259], which could potentially justify the wider range of RAEs observed for CaP than for struvite and other MgP [225]. According to the current state-of-the-art for technologies that seek to recover P from waste waters, it is difficult to guide the precipitation processes in a way that the formation of mono- and di-calcium phosphates become dominant [260]. Thus, the CaP commonly formed are unsuitable for most of the soils in Europe, of which pH value varies between 5 and 8 [261], at least, in the short-term. Regarding FeP, they are not currently registered as fertilisers under the REACH Regulation [248]. Ferric phosphates were initially proposed as end materials to be included in the newly proposed CMC, but finally discarded due to limited testing of the agronomic value (i.e., concerns over the plant availability of Fe-complexed phosphates and risk of Al/Fe forms inducing plant toxicity have been reported) [228]. Yet, there may be potential for P recovery from waste water as precipitated FeP mineral salts, which could be used as new input materials or intermediates [16], or as an alternative to other Fe fertilisers used to prevent Fe chlorosis [262].

Indeed, all the precipitated phosphate salts can behave as multi-nutrient fertilisers, since they contain a broad range of elements, including not only P, but also other nutrients for plants. This fact may help justifying the wide range of RAEs reported for these products. Nonetheless, those products recovered as MgP have been proven to supply equivalent amounts of plant-available P to other regular, high water-soluble, phosphate rock-based fertilisers, and to be more effective than other products recovered as CaP [63,64,225]. It is challenging to distinguish between effective and ineffective fertilisers due to all the factors influencing nutrient availability and release dynamics. From an agronomic point of view, MgP (e.g., struvite) are a desirable product due to the higher amount of plant-available P that they provide and the independence of its dissolution with respect to the soil pH value. Moreover, those CaP products recovered as hydroxyapatite are very similar in composition to the mined phosphate rock (i.e., apatite-type ores), so they can be used as feedstock in an industrial P production process [16,226]. The use of these secondary raw materials is not expected to result in large discharges of new contaminants into the environment. This scenario contrasts with the current import-based model of phosphate rock-derived P-fertilisers, which is associated with high consumptions of chemicals and new inputs of mobilised metals into the environment. Yet, local conditions should be taken into account in forthcoming scenarios based on closing nutrient cycles, working in close collaboration with all relevant stakeholders, since social and market acceptance of the technologies and recovered products is crucial for their successful implementation [263].

6. Conclusions

The recovery of precipitated phosphate salts from waste water may help in reducing dependence on phosphate rock as a critical raw material, while preventing environmental pollution and promoting more sustainable development. Several technological alternatives are feasible for this purpose. The increase in pH value and the dosage of metal ions (such as Mg^{2+} , Ca^{2+} , and Fe^{2+}) are factors commonly considered. In an integrated approach, the precipitation process can be applied before, during, or after biological N treatment. Some potential targets are: lowering the consumption of energy and chemical reagents, lowering the treatment cost, minimising the risk of toxicity for the microorganisms involved in the biological treatment, and recovering new valuable and marketable high-quality products in the framework of the circular economy. The typification of the end-products, in order to be covered by the EU fertiliser regulation, is currently ongoing. Phosphorus and organic carbon contents are the primary factors to be taken into account when assessing the characteristics of the precipitated phosphate salts. Those materials fulfilling the technical criteria under discussion will be directly usable as agricultural fertiliser, or as a by-product in the P-fertilisers industry.

7. Future Research and Development

The recovery of phosphates from waste water has been studied for years. Currently, it appears as a relatively easy way to improve the eco-design and sustainability of the WWTPs within the framework of the circular economy model, enabling the production of added-value products that can be recycled as fertilisers. A more frequent implementation of phosphate precipitation technologies at the full-scale for processing different kinds of waste water is expected to push into the development of new distribution channels and a consolidated market for the precipitated salts. Besides municipal and agri-food waste water streams, animal manure liquid phases are also promising as a source of precipitated phosphate salts, since they contain significant amounts of nutrients and specific applications are still scarce. The possibility that certain microorganisms help to produce particular products, either indirectly (e.g., involving EBPR-type processes) or even directly (i.e., inducing biological mineralisation), needs further study and will continue evolving. Moreover, the recovery of alternative products beyond MAP, able to supply P in a form easily available for plants, and the feasibility for integrating other nutrients such as K, will need further research efforts.

The development and implementation of P recovery technologies to produce marketable by-products most probably can help to reduce dependence on finite raw materials, while providing side-benefits in WWTP sludge lines. However, net impacts related to global warming are highly dependent on the structure of the productive sector at the regional level (e.g., nutrient balance, local stakeholders, and existence of enterprises dedicated to produce fertilisers). The materialisation of P-recovered fertilisers is not only cost-dependent, but it is also subjected to other decisions that impact on the need to process eligible input materials. Systematic studies based on mass flow analysis, life cycle assessment, and the definition of objective indicators to quantify sustainability and costs will help to assess the final benefits of the technological alternatives here described. A holistic approach, taking into account the water–environmental technology–agronomy nexus will favour the achievement of those requirements needed for an optimised production of fertilising products. Nowadays, most of the data used to assess the agronomic efficiency of these recovered products have been obtained in pot experiments. More field tests are, therefore, required for a better assessment of the performance of these products as fertilisers. In this regard, there is a lack of information about their performance in the long-term and their effect on both plant production and soil quality. The accumulation of plant-unavailable P in the soil may lead to an increased risk of P-losses through leaching and run-off. Moreover, the accumulation of other organic (micro)pollutants may also trigger contamination events affecting biodiversity, key soil functions, and its potential transference to crops (which, in turn, might be associated with impacts on human health).

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/10/7/1039/s1>, Relevant words included (or discarded) in the multi-term topic search assessed via the Web of Science Core Collection (Clarivate Analytics, USA).

Author Contributions: Conceptualization, A.M. and M.C.-S.; methodology, A.M.; software, A.M.; validation, A.M.; formal analysis, A.M.; data curation, A.M.; writing—original draft preparation, A.M. and M.C.-S.; writing—review and editing, A.M., M.C.-S., C.B. and J.C.; project administration, A.M.; funding acquisition, C.B. and J.C. All authors have read and agreed to the published version of the manuscript.

Funding: At University of Girona (UdG), this paper was written in the framework of the research project DigesTake (Resource recovery and valorisation from urban digestates in the framework of the circular economy) [COMRDI16-1-0061] funded by ACCIÓ–Generalitat de Catalunya within the program Comunitat RIS3CAT Aigua. The Laboratory of Chemical and Environmental Engineering (LEQUIA) (<http://www.lequia.udg.edu/>) is member of the TECNIO network, and it has been recognised as a consolidated research group by the Catalan Government [2017 SGR 1552]. At the Institute of Agrifood Research and Technology (IRTA), this paper was written in the framework of the research project LIFE ENRICH (Enhanced nitrogen and phosphorous recovery from wastewater and integration in the value chain) [LIFE16 ENV/ES/000375]. IRTA received the support of the CERCA Program–Generalitat de Catalunya.

Acknowledgments: The authors thank the efforts made by Dr. Rafaela Cáceres to make this scientific collaboration between UdG and IRTA possible. The authors would also like to acknowledge the constructive comments posed by the anonymous reviewers during the peer-review process, which helped to improve the final version of the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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