

Phosphorus removal from livestock effluents: recent technologies and new perspectives on low-cost strategies

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Abstract

Phosphorus is an essential element in the food production chain, even though it is a non-renewable and limited natural resource which is going to run out soon. However, it is also a pollutant if massively introduced into soil and water ecosystems. This study focuses on the current alternative low-cost technologies for phosphorus recovery from livestock effluents. Recovering phosphorus from these wastewaters is considered a big challenge due to the high phosphorus concentration (between 478–1756 mg L⁻¹) and solids content (>2-6% of total solids). In particular, the methods discussed in this study are i) magnesium-based crystallization (struvite synthesis), ii) calcium-based crystallization, iii) electrocoagulation and iiiii) biochar production, which differ between them for some advantages and disadvantages. According to data collected, struvite crystallization achieves the highest phosphorus removal (>95%), even if combined with the use of seawater bittern (a by-product of sea salt processing) instead of magnesium chloride pure salt as the magnesium source. Moreover, the crystallizer technology used for struvite precipitation has already been tested in wastewater treatment plants and data reported in this review showed the feasibility of this technology for use with high total solids (>5%) livestock manure. Furthermore, economic and energetic analyses here reported, show that struvite crystallization is the most practicable among the low-cost phosphorus recovery technologies for treating livestock effluents.

Keywords

Phosphorous recovery; Struvite; livestock treatment; by-product reuse

Abbreviations

CEC: cation exchange capacity

EC: electrocoagulation

HRT: heated retention time

MAP: magnesium ammonium phosphate

MTD: minimum theoretical equivalent diameter

SWB: seawater bittern

UWWTD: Urban Wastewater Treatment Directive

1. Introduction

Today, the world population is progressively increasing, adding about 83 million people annually (United Nations, Department of Economic and Social Affairs, 2019). Thus, population is projected to grow by just over than one billion people over the next 13 years and it is estimated that in 2050 the number of its inhabitants will grow to almost 10 billion (United Nations, Department of Economic and Social Affairs, 2019).

The world population growth has also coupled with an increase in food demand by developing countries (FAO, 2017; United Nations, Department of Economic and Social Affairs, 2019; Vaccari et al. 2018). This has led to a rise of food production and consumption; in particular, meat production is progressively increasing (FAO, 2017; Vaccari et al. 2018), with 210 million tons produced in Europe in 2014 (FAO, 2017).

The global growing food consumption translates into an increment of effluents and waste production (FAO, 2017; Jadhav et al. 2017; Nghiem et al. 2017). As described by the Eurostat report (Eurostat - Statistic explained, n.d.), the total amount of wastes generated by all economic activities and households in the European Union, reached a production peak of 2,503 million tons in 2014. Nevertheless, the trend of total wastes production has been quite stable from 2014 to 2017 and the waste amount (excluding major mineral waste) generated by agriculture, forestry and fishing has fallen by 68.7% (Eurostat - Statistic explained, n.d.).

Another issue that arises along with the increasing food supply is the growth of global demand for fertilizers (FAO, 2017; IFA, 2014), specifically nitrogen (N), phosphorous (P) and potassium (K). In the following years the fertilizer production is expected to reach 201.66 million tonnes by the end of 2020 (FAO, 2017), with an average annual increase of 1.9 %. These are alarming data, considering not only the steady increase in demand for fertilizers but also the potentially pollutant nature of nitrogen and phosphorus (FAO, 2017). Taking this into account, in the last decade, the common purpose has been to limit the nitrogen damage due to livestock effluents pollution (Nitrates Directive 91/676/EE), in consideration of the fact that animal sewages contain the highest amounts of total nitrogen and phosphorus (Fleming and Ford, 2004; Vaccari et al. 2018). Specifically, one human daily produces 9.1 g of total N and 1.8 g of total P, while a dairy cow produces respectively 260 g and 55 g a day and a feeder pig 27 g and 9.4 g (Fleming and Ford, 2004). In summary, 1,000 humans generate as much total nitrogen as 340 pigs or 40 cows and as much total P as 190 pigs or 30 cows (Fleming and Ford, 2004).

Unfortunately, the nitrogen targeted measures of the European Union (Nitrates Directive 91/676/EE) are insufficient for dealing with the land disposal of manure (Szogi et al., 2015; Szögi et al., 2015). Farmers, in fact, apply manure following N-based criteria, but the unbalanced nitrogen-phosphorus ratio for crop production leads to the overloading of phosphorus in soils (Szögi et al. 2015). Manure phosphorus concentration is higher than the amount removed in harvested crops and while nitrogen gets adsorbed, phosphorus increases in the soil with potential risks of water pollution (Szogi et al. 2015).

Global human activity discharges annually 1.62 million tons of P into the major freshwater pools on Earth (Seitzinger et al. 2010; Mekonnen and Hoekstra, 2018), surpassing the planet assimilation capability for the phosphorus excesses in water bodies (Mekonnen and Hoekstra, 2018; Vaccari et al. 2018). Reports in 2018 referred that the phosphorus massive input in freshwater bodies exceeded the assimilation capacity on the 38% of the land surface (Mekonnen and Hoekstra, 2018). This is a worrying report since the massive input of phosphorus into natural water bodies is the main cause of eutrophication, which affects the survival of many aquatic species (Ashley et al. 2011). Eutrophication occurs when the nutrients in water exceed the amount required for normal growth and the proliferation of algae generates a cover at the top of the water, preventing sunlight from reaching aquatic plants (Ashley et al. 2011; Seitzinger et al. 2010). This triggers algae death, leading to a decrease in water oxygen levels and consequently causing the death of all the aquatic organisms (Seitzinger et al. 2010). In order to overcome this problem, the European Commission has been taken several actions, such as the improvement of the Urban Wastewater Treatment Directive 91/271 (UWWTD) (Council of the European Communities, 1991) and the Regulation n.259/2012 (Parliament, 2012), which have led to a development of a new wastewater treatment system regulations in the European countries (Jaffer et al. 2002).

The P pollution problem runs alongside the rising demand for phosphatic mineral fertilizers. To meet the food and industries demand, phosphorus is obtained from phosphate rocks, a limited and non-renewable source which is going to decrease from 2050 onwards (Ashley et al. 2011; Kataki et al. 2016a; Vaccari et al. 2018). Moreover, due to the current economic and technological conditions the majority of this world phosphate reserves, estimated to be about 300 billion tons (U.S. Geological Survey, n.d.), is not available for extraction. Although wide deposits have been found in the oceanic continental shelves (Vaccari et al. 2018), the use of these deposits is reasonably unaffordable. Currently, the major quantities of phosphorus are mined in China while Morocco detains the 74% of the available global deposits of phosphate rock and South Africa exports the biggest quantity (Desmidt et al. 2015; Kataki et

al. 2016a; Sørensen et al. 2015; Azam et al. 2019). Europe is the region most dependent on imports which are the 86% of its total demand due to a very low local phosphorus production (IFA, 2014). Therefore, the geopolitical situation can have a significant impact on the P availability and price (Guedes et al. 2014). The increasing perception of a global phosphorus crisis could therefore determine serious international tensions due both to the Earth's reserves distribution and their control and to the world population growth (Vaccari et al. 2018).

In consideration of these questions related to the phosphorus issue, the strategies and technologies aimed to recover this element represent the resolution to respond both to the forthcoming collapse of the fertilizer's supply and to the rising eutrophication problem. The most promising technologies to overcome these concerns are the P-recovery processes which can achieve phosphorus-free effluents from wastewater treatment plants (WWTPs) and which focus on by-products reusable for other purposes (Azam et al. 2019). Nowadays, these processes are mostly applied to urban and industrial sewage, while there are few approaches available for treating livestock manure due to the lack of suitable markets for processed residues and the ready availability of low-cost alternatives (Vaccari et al. 2018). By the way global meat production is expected to double in 2050 (Mekonnen et al., 2018) with further intensification of the livestock effluents that cannot be fully recycled on the nearby land and can seriously affect freshwater systems (Tambone et al. 2017). Livestock effluents contribute to the contamination of surface water and groundwater because of their uncontrolled input of nutrients, in particular phosphorus (P) and nitrogen (N), to the soil. However, livestock effluents contain nutrients that could be used for replacing synthetic fertilizers by using new and more eco-friendly approach (Pepè Sciarria et al. 2019).

By the way, livestock manure has a high total solid (TS) content (TS >5% DM) which seems to be one of the main limitations for the recovery of P from the influent solution (Yetilmezsoy et al. 2017; Tarragó et al. 2018). While the fields needs further studies, other methods use several metal salts such as iron (FeSO_4 , FeCl_3) and aluminum compounds (alum, $\text{Al}(\text{OH})_3$) to obtain a rapid and effective phosphate

precipitation (Cordell et al. 2011). However, the limitations arise from the toxicity of the resulting products, which can be hardly reused in agriculture (Cordell et al. 2011). Another example is the use of lime products (CaO , $\text{Ca}(\text{OH})_2$) for soluble phosphorus precipitation as Ca or Mg phosphates in alkaline conditions (Cieřlik and Konieczka, 2017). The final products may be employed as slow-release fertilizers; however, the method requires high amounts of lime and could involve high chemical inputs and handling costs but also excessive slurry generation (Cieřlik and Konieczka, 2017).

In farms, phosphorus recovery from animal manure is largely limited by logistical and economic barriers, especially in small units where equipment and input costs quickly become prohibitive (Szogi et al., 2015). For zootechnical wastewaters, solid-liquid separation is commonly the first step, removing the P bounded to particles, solids and organic matter, which may affect following treatments (Szogi et al. 2015; Tambone et al. 2017). There are several technologies for P recovery and fertilizer production from animal slurries and some of them can achieve efficient P inorganic removal while keeping the operations relatively low-cost, i.e. chemical precipitation, biochar production (Tab. 1) (Fig. 1) (Guadle et al. 2013; Hu, 2016; Kiran et al. 2017; Schoumans et al. 2017; Yetilmezsoy et al. 2017; Zhang et al. 2019).

For the best of our knowledge, the large part of the reviews on nutrients recovery, have been written on urban and agricultural wastewaters, i.e. wastewaters with low content of total solids (TS) while in this review, a special attention on livestock effluent P resource recovery has been given. In consideration of what mentioned above, this article, reviews the low-cost techniques which remove and recover P from livestock wastes, evaluating their applicability to phosphorus sustainability. Special attention is given to the use of by-products such as alternative sources of Mg^{2+} in P recovery for the induction of struvite precipitation in crystallizer prototypes. Moreover, the discussion has been focused about how these by-products, can lead to a considerable decrease of the total cost of P recovery technologies and the impact of this decrease on real application.

Table 1: Summary of recent technologies for P recovery from livestock effluents.

Recovery and removal technologies	Substrate	Objective	Advantages	Disadvantages	References
Precipitation					
Struvite (MgNH_4PO_4)	Urine Sewage sludge Synthetic wastewater Synthetic wastewater - Swine digestate -	Fertilizer production, P removal	Low cost; Re-use of byproducts (seawater bittern as Mg source); Fertilizer production.	Zonal availability of seawater bittern	Etter et al. 2011; Cièslík et al. 2017; Crutchik et al. 2017; Yetilmmezsoy et al. 2017; Vaccari et al. 2018; Tarragò et al. 2018; Li et al. 2019.
Calcium phosphates ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, $\text{CaNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$)	Swine manure Anaerobic supernatant Swine slurry -	Fertilizer production, P removal	Large scale plants; High availability feedstock; Fertilizers production	Chemical input and related costs; Excessive sludge generation at high dosage	Cordell et al. 2011; Makara and Kowalski, 2015; Dai et al. 2017; Schoumans et al. 2017; Vaccari et al. 2018.
Electrocoagulation					
Electrodes made by low carbon steel, grey cast iron, flat bar for industrial use, aluminum, magnesium.	Municipal wastewater Swine wastewater Synthetic wastewater Swine manure	P removal and recovery	Low-cost; Simple set-up	Good as a pretreatment; Set-up from small to big scale for livestock effluent	Stafford et al. 2014; Mores et al. 2016; Omwene et al. 2018; Zhang et al. 2018.
Biochar production					
Pyrolysis of organic matter (biomass, residues, manures, wastes, etc.)	Swine manure Cow manure Swine slurry Swine manure	Waste recovery and energy production	P-rich ashes; Amending properties product	Needed further sperimentations	Azuara et al. 2013; Kiran et al. 2017; Schoumans et al. 2017; Szögi et al. 2018

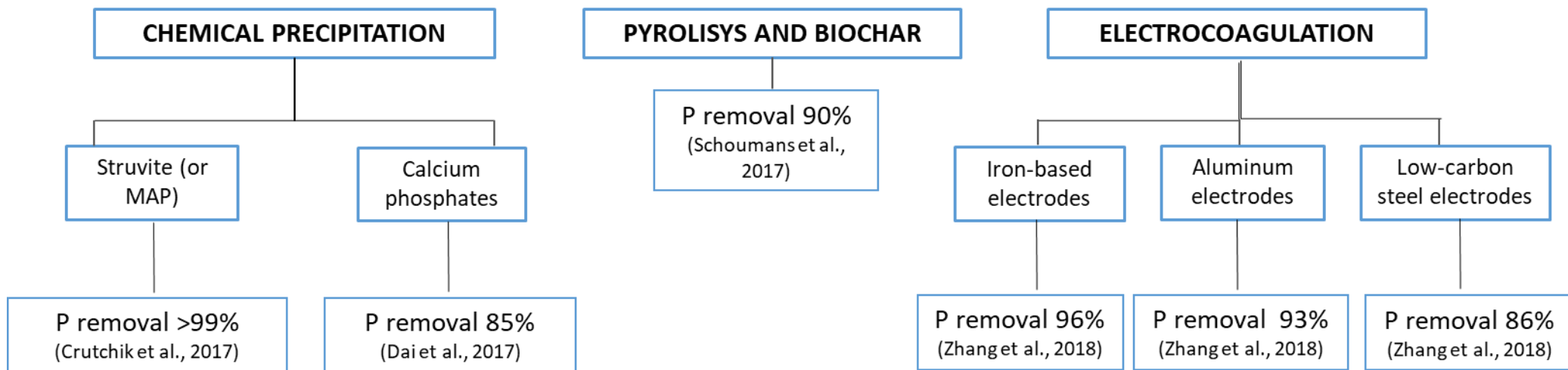


Fig. 1 Efficiencies of the described P recovery approaches

2. Low-cost strategies for phosphorus removal from animal manure

2.1 Chemical precipitation

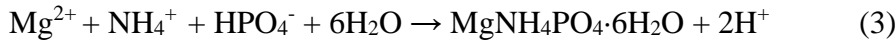
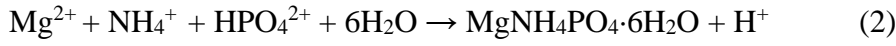
Chemical precipitation, also called crystallization, is a process that occurs spontaneously when phosphate concentration reaches the optimum for achieving thermodynamic super-saturation (Rittmann et al. 2011). Precipitation usually is induced by the addition of a metal ion, such as magnesium (Mg^{2+}), aluminum (Al^{3+}), ferric iron (Fe^{3+}) or calcium (Ca^{2+}) (He et al. 2007). The salts precipitate as insoluble hydroxides and are then subjected to co-precipitation and adsorption to the metal hydroxides (Vaccari et al. 2018). The choice between the different metal salts normally used to start the precipitation affects the potential of the P removed to be reused for agricultural and industrial applications (De-Bashan and Bashan, 2004; Rittmann et al. 2011; Zhang et al. 2018).

2.1.1 Magnesium-based precipitation

The use of magnesium salts (MgO , $Mg(OH)_2$ and $MgCl_2$) determine soluble phosphorus precipitation as different Ca and Mg phosphates at alkaline conditions if provided with the magnesium and calcium surplus necessary for P abatement (Katakai et al. 2016b). The final products are relatively insoluble but may be used as slow-release fertilizers (Rittmann et al. 2011).

The most promising compound for P recovery is struvite ($MgNH_4PO_4 \cdot H_2O$), which precipitates spontaneously once phosphates reach 100-200 mg L⁻¹. Struvite is formed from the combination of magnesium, ammonium, and phosphate at a stoichiometric molar ratio of $Mg^{2+}: NH_4^+-N: PO_4^{3-}-P = 1:1:1$ (Yetilmezsoy et al. 2017;).

The process of struvite crystallization is described in the Eq.1-2-3, whereas the reaction of HPO_4^{2+} is the dominant in the pH range of struvite precipitation (pH 7–11) (Jaffer et al. 2002).



Supersaturation is considered to be the engine in struvite formation and in all crystallization processes since it considerably affects the induction time of crystallization and the crystal growth rate (Shih and Yan, 2016). The struvite developing induction time is inversely proportional to the supersaturation of the solution (Li et al. 2019). The struvite supersaturation can be described through the saturation index (SI) shown in Eq.4 (Stolzenburg et al. 2014).

$$\text{SI} = \log ((a_{\text{Mg}^{2+}} \cdot a_{\text{NH}_4^+} \cdot a_{\text{PO}_4^{3-}})/K_{\text{struvite}}) \quad (4)$$

where K_{struvite} is the struvite solubility product while a_i is the activity of species' ion.

The dynamics of struvite formation are illustrated in Fig. 2, where line 0 represents the solubility curve of struvite and line between a and b represents the supersaturation curve. The unstable supersaturated area (point a) is where crystal nucleation takes place, while is in the metastable supersaturated area (point b) is favorable for the crystals growth. In the unsaturated stable area below line AB (point c) the SI is below 0, which is not favorable for the crystals nucleation (Fang et al. 2016).

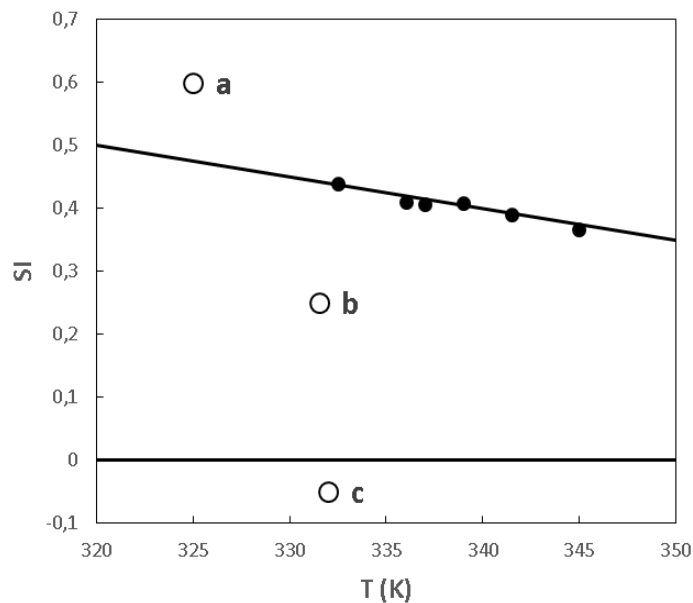


Fig.2 Relationship between the degree of supersaturation of struvite solution and struvite crystallization (Data source: Fang et al. 2016)

Struvite simultaneously recovers both nitrogen and phosphorus and has multiple commercial uses, including fertilizers and animal feed, cosmetics and detergents, fire-resistant panels and cement (De-Bashan and Bashan, 2004). It has excellent fertilizing properties and the low aqueous solubility of its crystals allows a prolonged duration of its fertilizing action over time (Li et al. 2019).

Many technological approaches are being developed to enhance struvite precipitation but few of them are suitable for livestock effluents, which are characterized by high suspended-solids concentration (3 g TSS L⁻¹) that affect the struvite crystallization rate (Li et al. 2019). The struvite crystallizer technology has been developed in different prototypes (Tab. 2) and put into production successfully abroad (Le Corre et al. 2009; Rahaman et al. 2014; Desmidt et al. 2015; Marchi et al. 2015; Tarragó et al. 2016; Crutchik et al. 2018; Zhang et al. 2018; Li et al. 2019; Gosh et al. 2019). The Tarragó et al. (Tarragó et al. 2018) prototype, in evaluating struvite removal, was able to reduce the influent concentration in pig slurries from ~370 mg PO₄³⁻ L⁻¹ to ~15 mg PO₄³⁻ L⁻¹ with >95% recovery

efficiency. Moreover, the outcomes showed that solids (1-3 g TSS L⁻¹) didn't affect struvite formation, since they have a significant role in struvite crystallization, acting as surface for crystals nucleation (Tarragó et al. 2018).

Struvite technology is close to commercialization, although the costs of chemical inputs are very high when MgCl₂ or another Mg source (magnesia or magnesite, wood ashes or MgO production by-products) are used in the process (Jordaan et al. 2009; Kataki et al. 2016a; Cieřlik and Konieczka, 2017; Cao et al. 2019). However, a promising strategy for P removal is the use of seawater bittern (SWB), which is a by-product of sea salt production and a source of magnesium obtainable for free at the production site (Etter et al. 2011). Similarly to spontaneous struvite formation, this is the cheapest strategy if it is locally produced (Etter et al. 2011) and the most efficient, allowing operators to remove from wastewaters 83% of the ammonia and 99% of phosphorus at a pH of 10.5 (Shin and Lee, 1998; Crutchik et al. 2018). The high potential of this strategy for P removal and struvite recovery from livestock effluents will be analyzed in detail later in this review.

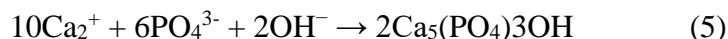
Table 2: Summary of reactor used for struvite crystallization and their efficiency

Crystallizer	Substrate	Efficiency (% P recovery)	References
Fluidized bed reactor (FBR)	Dewatered filtrate from anaerobic digestion	90%	Ishikawa et al. 2004; Guadie et al. 2014;
Bach test and pilot reactor (air-lift)	WWT's digested sludge	Pilot reactor:58-90%	Stumpf et al. 2008
Stirred tank reactor (reaction and settling zone)	Rejected liquors of different sludge treatments	70-90%	Martì et al. 2008; Li et al. 2019
Short-long column	WWT's digestate	70-90%	Bergmans, 2011
Air-lift crystallizer	Synthetic saturated solution	n.d.	Soare et al. 2012
U-shape reactor	Anaerobic digested effluents (swine)	n.d.	Zhang et al. 2014 Li et al. 2019
Air-lift reactor with a settler	Synthetic wastewater	>95%	Tarragò et al. 2016
Semi-CSTR	Swine	n.d.	Romero-Güiza et al. 2014; Li et al. 2019
Completely stirred tank reactor (CSTR)	Synthetic wastewater	84-87 %	Kuglarz et al. 2015; Crutchik et al. 2017; Liu et al. 2019

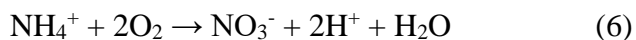
2.1.2 Calcium-Based Precipitation

In animal slurries, phosphorus may be initially released as H_2PO^- , HPO^{2-} and/or PO^{3-} by lowering the pH and can be subsequently recovered by the addition of an alkaline source (e.g. calcite (CaCO_3), hydrated lime (Ca(OH)_2), bone charcoal etc.), forcing precipitation of a Ca-P. The product can finally be removed from the solution by filtering the suspension (Makara and Kowalski, 2015; Schoumans et al. 2017). This leads to a relatively small volume of precipitates which are highly concentrated in phosphorus and which can be easily used as a secondary resource of P fertilizer (Desmidt et al. 2015; Schoumans et al. 2017).

The use of calcium compound for P removal determines first the precipitation of Ca phosphate minerals as hydroxyapatite, brushite, monetite etc. The most widespread phosphate mineral is hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which formation is described in Eq. 5 b (Vanotti et al. 2003).



The high buffering capacity of liquid manure affects P precipitation in livestock effluents when alkaline compounds such as calcium hydroxide (Ca(OH)_2) are used (Vanotti and Szogi, 2009). The pre-nitrification step could solve this problem (Eq.6-7), reducing the bicarbonate alkalinity and the concentration of NH_4^+ (Vanotti et al. 2003).



Hydrated lime (Ca(OH)_2) or the Ca(OH)_2 and Mg(OH)_2 combination are low-cost products (ICIS, 2018) which allow both the pH increase and the calcium addition. They also have been shown to be valuable in simple reactor tests for P precipitation from wastewaters (Vanotti and Szogi, 2009; Desmidt et al. 2015).

This calcium phosphate removal process may also be used to remove P in animal waste treatment systems both with and without anaerobic lagoons (Vanotti and Szogi, 2009). Vanotti and Szogi (2009) also reported that this technology (pilot scale) obtained the 95–98% of P removal as a phosphate from the anaerobic lagoons' streams. In systems without a lagoon, an initial solid-liquid separation process removed most of the carbon compounds from raw liquid manure (Vanotti and Szogi, 2009). Once separated, the wastewater is both treated with nitrification and soluble P removal. In the latest improved methods, the P recovery process became more efficient, reducing equipment needs and chemicals with the introduction of a combined solid-liquid separation (Schoumans et al. 2014).

Schoumans et al. (2014) reported also the use P recovery by calcium- based precipitation on pig slurries with or without a previous acidification step. The authors showed that by coupling the acidification step, i.e. decreasing the pH to 4-5 by adding HCl or H₂SO₄, Phosphorus that has been released (mainly as PO₄³⁻), at the lower pH, can be recovered by separation of this acid liquid phase and addition of an alkaline source, for example Ca(OH)₂, forcing precipitation of a Ca~P which can be removed from solution by filtering the suspension. Approximately 80% of the P can be recovered from the liquid phase at pH values below 5.5 while at pH levels between 6 and 6.5 the P recovery varies between 40 and 70%. By the way, the costs of chemicals to recover most of the P from pig slurry are high (2.63 – 10.85 € per ton pig slurry) due to the high pH-buffering capacity of the pig slurry.

A second approach is to recover P from the liquid fraction of pig slurry without the acidification step, since soluble P can be precipitated Ca²⁺ at high pH. The pH increases by adding Ca(OH)₂ that lead to soluble P precipitation as amorphous calcium phosphate (ACP, Ca₃(PO₄)₂·xH₂O) but also calcite (CaCO₃) can be formed (Schoumans et al. 2014). Other calcium phosphates have been identified as Ca₄H(PO₄)₃·3H₂O, dicalcium phosphate (CaHPO₄·2H₂O), and inorganic salts of ammonium and calcium (NH₄CaPO₄·H₂O). Nevertheless, only 25-40% of P recovery was achieved by maintaining the pH between 7.27 and 7.85 (Schoumans et al. 2014).

Although the use of lime it has been reported to determine the 95% of removal efficiency using animal manure, the necessity of high amount of this Ca mineral may result both in high chemical input and excessive sludge production and costs (Schoumans et al. 2014).

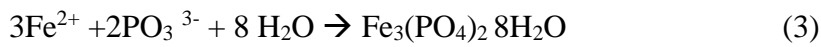
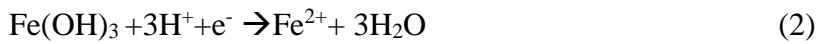
2.1.3 *Ferrous iron phosphate (Vivianite) crystallization*

The ferrous iron phosphate mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is one of the most common and most stable iron phosphate minerals which is often found in anaerobic environments, Fe-rich soil, lake sediments, bogs hydrothermal deposits, and plant roots (Wu et al. 2019). Previous studies showed the presence of vivianite in anaerobic systems with relatively low sulphide concentrations with the simultaneous presence of iron and phosphate, such as municipal wastewater treatment plants (MWTPs), specially during anaerobic sludge digestion (Wilfert et al. 2018). In WWTPs, vivianite is the predominant iron phosphate compound in different sludge in which it has been traceably discovered, including activated sludge, excess sludge and digested sludge.

Vivianite formation

Fe ions in natural water might be derived from the dissolution of iron minerals (as $\text{Fe}(\text{OH})_3$ and hydrous ferric oxide), while in WWTPs, Fe ions often come from Fe salts used as a flocculating agent to remove P (Fan et al., 2018). Contrarily, P in natural water could be derived from agriculture, plants, animal or domestic sewage and industrial wastewater, while in wastewater, P comes from human activities such as excretions, industrial pollution, household waste. In water, P is in the form of organic phosphorus, inorganic phosphorus, and polyphosphorus. Usually, in the presence of organic matter (OM) and reducing environments, Fe^{3+} is reduced to Fe^{2+} by dissimilatory metal-reducing bacteria (DMRB), while organic phosphorus is converted to phosphate by anaerobic microorganisms. If these two microbial processes continue to take place, the localized concentrations of Fe^{2+} and PO_4^{3-} can reach higher levels since the value of solubility product (K_{sp}) has reached target requirement and the formation of vivianite would occur (Nriagu,1972).

The following equations describe vivianite formation process in natural water.



Several factors can influence vivianite formation process as reducing redox environment, i.e low level or absence of oxygen, alkaline conditions moreover high Fe (II) ion amount, adequate phosphate activity, and low sulfide activity are required to stabilize vivianite precipitation in chemical systems (Azam et al. 2019). Within these factors, microorganisms play an important role in vivianite formation; directly transformation from Fe^{3+} to soluble Fe^{2+} via the reduction and electron transfer take place by the action of dissimilatory metal-reducing bacteria (DMRB); organic phosphorus to inorganic PO_4^{3-} by the anaerobic oxidation of methane (AOM); and SO_4^{2-} to S^{2-} through the reduction by sulphate-reducing bacteria (SRB) (Wu et al. 2019). The indirect effects are related to the modification of the reducing environment by the consumption of electron acceptors such as O_2 , NO_3 , and Fe^{2+} ; and the production of CO_2 , which lowers pH values. Moreover, the cell surfaces of microorganisms can act as nucleation sites to induce vivianite formation. Several authors reported the action of microorganism in inducing vivianite crystallization in sewage sludge; Wang et al. (2018) selected *Geobacter* as the primary functional microorganism to generate vivianite formation, reaching higher vivianite recovery rates (20-48%) than sewage biomass (7-33%). pH is also an important factor in vivianite formation. In natural systems, vivianite is stable under pH 6–9 conditions but in the absence of sulphide, vivianite was observed at pH 6 and 8.5 When sulphide was available, vivianite was only stable at pH 7 (Azam et al. 2019).

In terms of real approach, P recovery as vivianite has been investigated mainly on municipal and industrial wastewaters. For example, Priambodo et al., 2017, reported P recovery by vivianite formation in wastewater that was produced in the manufacture of thin film transistor-liquid crystal displays (TFT-LCD). By using a Fe/P ratio of 1.5 at pH 5-6, the authors reached a maximum P removal of 95%. Wilfert et al. (2018) showed that 70-90% of all phosphate was bound in vivianite in

sewage sludge with the highest iron content (molar Fe:P= 2.5).

The results obtained with vivianite crystallization showed (together with struvite) that potentially if one of the major methods for P recovery. By the way, P removal and recovery during vivianite formation have not been studied as much as those for struvite. Moreover, for the best of our knowledge, vivianite crystallization has not been reported as P recovery method in livestock effluents; this is due probably to the fact that instead of struvite it was not possible to recovery also N.

2.2 Electrocoagulation

Electrocoagulation (EC) is an effective method for phosphorus (Nguyen et al. 2014; Stafford et al. 2014) and solids removal (Hutnan et al. 2006) from several types of wastewater, such as synthetic wastewater (Bouamra et al. 2012; Attour et al. 2014; Inan and Alaydin, 2014), textile industries wastewaters (Chavan and Arega, 2018) and livestock effluents etc. (Zhang et al. 2018).

The EC process applies electricity to electrodes (usually aluminum or iron) immersed in the solution to be treated and connected externally to a direct current power supply (Fig. 3) (Symonds et al. 2015). The anode oxidation of metal electrodes releases metal ions that can work as coagulants, binding phosphate and enhancing the suspension of particles (Hu, 2016). In particular, during EC the coagulating ions are generated continuously by electrochemical dissolution of the sacrificial anode (Hakizimana et al. 2017). These ions spontaneously undergo hydrolysis in water forming different coagulant species including metallic hydroxide precipitates, which eliminate contaminants by adsorption or settling (Hakizimana et

al. 2017). The floc formation (as a result of the coagulation process) is characterized by the presence of metal hydroxy complexes in larger agglomerates, which in wastewaters can be treated by using physical separation process, such as screw press or filtration, floating or gravitational sedimentation (Stafford et al. 2014; Zhang et al. 2018).

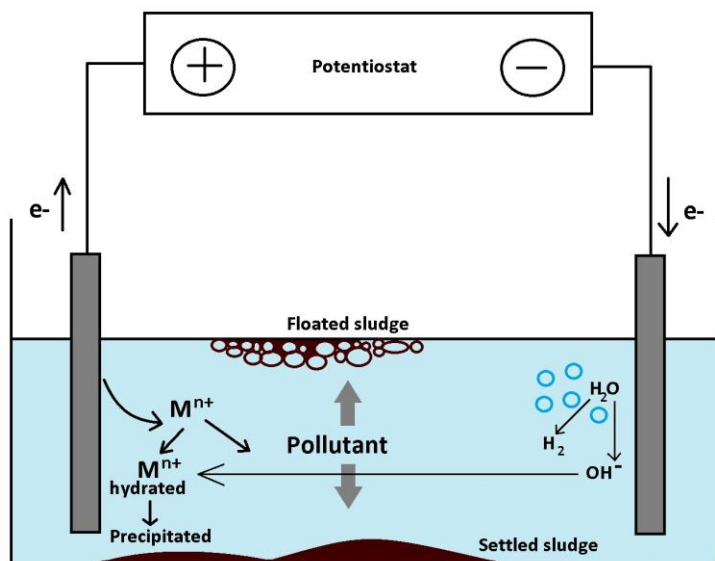


Fig.3 Simple electrocoagulation cell with reaction taking place during EC

Several electrode materials were tested as electrodes, e.g. lower steel carbon, aluminum, iron etc. Mores et al. (Mores et al. 2016) tested iron steel electrodes obtaining 96.3% of P removal, although this last result was reached by processing swine manure with an initial P concentration of 70 mg L⁻¹, which is much lower than the usual concentration of 478–1756 mg L⁻¹ in swine manure (Hernandez and Schmitt, 2012). Zhang et al. (Zhang et al. 2018) evaluated low carbon steel electrodes and the results showed that EC method, followed by 1 day spontaneous precipitation, obtaining the 72.6–86.3% of phosphorus removal from liquid centrifuged swine manure with an initial P concentration around 65-85 mg L⁻¹

Electrocoagulation could be considered as an alternative to chemical coagulation (Stafford et al. 2014; Zhang et al. 2018, 2016) since it offers some advantages: i. it has a simple set-up requirement and it can be automated; ii. it cuts the chemical cost by using cheaper materials (Zhang et al. 2016; Omwene et al.

2018); iii. gas bubbling promotes coagulation and the formation of bigger flocs; iv. pH is easily maintained because the cathode reaction consumes protons (Zhang et al. 2018, 2016). The findings of these recent studies indicate that EC is a potential technology for swine manure high-concentration P removal (Zhang et al. 2018).

2.3 Pyrolysis and Biochar

There is a rising interest worldwide in the pyrolysis of biomass and organic residues (Azuara et al. 2013; Lů et al. 2013; Liu et al. 2018; Masebinu et al., 2019). Biochar production allows producers to employ the energy from biomass and organic wastes and it is a product which may have soil quality amending properties (Lehmann, 2009; Spokas and Reicosky, 2009; Steinbeiss et al., 2009; Cayuela et al. 2010; Angst and Sohi, 2013; Foereid, 2015; Bedussi et al. 2015). Moreover, due to its high nutritive value, biochar derived from animal manure contains essential plant nutrients and a high cation exchange capacity (CEC) (Kiran et al. 2017).

The organic matter (e.g. biomass, manures, residues and wastes) is heated inside a pyrolysis reactor, in an oxygen-free atmosphere, to a temperature between 350-700°C (under pressure). This produces biochar which is composed of carbon and inorganic material, including P-rich ashes (Fig. 4). The pyrolysis also produces a gaseous fraction (methane, hydrogen, carbon monoxide, carbon dioxides, etc.) and a liquid fraction consisting of tar and pyrolytic oil (Azuara et al. 2013).

Schoumans et al. (Schoumans et al. 2014) produced biochar from pig, poultry and cattle manure, and tested for its soil improvement potential. The results showed that the soil phosphorus availability increased considerably, suggesting that the biochar-derived phosphorus provided the plant-available phosphorus in the soil. Further testing is needed on potential biochar applications, as well as a general evaluation of the pyrolysis of solid manures.

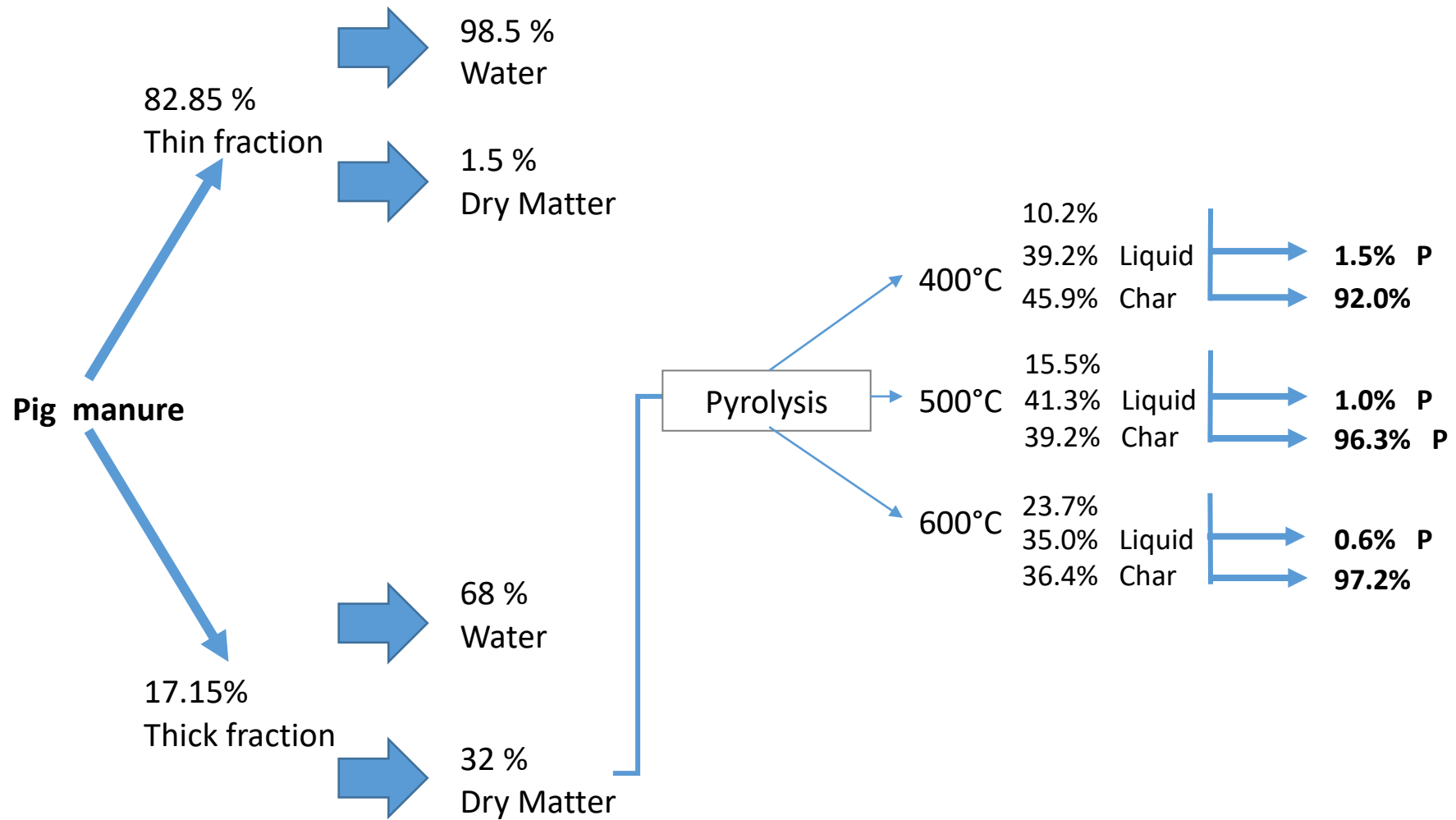


Fig.4 Distribution of products in pig manure pyrolysis and phosphorus mass balance (Data source: Azuara et al. 2013)

3. Struvite crystallization for P recovery from by-products

As described above, chemical precipitation, electrocoagulation (EC) and biochar production differ, with some advantages and disadvantages (Tab. 1). In particular, calcium phosphates precipitation is already applied at the large-scale (Schoumans et al. 2017), but it still needs massive chemical input which leads to an excessive sludge generation (Schoumans et al. 2017). Egle et al. (Egle et al. 2016) estimated that the total cost for a Ca-based crystallization process is about 1.5 € kg P⁻¹ including profit (with wastewater as treated effluent), while for the struvite crystallization the total cost is much lower, estimated at 0.01-0.22 € kg struvite⁻¹ (about 0.6 € kg P⁻¹) including profit (using treated seawater as the Mg source) (Quist-Jensen et al. 2016). Biochar production also has higher expenses compared to struvite production: Azuara et al. (Azuara et al. 2013) estimated that the pyrolysis process for P removal from pig manure had approximately a total cost of 3 € kg P⁻¹ (Tab. 4). Finally, considering that EC is a newly emerged, potentially valuable technology there are some difficulties in estimating the production costs for a pilot-scale plant due to the low number of published works on the topic. The only available data were reported by Hu et al. (2016) referring to an EC pilot-scale plant treating 100 L day⁻¹ of deep pit swine manure. According to the total cost reported, it was possible to estimate a recovery cost of 61.7 € kg P⁻¹. As discussed before (Section 2), EC is a promising technology in livestock effluent treatment and the high recovery cost calculated here may be reduced soon by employing cheaper and re-usable materials.

A comparison of the energy consumption for these processes is also necessary to appreciate the advantages of the struvite synthesis approach (Tab. 4). Nevertheless, there are different factors which could influence the energy consumption in P-recovery, such as the amount of material processed, reagents used or the scale of the process considered (laboratory test, pilot or full-scale plant). Moreover, the energetic balance data for these P-recovery processes are not easily accessible, thus the energy analysis performed in this work will consider only struvite crystallization and the EC technologies.

Schoumans et al. (Schoumans et al. 2017) reported that a full-scale plant for the production of struvite from livestock effluents consumes 157 kWh for the treatment of 100,000 ton of digestate. The available data on the electrocoagulation process consumption refer to an EC pilot-scale plant, which utilizes about 0.453 kWh in processing 10 kg of manure (Hu, 2016). Although it is difficult to compare data from such different scale processes, it could be approximately estimated that the energy consumption for the treatment of 10 kg of digestate by a full-scale crystallization plant is $1.6 \cdot 10^{-5}$ kWh (Hu, 2016). Therefore, the energy required by crystallization is four orders of magnitude lower than the energy spent in EC process and even if the calculation is affected by a standard deviation of two orders of magnitude (due to the different process scales), we can realistically affirm that the energy normally consumed by the crystallization process is far lower than the energy consumed by electrocoagulation.

Data discussed above indicate that among P recovery technologies, struvite crystallization has a great potential in the fertilizer market if the formation is promoted by using low-cost Mg sources and the recovery is controlled by crystallization technologies (Etter et al. 2011; Quist-Jensen et al. 2016; Crutchik et al. 2018; Tarragó et al. 2018, 2016). In the last years, struvite crystallization has gained more interest as a method for phosphorus and nitrogen recovery from animal slurries (Fukumoto et al., 2011; Wang et al., 2013; Wilsenach et al., 2007) and digestate (Pepè Sciarria et al. 2019; Cao et al., 2019) we will now describe in more detail the struvite formation and potential.

Struvite is a slow-release fertilizer which offers many advantages compared to the other conventional products. Specifically, it could be used to manage nutrient release, reducing the nutrient loss (Li et al., 2019), it has low leach rates (Münch and Barr, 2001) and thus it may have a relevant use in grassland and forest, which need one fertilizer application in several years (Cerrillo et al. 2015; Rahaman et al. 2014). If a high dose of fertilizer is applied, there is no damage to growing plants (De-Bashan and Bashan, 2004) and it is also an alternative for crops which require magnesium (Li et al. 2019). Finally, using struvite as fertilizer, the P uptake by plants shows high efficiency (Johnston and Richards, 2003).

Struvite crystallization technologies also have a role in nitrogen removal and recovery (Li et al. 2019). Although ammonium removal through struvite crystallization technology is practicable, it is not cost-effective due to the magnesium and phosphate salts high costs (Li et al. 2019). To face this difficulty, the recovered struvite can be subjected to pyrolysis in alkali solutions for further ammonium removal (H. Huang et al. 2011; Huang et al. 2012; H. M. Huang et al. 2011; Kataki et al., 2016a, 2016b). For example, using landfill leachate has been observed the 96% NH_4^+ removal under optimal conditions (OH^- : NH_4^+ of 1:1, temperature of 90°C and time of 2 h) (He et al. 2007). It was also reported the 87% of NH_4^+ recovery for yeast industry anaerobic effluent, in ideal conditions of OH^- : NH_4^+ ratio of 1.5:1, pH of 9 and temperature of 110°C, during an interval of 3 hours (Uysal et al. 2010).

Furthermore, struvite recovery gives some economic advantages. The spontaneous precipitation of struvite inside treatment plant pipes in fact, makes plant operating less efficient and costlier (the crystals must be broken by hand or dissolved with sulfuric acid) (Stratful et al. 2004;). The solution to this economic and efficiency problem could be the precipitation of struvite in a specific reactor, instead of allowing spontaneous formation. Technologies for struvite crystallization have recently improved and many types of reactors have been developed (Table 2) (Stumpf et al. 2008; Bergmans, 2011; Soare et al. 2012; Marchi et al. 2015; Crutchik et al. 2018; Tarragó et al. 2016, 2018,; Wang et al. 2019). The crystallizer performances are evaluated in terms of efficiency (P-recovery), heated retention time (HRT), minimum theoretical equivalent diameter (MTD), the struvite production rate (i.e. the amount of struvite produced in a fixed time), a very important reactor parameter for efficiency estimation (Li et al. 2019).

To develop a low-cost phosphate recovery technology, the attention has recently focused on seawater bittern use as the Mg additive for struvite synthesis. Magnesium is the second cation for abundance in seawater (Mg content $\sim 1,300 \text{ mg l}^{-1}$) coming from the Mg minerals erosion (Shin and Lee, 1998; Kumashiro et al. 2001). Seawater bittern is the salt suspension remaining after crystallization of NaCl from seawater and it is characterized by a high Mg content of 9,220–32,000 mg L^{-1} . Bittern has been demonstrated valuable for struvite precipitation in animal and municipal wastewater, urine, coke and

landfill leachate (Shin and Lee, 1998; Lee et al. 2003; Etter et al. 2011). In particular, the tests reported a total PO_4^{3-} recovery of 99% on coke manufacturing wastewater (Shin and Lee, 1998), 94% of P removal in urine (Merino-Jimenez et al. 2017) and 76% in swine wastewater (Lee et al. 2003; Kataki et al. 2016a; Pepè Sciarria et al. 2019).

The real value of bittern in struvite synthesis is thus proved, but the growing interest in this resource is because of its high availability and low cost. In fact, the use of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or other magnesium salts, affects the costs and sustainability of the struvite synthesis process (Quist-Jensen et al., 2016). Economic evaluations (Etter et al. 2011; Quist-Jensen et al. 2016; Yetilmezsoy et al. 2017) of Mg sources normally used in the struvite crystallization process are reported in Tab. 3.

Table 3: Economic analysis of magnesium sources normally used in the struvite crystallization process

Common magnesium sources	Total cost (€)	References
Magnesium chloride hexahydrate: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	€ 656.25 ton^{-1}	Dalian Chem Imp.& Exp. Group Co., Ltd. (2016)
Magnesium sulfate heptahydrate: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	€ 473.5 ton^{-1}	Shijiazhuang Xinlongwei Chemicals Co., Ltd. (2016)
Magnesium oxide: MgO	€ 612.5 ton^{-1}	Liaoning Metals & Minerals Enterprise Co., Ltd. (2016)

Seawater bittern has no cost of production since it is a waste brine remaining after salt (NaCl) extraction from seawater. Nevertheless, the transportation costs from the coast might be an influence on the total expenses of the process. For example, Etter et al. (Etter et al. 2011) estimated the cost of SWB to be 0.22 € kg struvite^{-1} considering the transport to a pilot test site in Nepal located in an area far from the coast. Thus, SWB is a very low-cost resource and even if in the potential areas of production the

magnesite is locally extracted, the price difference is small (the magnesite locally costs 0.12 € kg struvite⁻¹) (Etter et al. 2011).

4. Directions for future research

The overview of technologies reported previously highlighted that chemical P mineral precipitation has become recently a significant removal method (Schoumas et al., 2014; Azam et al. 2019). As the demand for P continues to increase rapidly, a technical easily and effective P recycling method such as chemical P mineral precipitation from animal slurries is needed to obtain an alternative source of P.

Moreover, these techniques are relatively simple and are expected to be feasible at small industrial scale and at larger innovative livestock farms. (Schoumas et al., 2014; Gosh et al. 2019). Within Mg and Ca-based precipitation, the cost of chemicals of the Mg approach at pH 8 was lower compared to the acid-base approach (Schoumas et al., 2014; Gosh et al. 2019). One of the advantages of struvite crystallization is that it can simultaneously remove phosphorus and nitrogen (12% P and 5% N by mass) that usually the main issue in livestock effluents treatment (Schoumas et al., 2014; Tambone et al. 2017; Daneshgar et al. 2018)

Any deficiency of Mg²⁺, for P recycling as struvite can be supplemented utilizing alternative sources of such ion leading to cost-effective and maximum recovery of struvite (Kataki et al. 2016). Moreover, the use of a by-product in fertilizer synthesis is fundamental for an ecologically and socially sustainable economy. This makes the seawater bittern solution attractive on the market (small and industrial production) and though its use is yet to be evaluated on a commercial scale, it may be an economic Mg source in regions neighbouring the sea (Shin and Lee, 1998; Matsumiya et al., 2000; Lee et al., 2003; Etter et al., 2011; Crutchik et al. 2018)..

For example, the Dutch agricultural sector produces about 75 million kg P y⁻¹ as animal manure of which 25% cannot be applied to land in the Netherlands because of P application limits for agricultural land (Smit et al., 2015; Schoumans et al. 2017). This issue could be resolved by using the struvite

crystallization approach (especially if enhanced by the SWB employment), considering that this low-cost technology could recover more than 90% of this discarded P (the equivalent of 17 million kg P y⁻¹) in a highly usable product. Smit et al. (Smit et al. 2015) estimated that the import of P mineral fertilizer into the Netherlands is about 7 million kg P y⁻¹. Thus, the recovery of P which cannot be applied as fertilizer in the Netherlands (i.e. 22% of the total 75 million kg P y⁻¹ produced) could potentially replace the demand for this mineral fertilizer, removing both the import costs and the issue of animal manure disposal.

In this context, another issue arises concerning the treatment of livestock effluents, since their high amounts of suspended solids (TS >5%) and organic matter may limit struvite crystallization (Havukainen et al., 2016).. According with data reported previously this problem seems to be overcome since the action of solids in the entering stream has an influence on the nucleation stage (Tarragó et al. 2018), acting as the nuclei for struvite crystallization and reaching high P removal (>90%) as demonstrated by Tarragó et al. (Tarragó et al. 2018). Moreover, in terms of technology, chemical P crystallization is a well-established method, as opposed to lesser-used biological removal processes (Gosh et al. 2019). Furthermore, as highlighted in Table 4, Chemical P crystallization (in particular struvite) is effectively one of the cheapest technology for P removal and future researches should follow the use of alternative source of ions, such as seawater bitter for Mg²⁺, to decrease chemical P crystallization cost .

Table 4: Summary of the analyzed technologies with respective P-recovery, economic and energetic balance.

Low-cost P-recovery technologies	Efficiency of the process (% P removed)	Total costs	Energy consumption*	References
Crystallization (Struvite)	>99 %	-	-	Crutchik et al. 2017;
	-	0.6 € kg P ⁻¹	-	Quist-Jensen et al. 2016;
	92%	-	1.6 · 10 ⁻⁵ kWh	Hu et al. 2016;
	>99 %	-	-	Yetilmezsoy et al. 2017
Calcium phosphates precipitation	85 %	1.5 € kg P ⁻¹	-	Egle et al. 2016;
	86 %	-	-	Dai et al. 2017;
Electrocoagulation	98%	-	-	Fernandes et al. 2012
	96 %	61.7 € kg P ⁻¹	0.453 kWh	Hu et al. 2016;
	>99%	-	-	Omwene et al. 2018;
	86 %	-	-	Zhang et al. 2018;
Pyrolysis and Biochar	90 %	3 € kg P ⁻¹	-	Azuara et al. 2013;
	97%	-	-	Szögi et al. 2018

*for the treatment of 10 kg of animal digestate.

5. Conclusions

The growth of population and urbanization are promoting the diminishing of essential natural resources exerting pressure on the environment. Phosphorus is an essential element on Earth as a good nutrient source and it is necessary for food production. Unfortunately, the mineable P reserve will decrease rapidly if no other renewable sources are found. Moreover, nutrients excess in soil as fertilizer can cause serious environmental problems such as eutrophication. One solution, could be the recovery of P from various sources, especially agricultural, industrial, and municipal wastewaters. Therefore, P removal from polluted environments is a way for achieving a clean and safe environment. Recycling P as mineral precipitates from livestock effluents can reduce the cost of fertilizers in the agricultural sector. From the analysis performed in this review on P recovery technologies, it emerges that: i) struvite crystallization is the best P removal system, above all if it is combined with the use of seawater bittern as a low-cost Mg source; ii) P recovery by air-lift crystallizer technology has been already tested in wastewater treatment plants and data reported in this review showed the feasibility of this technology also in treating high total solids (TS>5%) livestock manure; iii) energetic and economic analysis revealed the value of the seawater bittern struvite as a competitive alternative to conventional phosphatic fertilizers.

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