10 Municipal Wastewater as a Potential Resource for Nutrient Recovery as Struvite

Nageshwari Krishnamoorthy,[1] Alisha Zaffar,[1] Thirugnanam Arunachalam,[1] Yuwalee Unpaprom,[2] Rameshprabu Ramaraj,[2] Gaanty Pragas Maniam,[3] Natanamurugaraj Govindan,[3] and Paramasivan Balasubramanian[1]

[1]Department of Biotechnology & Medical Engineering, National Institute of Technology Rourkela, Odisha, India
[2]Maejo University, Chiang Mai, Thailand
[3]Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Pahang, Malaysia

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10.1 INTRODUCTION

Rapid industrialization and urbanization have become remarkable trends world-wide that have caused negative insinuation on the environment. Due to the increasing population, notable issues such as land and environmental degradation, pollution, and climate change arise. One such problem is wastewater generation caused by several anthropogenic activities that demand major concern and treatment (Addagada, 2020, Krishnamoorthy *et al.,* 2021a). Of the various sources of wastewater, municipal wastewater serves to be a chief contributor of nutrients and harmful pollutants. It mainly comprises household waste, medicinal waste, plastics, human feces, urine, heavy metals, organic, and inorganic waste. In this regard, it contains vital nutrients such as phosphorus, nitrogen, sodium, and potassium (Kataki *et al.*, 2016; Luo *et al.*, 2014; Mahy *et al.*, 2019). Human urine alone contributes ~50% phosphorous and ~80% of ammonium nitrogen to municipal wastewater (Krishnamoorthy *et al.,* 2021b; Wilsenach & Van Loosdrecht, 2004). Around 38.88 km^3 of wastewater is generally produced in various regions of southern parts of Asia. India alone produces ~109,598 tons of solid waste/day, of which only 7% is treated (Evans *et al.*, 2012; Jasinski, 2014). This mineral-enriched water when let into ponds and natural streams will aid in algal growth and eutrophication leading to oxygen depletion in the water bodies. The hypoxic conditions prevalent will decrease life underwater (Gilbert, 2009). A feasible solution should be arrived at to establish a sustainable circular bio-economy.

On the other hand, the alarming depletion of phosphorous resources has triggered a rising need for the recycling and recovery of this non-renewable nutrient. Phosphate reserves are scarred around the world, mentionable in Morocco, Iraq, China, and Algeria (Desmidt *et al.*, 2012; Gurr, 2012; Zhang *et al.*, 2013). According to an article published by International Fertilizer Development Center, the United States, phosphate rock mining for fertilizer production is increasing at a rate of 180–190 million tons per year as a result of the increase in population (Gurr, 2012; Van Kauwenbergh *et al.*, 2013). The shooting up of per capita phosphorous demand due to an increase in population and a rise in phosphorus consumption suggests that the reserves will be depleted in the next few years (Gilbert, 2009). Such critical situations have urged the researchers to explore sustainable solutions not only to recover nutrients but also to utilize them as organic fertilizer for the enrichment of plant growth. Retrieval of P from municipal wastewater in the form of struvite ($MgNH_4PO_4 \cdot 6H_2O$) can be an alternative approach for the cessation of a leak in the phosphate cycle.

Struvite is a phosphate-rich mineral comprising mainly of phosphate, ammonium, and magnesium equimolar ratio). The research and commercialization of struvite are emerging in recent decades for utilization as a potential substitute to commercial fertilizers extracted from phosphate rocks. It has an NPK value of 6:29:0 (Barak & Stafford, 2006). Considering the nutritional composition of municipal wastewater, it is likely to be used for struvite precipitation. Domestic wastewater collected in China is estimated to contain approximately 5.5% of total phosphate as compared to the consumption of chemical fertilizer (Krishnamoorthy *et al.*, 2020). Solid waste accounts for up to 50% of the organic waste, comprising mainly of food scraps with a P concentration of ≤4 g/kg dry matter. An added advantage is that the flue gas produced by incineration of solid waste contains 10–15% of CO_2 which can reduce chemical cost by serving as a carbon source for calcium pre-treatment (Wu *et al.*, 2018).

The struvite precipitated can be directly marketed as a soil-conditioning slow-release fertilizer. The risk of heavy metal co-precipitation with struvite is low as the metal content is much lower than the ground itself, reducing the hazard of chemical contamination (Maaß *et al.*, 2014; Saerens *et al.*, 2021). This chapter converses the nutritional composition and aptness of municipal wastewater for struvite recovery and various principles that are employed for efficient struvite crystallization. Chemical and electrochemical precipitations are the common methods used for lab-scale and industry-scale production and several reactor designs have been discussed in detail. The chapter also highlights the most significant process parameters that need optimization for improved quality of struvite. In addition, it provides insights on the research gaps, challenges that should be overcome, and future perspectives of struvite research that require further attention.

10.2 NUTRITIONAL COMPOSITION OF MUNICIPAL WASTEWATER

Several works of literature have reported that municipal wastewater has a nutritional value equivalent to that of commercial fertilizers to be used in the agricultural field. It holds numerous macro and micronutrients, organic matter, and high NPK value that can be used for fertilizing applications (Saerens *et al.*, 2021; Srivastava *et al.*, 2018; Theregowda *et al.*, 2019). Among these nutrients, phosphorus, nitrogen, and magnesium are the most essential nutrients required by the plants for their growth and hence serve as a source of struvite. Animal waste in municipal wastewater alone constitutes up to 34% of the total nitrogen that enters the agricultural field (Matassa *et al.* 2015). There are many physicochemical methods for recovering the nutrients, of which struvite precipitation has gained momentum in recent years.

P is a vital nutrient present in municipal wastewater that is required by the plants for various processes like photosynthesis, cell division, growth, energy transfer, and quality of fruits and crops. It can be incorporated into the food chain by the application of phosphate-rich fertilizers (Theregowda *et al.*, 2019). Every year approximately 27 million tons of P is used in agriculture, among which only

10–11% is actually utilized. The remaining proportion is dumped into the water bodies through diffusion resulting in eutrophication. Struvite precipitation can address this issue by recovering P in its most redeemable form, phosphate. In addition, crystallization of struvite is considered a biological way of water treatment as it recovers nitrogen in the form of ammonium, the most accessible form by the plants. Plants can easily take up ammonium and convert it to nitrate through nitrification and further alter nitrate to nitrogen by denitrification (Theregowda *et al*., 2019; Williams *et al*., 2015).

Potassium is another important essential nutrient present in municipal wastewater which is required for enrichment of soil and crop yield (Ryu *et al*., 2012; Zhang *et al*., 2012). It can be efficiently recovered as K-struvite by slightly varying the conditions of usual struvite precipitation. This isomer analog of struvite is formed by the replacement of ammonium by potassium and potentially used as a slow-release fertilizer. However, high concentrations of ammonium and sodium in municipal wastewater can inhibit the K-struvite formation. In order to avoid this, pre-treatment strategies such as ammonium stripping can be adopted. So far, there are no such approaches for preventing the effect of sodium, and further studies on understanding the variation in process and experimental conditions can provide insights on eliminating the inhibitory effect. Also, there is literature shred of evidence of co-precipitation of struvite, K-struvite, and other struvite family crystals which can serve as a value-added fertilizer (Huang *et al*., 2019; Li *et al*., 2020). Municipal wastewater also constitutes a high concentration of heavy metals such as copper and zinc and other micropollutants like pharmaceuticals, pesticides, organic, and inorganic pollutants (Decrey *et al*., 2011). Pre-treatment methods have been widely explored to reduce heavy metal amounts for efficient water treatment and reuse of irrigation. The presence of minuscule of such metal ions can help as co-factors of bacterial enzymes involved in anaerobic digestion. The list of nutrients, heavy metals, organic, and inorganic compounds present in municipal wastewater are shown in Table 10.1.

10.3 TECHNOLOGIES INVOLVED IN STRUVITE PRECIPITATION

Recovery of nutrients from wastewater is quite tedious concerning the concentration and form of ion species. In this regard, struvite recovery has bloomed to be an interesting approach not only for efficient recovery of P and nitrogen but also to serve as a sustainable alternative for chemical fertilizers. Several technologies such as chemical, electrochemical, and biological precipitation have been developed for this purpose to promote recycling, and reuse of nutrients and to avoid consumption of non-renewable natural resources.

10.3.1 Chemical Precipitation

A chemical method for the struvite precipitation is one of the most common processes by which nutrients can be managed to be removed from wastewater. Chemical precipitation requires the addition of magnesium as it is present in

TABLE 10.1

Nutritional Composition and Constituents of Municipal Wastewater

	Constituents	Concentration (mg/L)
Nutrients	Nitrogen	20–35
	Phosphorus	5–30
	Potassium	13–20
Heavy metal (mg/kg)	Iron	20,000
	Cadmium	3
	Arsenic	3–230
	Chromium	1–3,410
	Copper	80–2,300
	Nickel	2–179
	Lead	13–465
	Zinc	101–49,000
	Sulfate	20–50
Organic and inorganic substances	Dioxins, polychlorinated biphenyls (PCBs), furans, organochlorine pesticides	8–35
	Inorganic substances	3–10
Physicochemical parameters	Alkalinity	50–200
	Total Solids (TS)	350–1,200
	Total Dissolved Solids (TDS)	250–850
	Suspended Solids (SS)	100–350
	Volatile compounds	80–275
	Volatile organic compounds	100–400
	Total Organic Carbon (TOC)	80–290
	Biological Oxygen Demand (BOD)	110–400
	Chemical Oxygen Demand (BOD)	250–1,000

Source: Esakku et al. (2005), Liu *et al.* (2013), and Werle and Dudziak (2012).

restricted quantities in sludge liquors of municipal wastewaters. The common magnesium salts used for precipitation include magnesium chloride, magnesium sulfate, magnesium oxide, and other cheap sources such as bitter, wood ash, and seawater (Borojovich *et al.*, 2010; Krishnamoorthy *et al.*, 2020; Sakthivel *et al.*, 2012). pH is reported to be the most influential parameter and hence, the addition of alkaline chemicals is required to increase the pH necessary for struvite crystallization. It has been reported in the literature that alkaline pH conditions and an appropriate molar ratio of external magnesium input are favorable for unintended precipitation of phosphate as struvite (Liu *et al.*, 2013). Figure 10.1a diagrammatically represents the processes taking place in chemical precipitation. In the case of anaerobic digestate, CO_2 stripping has been shown to improve pH (Hu *et al.*, 2020; Song *et al.*, 2011). Similarly, temperature conditions above 20°C with high constituent ion concentrations are shown to be ambient (Tilley *et al.*, 2008).
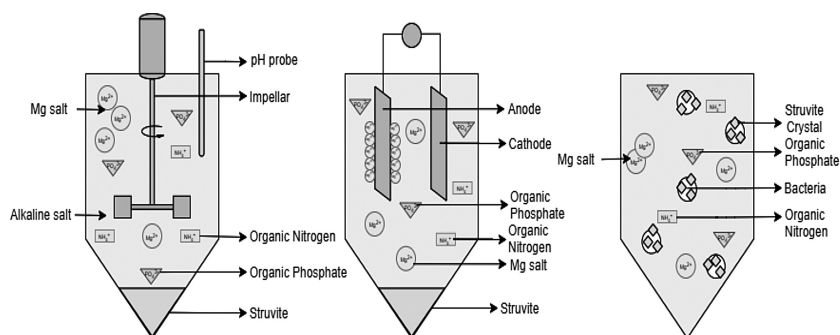
FIGURE 10.1   Diagrammatic representation of working principles of (a) Chemical, (b) Electrochemical, and (c) Biological precipitation of struvite.

The optimal range of operational parameters is subject to differ with a source of wastewater and has been discussed in detail in Section 10.4. However, deviation from these conditions can lead to the formation of struvite analogs such as ferrous phosphate (vivianite), hydroxylapatite, and brushite (Capdevielle *et al.*, 2016).

In municipal wastewater, up to 90% of the phosphate is attached chemically or biologically to the surface of the solids. In order to make the P available for struvite precipitation, the wastewater has to undergo a series of steps. Initially, the bound phosphates have to be dissolved into the sludge with the help of thermal or chemical treatments. Sometimes, sulfuric acid is used to dissolve the P bound to heavy metals. Other means of improving phosphate dissolution include the wet oxidation process and metallurgical smelt-gasification process. The latter is a thermal treatment where the sludge will be smelted at 2,000°C with metallurgical coke for slag formation. Later, magnesium and alkaline salts are added to precipitate out struvite (Hester & Harrison, 2013).

Law and Pagilla (2018) have reported the highest P recovery potential up to 90% from municipal sludge influent. But, this is not the case with treated effluents, where recovery of only 10% was recorded. In addition, the process was claimed to be cost-intensive. P extraction from secondary effluents was performed by Hester and Harrison (2013) using a combination of ion exchange and precipitation techniques. It was concluded that the procedure demanded a high amount of chemicals making it economically unviable. The nitrogen and phosphate recovery as struvite from various municipal sources are shown in Table 10.2. Agitation of solution can improve nucleation and thus the crystallization. However, high stirring can produce unrecoverable struvite fines (Doino et al., 2011; Oliveira *et al.*, 2020). Studies have reported the use of such fines for seeding purposes when recycled (Liu *et al.*, 2011). Though the chemical process may sometimes be efficient, the high costs incurred by NaOH in addition to controlling pH and magnesium supply for struvite precipitation make the process impractical. The main benefit of the chemical method is its simplicity of operation.

TABLE 10.2
Various Technologies and Operational Parameters Involved for Struvite Precipitation from Municipal Wastewater

Source of Municipal Wastewater	Precipitation Technology Involved	P concentration (mg/L)	Mg:P	pH	Mixing Speed (rpm)	Mixing Time (min)	Recovery	Reference
Urine	Electrochemical	256±8.6	1.3	9.20	160	5	96% P	Liu et al. (2013)
Urine	Chemical	1,000	1.4	9.3	–	30	94% P	Morales et al. (2013)
Swine manure	Chemical	2,700	1.2	8–8.5	100	60	88.6% P	Lee et al. (2015)
Medicinal waste	Chemical	–	1	9.6		60	91% N	Li et al. (2018)
Digestate	Electrochemical	108.51	1.5	10.5	600	60	–	Corona et al. (2020)
Domestic sewage	Chemical	64.4	1.6	8.28–8.41	–	2 h	90% P	Quintana et al. (2004)
Poultry manure	Chemical	1,318	1	9.0	–	15	85.4% N	Yetilmezsoy and Sapci-zengin (2009)
Digested manure	Chemical	800	1.3	9.0	–	60	80% P	Siciliano et al. (2020)
Swine wastewater	Electrochemical	780	0.8	8.0–9.0	3,500	15	79–82% P	Ichihashi and Hirooka (2012)
Digested swine wastewater	Electrochemical	116.2	0.6	8.0–11.0	200	–	90% P	Ye et al. (2018)
Food waste	Chemical	–	–	7.5–9.0	–	–	70–100% P	Campos et al. (2019)
Human waste	Electrochemical	0.6 mM	2.1:0.55	8.3	600	–	80% P	Cid et al. (2018)
Domestic waste	Chemical	5	–	8.5	–	–	87.5% P 91.6% N	Zou and Wang (2016)

10.3.2   ELECTROCHEMICAL PRECIPITATION

In electrochemical precipitation of struvite, magnesium electrodes are used for the discharge of magnesium ions into the sludge. Magnesium acts as a sacrificial anode and releases divalent ions to serve the purpose of struvite formation and pH elevation (Figure 10.1b). The diffusion of oxygen increases during electrolysis leading to the generation of OH^- ions. However, magnesium requirement is too high to precipitate all the phosphate which increases the overall cost of the process. Hence, alternate methods should be investigated for coupling pH adjustment with struvite precipitation. Aeration is one such technique reported to increase pH (Almatouq & Babatunde, 2016; Hug & Udert, 2013).

In the case of conventional wastewater treatment, several electrodes such as aluminum and iron are being used to supply necessary cations for the coagulation of particulate matter. However, magnesium electrodes are vital for struvite formation. Due to slower precipitation kinetics at high pH, phosphate removal was found to be slower in stored urine than fresh urine. But conditions prevailing in stored urine are relatively conducive for phosphate precipitation. Also, studies have proved that phosphate availability in struvite is significantly higher than aluminum or iron phosphates (Baierle *et al.*, 2015; Jardin & Pöpel, 2001; Sengupta & Pandit, 2011). Struvite precipitation using magnesium electrodes has not been widely described in the literature.

Struvite is considered the best alternative for recycling nutrients and direct application into agricultural fields. Struvite crystals with high purity were obtained by Kruk *et al.* (2014) through the electrolytic release of magnesium. Though such dosage setup seems simpler to handle, it is comparatively more expensive than chemical dosing. Nonetheless, in chemical magnesium dosage, the risk of struvite powder incrustation in screw feeder and to prevent this, magnesium salts have to be packed in smaller bags of polyvinyl alcohol. The electrochemical method is advantageous in the fact that it involves the direct dissolution of magnesium without additional mechanical feed mechanisms. Such systems are particularly suitable for decentralized reactors considering a simple and scalable infrastructure (Hug & Udert, 2013; Ishii & Boyer, 2015, Krishnamoorthy *et al.,* 2021a). The operational parameter conditions used in electrochemical struvite precipitation are shown in Table 10.2.

10.3.3   BIOLOGICAL PRECIPITATION

Biological precipitation is the process by which microorganisms mineralize the nutrients present in wastewater to form struvite like minerals on their surface for hardening the structural tissue. This process is also known as biomineralization (Figure 10.1c). Many bacterial species such as *Proteus mirabilis*, *Proteus vulgaris*, *Staphylococcus aureus*, *Enterobacter* sp., and *Ureaplasma urealyticum* exhibit this property. Such formation was initially observed in patients with urinary infection. Some researchers predict that the formation can be a result of dead bacterial cells present in the medium. The negatively charged surfaces of bacteria

release molecules such as phospholipids and proteolipids that not only generate free surfaces but also attract positive ions like magnesium. However, the exact mechanism behind this process is yet to be explored. It is also assumed that such urease-producing strains develop a conducive physicochemical environment suitable for struvite crystallization. Due to this activity, ammonia gets release leading to elevation in pH. Later, the supersaturation of solution takes place, followed by heterogeneous nucleation by cellular molecules with a low energy barrier. The mineralization can take place either intracellularly or extracellularly depending on the biological system. The process can take place actively by controlled mineralization (homogenous mineral) or passively by biological induction (heterogeneous mineral). The research on this aspect of struvite crystallization is still in the early stages and more studies have to be conducted in order to gain more insights on the actual mechanism, duration of struvite formation, reactor designing, and scale-up of the process (Bayuseno & Schmahl, 2020; Kataki *et al.*, 2016; Li *et al.*, 2015; Prywer & Torzewska, 2010).

10.4   OPERATIONAL PARAMETERS INFLUENCING STRUVITE PRECIPITATION

Research on the extraction of struvite from municipal wastewater has been going on for the last two decades. So far, several methods have been applied for struvite precipitation. Apart from the method, the most significant factors that govern struvite precipitation are the operational parameters that will guide the process and lead to a better yield. Various parameters that influence struvite precipitation are discussed below.

10.4.1   pH

The availability of the ions such as Mg^{2+}, NH_4^+, and PO_4^{3-} is the main component of struvite precipitation whose ionic forms are controlled by pH. Struvite precipitation occurs basically at a pH range of 8–11. During the process, H^+ ions are released decreasing the pH. In order to overcome this effect, NaOH is supplied to increase the pH and facilitate precipitation. The change in pH also results in the formation of phosphate ions like PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ which may enable the formation of other compounds along with struvite. pH > 11 leads to the formation of $Mg(OH)_2$ and NH_3 reducing the availability of NH_4^+ and Mg^+ ions leading to a decrease in the efficiency of struvite recovered (Crutchik & Garrido, 2011, 2016; Crutchik *et al.*, 2017). The presence of the ions (Na^+, SO_4^{2-}, Cl^-, etc.) in lower concentrations tends to form $MgSO_4$ and $NaPO_4$, hindering the formation of struvite. Thus, to eliminate the formation of such precipitates an optimum pH should be maintained. Apart from this, the stability of struvite crystals is reported to be very minimum at pH 10 (Lahav *et al.*, 2013). Sparging can also be used in place of NaOH to maintain the pH. Hallas *et al.* (2019) through their experiments have shown that there is a slight increase in the amount of struvite crystal formation when air sparging is used.

TABLE 10.3
Solubility Trend of Ions in Municipal Wastewater with Increase in Temperature

Temperature (°C)	pK_{sp}	K_{sp} ($\times 10^{-14}$)	Temperature (°C)	pK_{sp}	K_{sp} ($\times 10^{-14}$)
10	14.36	0.436	30	13.15	7.12
15	14.04	0.916	35	13.23	5.920
15	13.28	5.3	35	13.10	7.90
20	13.69	2.050	35	13.08	8.32
20	13.22	6.03	40	13.40	4.000
25	13.36	4.330	45	13.60	2.530
25	13.26	5.51	50	13.68	2.110
25	13.17	6.76	55	03.84	1.460
30	13.17	6.840	60	14.01	0.973

Source: Crutchik and Garrido (2016), Fang *et al.* (2016), and Hanhoun *et al.* (2011).

10.4.2 Temperature

Temperature plays a very important role in struvite precipitation as it has an effect on the solubility of ions. Several studies have concluded that the optimum temperature for struvite precipitation falls between 25 and 35°C. A study done by Salsabili *et al.* (2014) shows that the solubility of the crystals increases with an increase in temperature up to a certain limit, after which it declines. Fang *et al.* (2016) have concluded that the size of struvite crystals increases from 65 to 69 μm when temperature increases from 21 to 49°C. Hence, the solubility of the ion temperature may also influence the size and shape of the crystals. Table 10.3 below shows the trend of solubility with increasing temperature.

10.4.3 Magnesium Source and Dosage

There are many sources of magnesium that can be used for struvite precipitation. According to studies, the most common magnesium sources are crystals of $Mg(OH)_2$, MgO, $MgCl_2$, and $MgSO_4$. $MgCl_2$ and $MgSO_4$ have the advantage of being easily soluble leading to the formation of struvite crystals with more purity. Among all the crystals, MgO is the least harmful and one of the most efficient and cheapest sources of Mg^{2+} for struvite precipitation. Though it provides better yield, its insoluble nature decreases the efficiency of struvite formation (Capdevielle *et al.*, 2014). Many new technologies like silicon-doped magnesium oxide (SMG) have been developed that helps in the production of struvite by the process of adsorption (Li *et al.*, 2019).

In recent years, various cheap alternatives of magnesium like seawater, magnesite, bittern, and ash powder are being explored (Heinonen-Tanski & Van Wijk-Sijbesma, 2005; Sakthivel *et al.*, 2012; Siciliano & De Rosa, 2014). Though the theoretical

molar ratio of Mg:P is unity, it is suggested that an increase in magnesium concentration can improve struvite yield. The most obvious reason behind it is the more availability of magnesium. However, it may also lead to the formation of struvite analog resulting in the compromisation of purity. When Mg:P is in the range of 1–1.5, the yield and size of the crystals are reported to be optimum (Rahaman *et al.*, 2008).

10.4.4 Presence of Pollutants

The struvite crystals that are precipitated from municipal wastewater are not pure due to the presence of pollutants in the form of ions, inorganic metals, organic compounds, and metalloids depending on the method of struvite formation and wastewater source. Ions like Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, OH^-, Cu^{2+}, Zn^+, Cd^{2+}, Fe^{2+}, and Al^{3+} are formed at different phases of struvite precipitation which may or may not hinder the formation of struvite (Saidou *et al.*, 2015; Hallas *et al.*, 2019). Along with ions, heavy metals like As, Cd, Pd, Ni, and Hg are also present in municipal waste that can co-precipitate along with struvite crystals. Many organic pollutants like heptadecane, eicosane, tetra-tetracontane, 2-ethylacridine, 4-ethoxy-benzoic acid, PAH, and benzene have been detected in urban wastewaters (Saerens *et al.*, 2021). Sometimes, the organic carbon content in the struvite crystal can exceed beyond 6% which can pose certain disadvantages (Huygens *et al.*, 2019). The amount of TSS influences the purity and stability of the struvite crystals. TSS level above 153 mg/L can result in irregular-sized and broken crystals; however, a minimum of 20 mg/L TSS should be present to promote heterogenous precipitation, that can lead to formation of large crystals (Ping *et al.*, 2016). Table 10.4 depicts

TABLE 10.4
Literature References for Heavy Metals Concentration in Struvite Below Maximum Permissible Addition (MPA)

Heavy Metal	Saerens *et al.* (2021) (mg/kg)	Maaß *et al.* (2014) (mg/kg)	Latifian *et al.* (2012) (mg/kg)	Antonini *et al.* (2011) (mg/kg)	MPA (mg/kg)
As	<2	–	0.5	<15	4.5
Cd	<0.2	0.3	0.02	<0.2	0.76
Cr	8.2	11.0	0.42	17.8	3.8
Cu	6.8	39.0	7.26	44.3	10
Hg	<0.007	–	0.01	<4.2	1.9
Pb	<10	5	0.30	<0.9	2
Ni	<3	2	–	<4.2	10
Zn	41	0.1	11	90.2	16
Fe	–	–	350	44.3	15
Mn	–	0.2	–	4.14	0.5

Source: Kinuthia *et al.* (2020) and Vodyanitskii (2016).

the probable pollutants that can precipitate along with struvite, their concentration and permissible limits for application of struvite to the agricultural fields.

10.4.5 Stirring Speed

Struvite can be formed naturally without the help of stirring but the size of crystals remains small. In order to decrease the time of struvite crystal formation, promote nucleation and increase the size of the crystals, stirring is indispensable. Stirring can increase the mass transfer rate of ions in wastewater and enhance crystallization. The stirring speed for the precipitation of crystal of optimum size falls in the range of 100–200 rpm (Morales *et al.*, 2013). Stirring time also has to be taken into account for efficient struvite recovery. Stirring for a long time with a high mixing rate can lead to breakage of crystals resulting in the formation of unrecoverable struvite fines. An optimum of 15–60 minutes mixing time has been reported in literature followed by sufficient holding time (Liu *et al.*, 2008; Peng *et al.*, 2018; Rahaman *et al.*, 2008).

10.4.6 Seeding

Struvite formation requires nucleation from the embryo, followed by crystal growth. In this context, the lag phase of crystallization is usually quite long. In order to speed up the precipitation process and enhance crystal size, many seed materials have been used by researchers. The struvite powder itself is sometimes used for seeding the next batch. As a result of spontaneous precipitation, struvite fines tend to get settled at the bottom of wastewaters. Such pre-formed crystals can be recovered and used for seeding purposes. They provide surfaces for other fine crystals to deposit on the active spots influencing the crystal size and morphology. Seeds can enhance ammonium removal through struvite formation; however, no significant effect of phosphate recovery was observed. Seed addition cannot induce spontaneous nucleation but promote the growth and formation of clusters. Other than struvite, several other seed materials are being used for enhanced struvite precipitation including biochar, quartz sand, kaolinite, and steel powder. Modifications in biochar such as Mg-laden biochar have been shown to be very effective in crystallization (Addagada, 2020; Ali & Schneider, 2006; Liu *et al.*, 2020; Liu *et al.*, 2013).

10.4.7 Reactor Design

There are several reactor designs used globally for the precipitation of struvite. Some of the most common designs are fluidized bed reactor (FBR), stirred tank reactor (STR), bioelectric systems such as microbial fuel cells (MFC) and microbial electrolysis cells (MEC), ion exchange technology (IET), and membrane exchange technology (MBR). The operational conditions used in such reactors are shown in Table 10.5 and are discussed in detail below.

TABLE 10.5

Various Reactor Designs Used Along with Operational Conditions for Struvite Precipitation

Reactor Technology Involved	Operational Conditions	References
Fluidized bed reactor	**Mg:P:** 1.3 **Alkaline reagent:** 0.5 M NaOH **pH:** 9.0–9.3 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Flow rate:** 170–180 mL/min	Doino et al. (2011)
Fluidized bed reactor	**Mg:P:** 1.0 **Alkaline reagent:** 0.1 M NaOH **pH:** 8.5–9.5 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Flow rate:** 0.01 m/s	Ye *et al.* (2018)
Stirred tank reactor	**Mg:P:** 1.0 **Alkaline reagent:** 1 M NaOH **pH:** 8.5–9.5 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Stirring rate:** 500 rpm **Supersaturation range:** 1.83–3.44 **Temperature:** 25°C	Hanhoun *et al.* (2013)
Stirred tank reactor	**Mg:P:** 1.0 **Alkaline reagent:** 1 M NaOH **pH:** 8.0–8.5 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Stirring rate:** 300 rpm **Temperature:** 25°C	Mehta and Batstone (2013)
Inverse fluidized bed reactor	**Mg:P:** 1.0 **Alkaline reagent:** 4 N NaOH **pH:** 8.0–9.0 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Temperature:** 18.5–33.4°C	Sathiasivan *et al.* (2021)
Fluidized bed reactor	**Mg:P:** 1.3 **Alkaline reagent:** 1 M NaOH **pH:** 8.0–8.2 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Supersaturation ratio:** 2–6	Iqbal *et al.* (2008)
Fluidized bed reactor	**Mg:P:** 1.3 **Alkaline reagent:** 1 M NaOH **pH:** 9.0–9.5 **Mg source:** $MgCl_2 \cdot 6H_2O$ **Temperature:** 20°C	Zamora et al. (2017)
Fluidized bed reactor	**Mg:P:** 1.25 **pH:** 9.0 **Mg source:** $MgCl_2 \cdot 6H_2O$	Guadie *et al.* (2014)

(Continued)

TABLE10.5 (CONTINUED)

Reactor Technology Involved	Operational Conditions	References
Fluidized bed reactor	**Mg:P:** 1.0 **Alkaline reagent:** 1 M NaOH **pH:** 9.0 **Mg source:** $MgCl_2·6H_2O$	Su *et al.* (2014)
Fluidized bed reactor (Struvite precipitation & dewaterability technology)	**Mg:P:** 1.0 **Alkaline reagent:** 1 N NaOH **pH:** 8.13±0.05 **Mg source:** Brine **Temperature:** 25°C	Lahav *et al.* (2013)
Fluidized bed reactor	**Mg:P:** 1.0 **Alkaline reagent:** NaOH **pH:** 8.2±0.1 **Mg source:** $MgCl_2·6H_2O$	Liu *et al.* (2013)
Fluidized bed reactor	**Mg:P:** 1.0 **Alkaline reagent:** NaOH **pH:** 8.2±0.1 **Mg source:** $MgCl_2·6H_2O$	Ping *et al.* (2016)
Stirred tank reactor	**Mg:P:** 1 **Alkaline reagent:** 0.3 M NaOH **pH:** 8.8 **Mg source:** Seawater & $MgCl_2·6H_2O$ **Stirring rate:** 1,400 rpm	Aguado *et al.* (2019)
Stirred tank reactor	**Mg:P:** 1.0–1.2 **Alkaline reagent:** 1 M NaOH **pH:** 7.0–10 **Mg source:** $MgCl_2·6H_2O$	Rodrigues *et al.* (2019)
Microbial fuel cell	**pH:** 7.2–9.0 **Mg source:** $MgCl_2$ **Anode:** Mg; **Cathode:** Activated carbon with 20% polytetrafluoroethylene **Temperature:** 20±2°C	Merino-Jimenez *et al.* (2017)
Microbial reverse electrolysis cell (combined hydrogen production of 2.06 m^3 H_2/m^2 d)	**Voltage:** 0.4–0.12 V **Electrodes:** Titanium mesh cathode with platinum **Chamber:** Acetate fed single air chamber	Song et al. (2021)
Dual chamber microbial electrolysis cell (combined hydrogen production of 0.28 m^3 H_2/m^2 d)	**Mg:P:** 1.0 **pH:** 7.0 **Electrodes:** Carbon cloth connected by titanium **Membrane:** Nafion	Almatouq & Babatunde (2017)

TABLE10.5   (CONTINUED)

Reactor Technology Involved	Operational Conditions	References
Ion exchange and isothermal supersaturation	**pH:** 8.0–11.0 **Mg source:** Marine **Temperature:** 25°C **Ion exchange resin:** Amberlite 1RC86 macroporous sulfonic resin, Lewatit CNP80 macroporous carboxylic resin, Lewatit SICOO microporous sulfonic resin	Ortueta *et al.* (2015)
Forward osmosis (nitrogen and phosphorus recovery as struvite)	**Alkaline reagent:** 0.1 M NaOH **pH:** 9.0 **Membrane:** Thin-film polyamide composite	Volpin *et al.* (2019)
Pre-Anaerobic membrane reactor MBR	*Continuous stirred tank reactor* **Mg:P:** 2.0 **pH:** 9.0–10.0 **Mg source:** $Mg(OH)_2$ *Batch stirred tank reactor* **Mg:P:** 1.5–2.0 **pH:** 9.0–9.5 **Mg source:** $Mg(OH)_2$	Haroon *et al.* (2020)
Stirred tank reactor (Struvite precipitation & dewaterability technology)	**Mg:P:** 1.5 **pH:** 7.5 **Mg Source:** $MgCl_2 \cdot 6H_2O$ **Stirring rate:** 800 rpm **Temperature:** 24–30°C	Bergmans et al. (2014)
Continuous in liquid phase and batch reactor in solid phase	**Mg:P:** 2.0 **Alkaline reagent:** 0.4 M NaOH & aeration **pH:** 8.5–8.7 **Mg Source:** $MgCl_2 \cdot 6H_2O$	Pastor *et al.* (2010)

10.4.7.1   Fluidized Bed Reactor (FBR)

FBR is the most common reactor type used for struvite precipitation. Many commercial installations around the world have utilized this design for the efficient production of marketable struvite. This type of reactor has two components: a fluidized bed component with increasing diameter from the point of wastewater inlet at the bottom and a settling zone at the top (Figure 10.2a). The difference of diameter on various regions ensures proper mixing of the reactants (Iqbal, 2008). The two components of the reactor are joined by a funnel of polyvinyl chloride to avoid settling precipitates in the settling zone.

The supernatant of the sludge is fed in to the reactor with the help of a peristaltic pump. It has a pH controller with automated input of NaOH in the reactor

to maintain the pH. In addition, there are two other inlets for the supply of magnesium and recycled water fed at rates of 170–180 mL/min and 9–42 mL/min, respectively (Shim *et al.*, 2020). There are two outlets, one at the bottom to remove the larger crystals from the reactor and the second one at the top to remove the liquid along with small crystals which are again fed back into the reactor as seeds.

The large crystals are promoted to form in the fluidized bed and small crystals along with the fluid that settles upwards in the settling zone by plug flow method. These crystals are removed by the second outlet and send to the clarifier for recycling back to the fluidized bed to form larger crystals in successive batches. In many reactors, there is provision for additional hydrocyclone units that facilitate proper mixing and pelletization (Lahav *et al.*, 2013).

10.4.7.2   Stirred Tank Reactor (STR)

STR has a stirring system that helps in the homogenous mixing of reactants. These reactors possess several auxiliary devices for supplying reactants, wastewater, pH adjustment reagents, and struvite precipitate removal. In this reactor, the mixing of all the reactants occurs in the same region (Figure 10.2b). Stirring plays a major role in such reactors as it helps in mass transfer and hence the formation of crystals. The reactors are designed to perform both in batch and continuous modes. In the case of batch precipitation of struvite formation and precipitation occurs in the same reactor; whereas, in continuous precipitation, formation occurs at different regions. Many times, a mixed reactor is constructed where both the batch and continuous reactors can work side by side leading to the formation of struvite crystals. Stirred reactors are easy to build and manage and hence it is widely used for laboratory experiments (Guadie *et al.*, 2014; Mehta & Batstone, 2013; Rodrigues *et al.*, 2019). However, in the case of pilot-scale experiments, it requires high investment and the cost incurred by energy consumption is high making it impractical for large-scale applications.

10.4.7.3   Bioelectric System

Bioelectric systems for struvite precipitation are emerging as they help in simultaneous recovering of energy, biofuel, nutrients, or chemicals from wastewater. The process is carried out with the help of microorganisms that bring about redox reactions at the electrodes' vicinity. This system is cheap and easier to construct as compared to other fuel cells. The construction neither requires costly metal nor difficult working conditions. With the advancement of technology and the scope of science, these bioelectric systems are used to recover nutrients like struvite with instantaneous production of electricity (Kelly & He, 2014). There are two types of bioelectric systems generally being used for struvite crystallization namely MFC and MEC.

10.4.7.3.1   *Microbial Fuel Cells (MFC)*

MFC are used to produce electricity with the help of a variety of microorganisms. In this system, the microorganisms act as a catalyst for the production
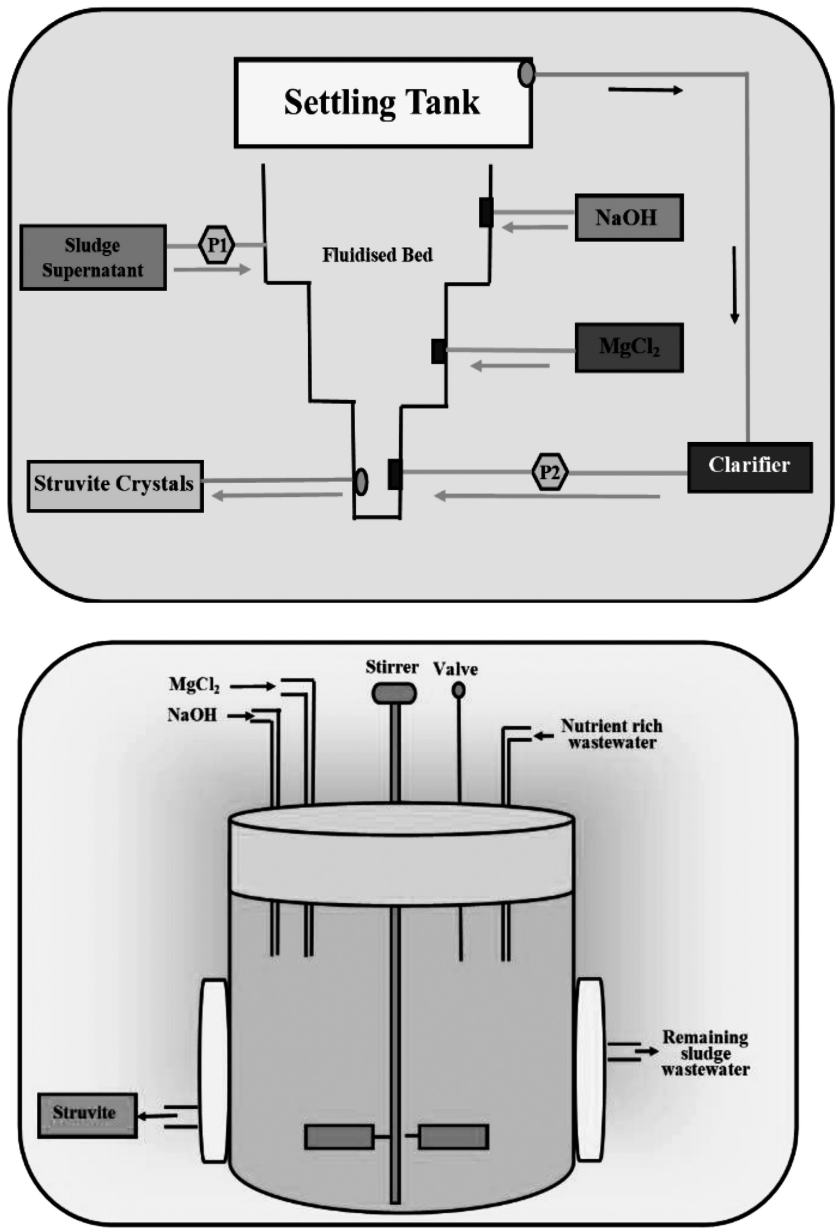
FIGURE 10.2   Reactor designs of (a) Fluidized Bed Reactor (FBR) and (b) Stirred Tank Reactor (STR) for struvite precipitation.

of electricity from the organic compounds present in wastewater. The oxidation of such compounds results in the release of electrons from anode that is later transferred to the cathode with the help of electron acceptors like oxygen for hydrogen production (Figure 10.3a). During the formation of struvite crystals, phosphate ions that are already present in wastewater along with nitrogen species reactor together. For the better formation of crystals, ammonium and magnesium salts are added externally. Though hydrogen and hydroxide liberation in the cell improves pH conditions suitable for struvite crystallization, pH is also maintained by supplying an alkaline medium for enhanced recovery (Merino-Jimenez *et al*., 2017; Almatouq & Babatunde, 2016; Ichihashi & Hirooka, 2012).

Many new advancements in reactor designs have been executed among which a three-staged reactor stands interesting. The setup consists of a STR unit coupled with two MFC. The advantage of possessing an MFC before is that it helps in urea hydrolysis to make the struvite precipitation easier. According to studies, this process is capable of recovering 82% of phosphorus from wastewater. In this process, chemical precipitation combined with microbial absorption plays a very important and efficient role in wastewater treatment and phosphate recovery as struvite (Merino-Jimenez *et al*., 2017; Siciliano *et al*., 2020).

10.4.7.3.2   *Microbial Electrolysis Cells (MEC)*

MEC utilizes the principle of electrolysis for the treatment of waste and production of biofuel and struvite with the help of microorganisms. When an electric current is supplied in presence of a catalyst (microorganisms), oxidation occurs at the anode followed by electron release. These electrons then flow to the cathode to initiate hydrogen evolution (Figure 10.3b). In this process, multiple products like H_2, CH_4, and struvite are being generated simultaneously. The system generally consists of stainless steel that acts as a cathode in a single-cell MEC chamber. The cathode may be in the form of a mesh or flat plate. Usually, flat plate cathodes have more efficiency as compared to mesh. Struvite crystals are formed at the cathode in the form of white solids having equal molar of ammonium, magnesium, and phosphate. But the accumulation of struvite crystal at the bottom of the cathode reduces its efficiency (Almatouq & Babatunde, 2017; Igos *et al*., 2017; Siciliano *et al*., 2020).

Though MFC and MEC are new technologies, it requires more advancement to be applied for the large-scale production of struvite. For better production of struvite, it might be coupled with other technologies but its scope is very limited.

10.4.7.4   Ion Exchange Technology (IET)

Ion exchange methods have been in use for several years for the process of nutrient recovery. This technology is very cheap, easy to use, recyclable, reusable, and regenerable. This technology is now being used for the production of struvite crystals with the help of certain resins. The resins used may be NH_4^+, PO_4^{3-}, or K^+ which are regenerated at the exchanger as ammonium or potassium
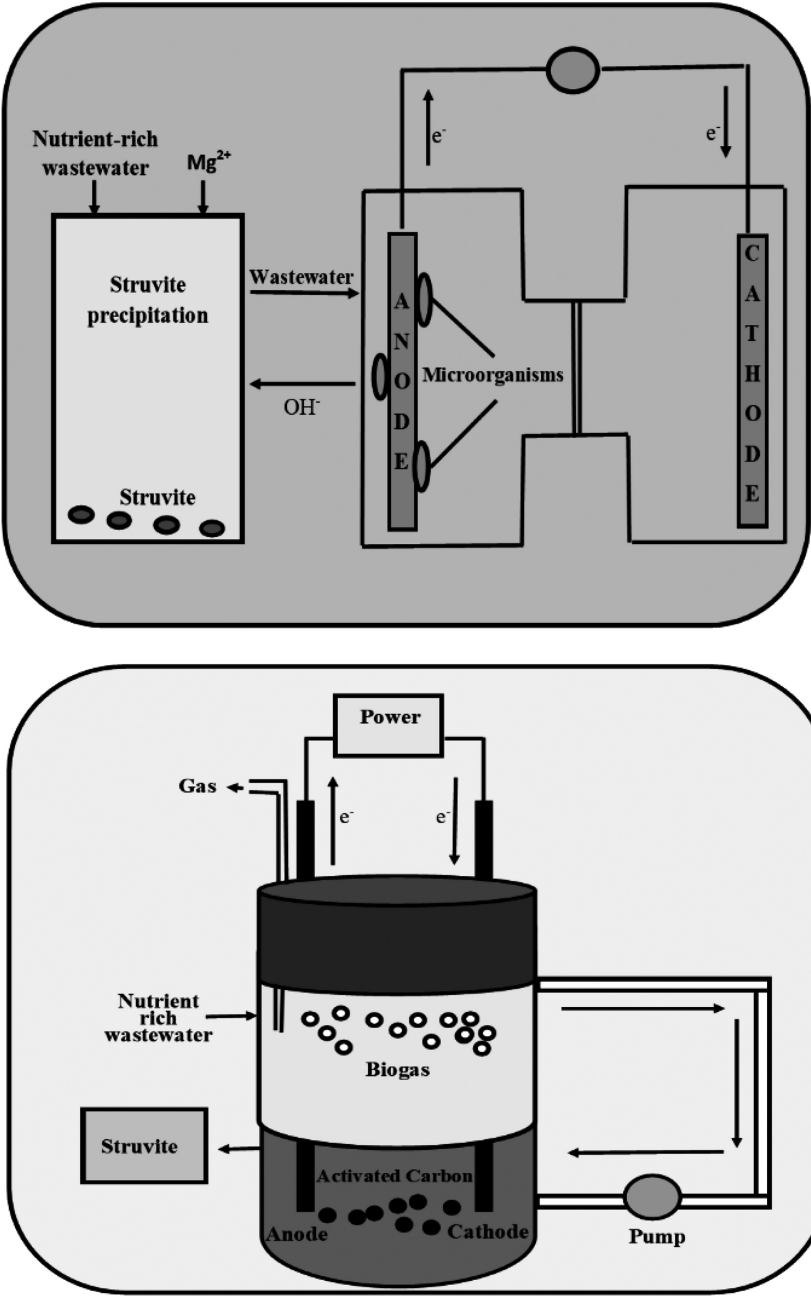
FIGURE 10.3 Reactor designs of bioelectric systems for struvite precipitation (a) microbial fuel cell and (b) microbial electrolysis cell.
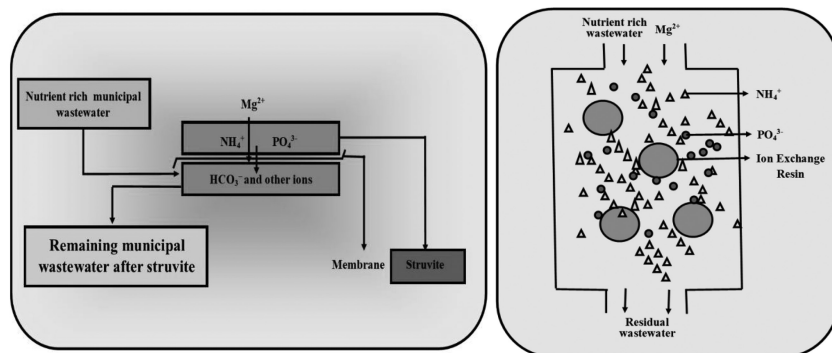
FIGURE 10.4 Reactor designs of (a) Membrane exchange technology and (b) Ion exchange technology for struvite precipitation.

struvite (Figure 10.4a). The only problem in the case of IET is that PO_4^{3-} selective sorbents are not easily available and reusable limiting the use of this technology. Many resins like Lewatit CNP80 macroporous carboxylic resin, Amberlite 1RC86 macroporous sulfonic resin, etc. have been widely used for struvite production. It is also suggested that, for better recovery of struvite from ion exchanger, the water should be pre-treated (Ortueta et al., 2015; Siciliano *et al.*, 2020).

10.4.7.5 Membrane Exchange Technology (MBR)

MBR is an emerging field for efficient wastewater treatment and struvite recovery. It makes use of porous membranes for wastewaters to passes through. It possesses two phases, one which passes through the membrane called permeate and the other which remains on the other side of the membrane called retentate (Figure 10.4b). Various membrane technologies have been in use for struvite precipitation that is classified based on the diameter of the filter as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis, forward osmosis, and electrodialysis. In this case, the main aim is to produce permeate or retentate-rich phosphate and nitrogen, so that they can be easily removed by further precipitation in an alkaline medium. Adjustment of pH is mandatory for making the conditions optimum for struvite precipitation. For large-scale production of struvite, this technology can be coupled with either FBR or STR. However, the technology is very expensive and the membranes are not easily available, which acts as a limitation for its use on a larger-scale (Siciliano *et al.*, 2020; Volpin *et al.*, 2019).

10.5 RESEARCH GAPS AND CHALLENGES ASSOCIATED WITH STRUVITE PRECIPITATION

Progress has been made in the field of struvite in the last two decades. However, there still exist some knowledge gaps and challenges that need to be addressed in further studies. Most of the work reported on struvite has been performed using

synthetic formulations of wastewaters (Gao *et al.*, 2020; Le Corre *et al.*, 2005; Tansel *et al.*, 2018). The results obtained from such experiments may not be suitable for real-time application. Hence, the focus should be shifted to real-time trails which also might help in the scale-up of the technology. Exploration of optimum physicochemical characteristics of wastewater in addition to operational parameters is necessary to gain better insights on reaction taking place and storage conditions. Most of the research deals only with the scope of struvite production. It has to be extended to plant growth studies for making it a commercial product. In addition, the mechanism behind struvite uptake by the plants is still unclear and more research on this facet has to be promoted. On the other hand, only the fertilizing applications of struvite have been widely considered (Oliveira *et al.*, 2020; Udert *et al.*, 2015). Other aspects and areas where struvite can be applied also have to be worked upon.

The external addition of magnesium is an important element of struvite crystallization. However, be it magnesium electrode or salt, it contributes to up to 75% of the total cost of the process. In order to address this issue, alternative low-cost sources of magnesium should be investigated. More attention to drying conditions of struvite should be given as it has a severe effect on sterilization and composition of mineral formed. The presence of harmful bacteria and heavy metal with struvite might be hazardous considering its application in the agricultural field (Bischel *et al.*, 2016; Decrey *et al.*, 2011). These are some of the areas that require more emphasis in further work for the development and establishment of the field on a larger scale.

10.6   CONCLUDING REMARKS AND FUTURE PERSPECTIVES

With the increase in population and urbanization, the generation of waste is increasing on an everyday basis. On the other hand, the infrastructure for effective treatment of sludge and reuse for drinking or irrigation purposes is still lacking. Struvite precipitation is an integrated field involving wastewater management, nutrient recycling, prevention of eutrophication, and production of organic fertilizer. In this view, struvite recovery from municipal wastewater can be economical due to the presence of high nutrient considered and ease of accessibility. This paper deals with various aspects of struvite crystallization from municipal wastewater with incorporated details of different precipitation technologies, significant operational conditions such as pH, temperature, source and dosage of magnesium, the concentration of co-present pollutants, and stirring rate. Several reactor designs that have been reported in the literature and commercially installed across the globe have been emphasized. In addition, research gaps and challenges associated with struvite production technologies have been highlighted for consideration in future studies. Some of the future perspectives of struvite research have been highlighted below:

- Source-separated collection of municipal wastewater can reduce the load of primary treatment, dilution, and improve assembly of concentrated nutrient-rich source for easy and effective recovery of struvite.

- Cost-effective pre-treatment techniques to improve solubilization of nutrients bound to organic compounds and heavy metals can enhance the amount of nutrients recovery.
- Seeding can improve the quality, size, and recovery rate of struvite crystals. Hence, future works on finding a lucrative seed material become essential.
- In addition to struvite formation, recovery of struvite analogs such as K-struvite and Na-struvite can improve retrieval of supplementary nutrients from wastewater.
- More research on emerging technologies such as MFC and MEC should be implemented to make the overall process economical as it involves simultaneous struvite, hydrogen, and electricity production.
- Incorporation of computational methods such as modeling, techno-economic, and life cycle assessments can provide better insights with respect to scale-up of struvite technologies.
- Biorefinery aspects such as combined algal growth prior to struvite precipitation can help in the assimilation of organic matter and heavy metal content for enhanced struvite recovery. This process can also benefit the utilization of algae for biodiesel or fertilizing applications.

DECLARATION OF INTEREST

The authors declare no conflict of interest to disclose.

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