Phosphorus Removal and Recovery from Digestate after Biogas Production

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1. Introduction

1.1. Anaerobic digestion

Anaerobic digestion (AD) is a commercially available industrial process that generates biogas (roughly consisting of 60% of CH_4 and 40% of CO_2) and breaks down organic materials by anaerobic microbes. It is a process that can greatly reduce the amount of organic matter which might otherwise be destined to be land filled or burnt in an incinerator, both scenarios generating strong public concerns. The use of AD is suitable for most types of organic wastes such as livestock manure, waste paper, grass clippings, municipal waste, food and fruit/ vegetable processing waste etc. AD provides benefits including substantial odor reduction, production of a renewable energy source (biogas), reduction of greenhouse gas (GHG) emissions, potential pathogen reduction, minimization of solid waste for disposal, and enhanced nutrient management (Borowitzka 1999). Different groups of microorganisms are working together as a food chain to degrade the organic materials to produce methane as the final product. Briefly, insoluble organic material is hydrolyzed to produce simple soluble materials such simple sugar, amino acid and long chain fatty acid. Acidogenic bacteria degrade them to produce volatile fatty acid (VFA) and hydrogen, which is called acidogenesis. Then, acetogenic bacteria produce acetate from VFA and solvents in acetogenesis. There is a group of acetogenic bacteria which can synthesize acetate from hydrogen and carbon dioxide, referred as homoacetogenesis. And finally methanogens use acetate or hydrogen to produce methane as the final product. There are also other bacteria groups involved in the AD, for example sulfate reduction bacteria. Of all the current bioenergy options, AD is a well-established technology in Europe with large scale systems developed primarily in countries such as German and Denmark. In the US, large dairy farms are the leading users of AD in agriculture. EPA's AgSTAR program estimates that 137 dairy farms and 23 swine operations are using anaerobic digestion in the US. The current rate of anaerobic digestion deployment contrasts with AgStar's estimates of 2,645 dairy and 5,596 swine operations that could use anaerobic digestion with current designs.

While AD is the widely recommended technology for bioenergy production and nutrient management for animal wastes, the literature on AD is vastly focused on the influence of reactor configuration and manure characteristics based on four goals: solids destruction, biogas production, odor reduction, and pathogen reduction [1]; and few has been done on regards to P dynamics and mechanisms of transformation during AD. It is commonly believed that organic phosphate is degraded during the anaerobic degradation and therefore converted to inorganic phosphate. Gerritse and Vriesema [2] worked on the fractionation of P into organic and inorganic portions, as well as phase distribution, i.e., dissolved vs. particulate P, in liquid cow manure samples, either raw and digested. Their results confirm the hypothesis that most P found in manure is inorganic (around 90%), and overall, the inorganic:organic ratio does not change significantly after digestion – having found inorganic P at 86% of total P in their digestate samples. Similar qualitative conclusions are found in other literatures [3-5]. In regards to AD on phosphorus availability, discussions are very discrepant among studies. While some state that this degradation process increases the nutrient availability for plants [6] or that it does not have direct effects [7], some state that AD has potentially the opposite influence, i.e., it decreases P availability for plants [8-10]. It is known that pH influences the solubility of P and micronutrients; e.g., raising the pH moves the chemical equilibrium toward the formation of dissociated phosphate ion, which facilitates the precipitation of such ion as insoluble Ca and Mg phosphates. Some other concerns, such as the binding form of other elements, as Fe, may be regulated by AD [11]. Also, during AD, the fraction of dissolved P becomes mineralized and it becomes associated with suspended solids [12]. Also, the water-extractable P-fraction decreases substantially during AD. Struvite formation, which will be further discussed in this chapter, is very likely to be formed and crystallized, due to a combination of mineralization of P, N, and Mg during AD, being regulated by many ionic species found in the digestate media, e.g., Ca^{2+}, K^{+}, CO_3^{2-} [13]. P loss, i.e., loss of phosphorus due to leaching, retention, etc, during AD are also in a wide range of results in the literature, being reported as smaller than 10% [14] or as high as 36% [15]. This is due to many factors, since AD systems are different among them with different operational conditions, which also include partial retention in the digesters during P precipitation [16]. Möller and Müller [7] suggested some losses could also occur via leaching and runoff after field application, even though no data has been published by then.

Since AD does not show any significant effects on phosphorus (P) removal [17], AD effluent still contain a high level of phosphorus (either organic or inorganic phosphate) that, when directly discharged, has a potential to cause various environmental issues, for instance, eutrophication, which severely damages aquatic ecological systems. In terms of manure management, large portions of the phosphorus can be removed by the solid–liquid separation of manure, which was proposed mostly in alignment with the AD of dairy manure. The phosphorus is relatively enriched in the solid phase while the liquid phase primarily only contains the soluble phosphate. The solid-liquid separation can be installed before the AD process and separating the solids from the liquid manure makes the liquid easier to pump and handle. However, it may significantly decrease the amount of organic materials available for the biogas production. The solid-liquid separation can also be installed after the AD process, where the solids can be used as the animal bedding materials. Numerous technologies have been developed to effectively and efficiently separate the solid and the liquid portions of the manure [18-23]; however, it is still considered as a pretreatment or as a first stage decontamination in highly polluted effluents with high content of particulate phosphorus. Even with the solid-liquid separation, the liquid waste still contains high concentration of phosphorus, while the phosphorus content of the solids is very low and the transportation of manure solids is still limiting the applications of phosphorus in a wider region.

As the animal industry is developing to larger production and operation to meet the increasing food and meat consumption as a result of the population growth and higher living standard [24], animal wastes, mainly animal manure in liquid, slurry, or solid forms, need more appropriate handling and utilization. Research on AD is boosted to a new level because of the recent research highlights on bioenergy and biofuel, so studies on methods for phosphorus removal and recovery from AD effluent needs investigation of the same level of attentions. In fact, recovery and recycle of P from AD effluent would offer a sustainable way of producing P fertilizer compared to the current approach that P is unsustainably mined from phosphate rock which according to some estimation that the reserve would be depleted within a century [25]. This book chapter will elucidate the mechanisms, processes and performances of some of the currently available P recovery technologies for manure and AD effluent, including chemical, electrochemical and biological methods.

1.2. Phosphorus in manure

Phosphorus (P) is one of the most abundant elements in the Earth's crust and it occurs in a large variety of forms, either in organic or inorganic forms, and also as monomeric (phosphates) or as constituent part of macromolecules (polyphosphates). Its discovery dates back to 1669, by Hennig Brand of Hamburg, through the distillation of urine. Its history proceeds to further characterization of some phosphorus compounds and production of phosphoric acid in the 18th century by Boyle. It was during the first half of the nineteenth century that some scientists, especially Liebig and Lawes, made very significant advances in the science of plant nutrition, and the first studies on the utilization of phosphates as fertilizers were recorded [26]. Some remarkable work in the 20th century in the field of biochemistry has been developed upon the understanding of phosphorus in biological systems, such as the discovery of adenosine triphosphate (ATP) in 1929; the concept of high energy phosphate bonds in 1941; and the elucidation of the molecular structure of nucleic acids (DNA and RNA) by Crick and Watson in 1953. These findings, and other outstanding results, led to the understanding that phosphorus plays a vital role in living processes. Phosphorus is usually not found free in nature and mostly occurs in the fully oxidized state as phosphate; and phosphates can be classified according to their molecular structure. The first attempt to classify them was introduced by

Graham, in 1833, in which he proposed the division into orthophosphates, pyrophosphates, and metaphosphates [26].

Phosphorus is present in agricultural residues and wastes, for instance, animal manure and litter. These residues are used as inexpensive fertilizer to improve soil quality. Soil tests have been conducted to estimate how much nutrient may be available for plant uptake during growth (Corbridge, 1985). For phosphorus characterization in soil, the values are aimed at identifying the labile P fraction, i.e., the fraction that is readily available for plants. From these observations, significant advances have been achieved over the last 65 years. The utilization of manure as fertilizer brought a different scenario for the analysis, due to the rich phase of phosphorus present in several samples reported in the literature [27]. Analytical techniques for phosphorus have transformed from simple gravimetric and volumetric titration methods to advanced new applications of 2D-NMR, chromatographic, spectroscopic, and microscopic methods. However, for several studies, understanding the chemical behavior of phosphorus is more relevant than predicting its molecular properties, like on sediments, soils, and residual materials. On these studies, the different phosphorus forms are usually categorized within their capability of being recovered by some physiochemical methods. The inorganic fraction are usually categorized under the following groups: (i) adsorbed by exchange sites; (ii) associated with iron, aluminum and manganese oxides; (iii) associated with carbonate; (iv) associated with calcium as apatite; and (iv) bound in a crystalline mineral form. The organic fraction is divided into: (i) labile organic substances; (ii) organic phosphorus associated with humic and fulvic acid; (iii) acid-soluble components; and (iv) residuals consisting of phosphate esters and phosphonates [28, 29]. The method of phosphorus fractionation relies on sequentially extracting compounds from a sample with selective solvents, that are able to isolate P pools of different solubility and of different chemical behavior. The major drawback of such analysis is that, it is unable to isolate discrete chemicals, though sophisticated methods of fractionation is used. Hence, extractants are usually designated to solubilize groups of minerals defined as P associated with Fe, Al, Ca, or even residual forms [30].

On regards to the variety and solubility of manure phosphorus, it must be understood that manure is a complex system and there are numerous interactions between the organic and inorganic phases within its matrix. It has been stated that manure relies on a sensitive and balanced dynamic equilibrium where minor changes, such as through chemical, physical or biological processes, affect the matrix as a whole [31]. Researchers defined the characteristics of four types of manures based on the different phosphorus contents and their characterization: i) Swine; ii) Beef and Dairy; iii) Chicken and Turkey; and iv) other species [27]. SEM images of swine manure samples revealed the presence of $MgNH_4PO_4 \cdot 6H_2O$ (struvite) and trace amounts of $MgKPO_4 \cdot 6H_2O$ (K-struvite); and found that these forms of struvite were in chemical equilibrium with beta-tricalcium phosphate (beta-TCP), and $CaHPO_4 \cdot 2H_2O$ (brushite) [32]. It was also found that swine manure has significant portions of brushite and $AlPO_4 \cdot 2H_2O$ (variscite) [33]. The majority of analysis shows that struvite and brushite are commonly present in swine manure [27]. Similar to swine manure, cattle manure analysis provides a range of phosphate minerals; struvite and $CaHPO_4$ (dicalcium phosphate, DCP) were found to be the main mineral forms of manure inorganic phosphorus as detected by SEM and X-ray diffraction [1, 31]. It was reported that [33] dairy manure predominantly has struvite and brushite, like swine manure. Chicken and turkey manure, shows significant amounts of brushite, beta-TCP, DCP, and struvite, but they vary with different studies [27]. Studies on other manures, such as horse, deer, sheep, and goat, have been reported as being constituted by a mix of struvite and at least one form of Ca-phosphate mineral, usually brushite [26].

Land application of manure has been a more sustainable practice to provide an alternative source for nutrients in order to improve agricultural crop production. Over the past few decades, livestock production has undergone an industrial revolution, resulting in the large-scale generation of livestock manure [34]. Recent developments in corn ethanol production are also transforming the feed industry for wide applications of corn ethanol coproducts such as dry distiller's grains with solubles (DDGS) and corn gluten feeds (CGF) in animal diets. These new feeding materials are causing an increase in P excretion in animal manure [35]. There are multiple barriers to the land application of manure for P utilization and uptake by plants. First, the application is limited to the site close to the livestock, due to the low nutrient content (less than 1% of P in dry volatile solids, and solid content of swine manure around 6%) and subsequent high transportation cost. With the increasing size of livestock farms, especially in the areas where animal farming is highly concentrated, tremendous amounts of surplus manure must be discharged while the land in the surrounding area is oversaturated with P. Second, land application of animal manure is limited by its composition. For example, nutrients such as nitrogen (N) and P are present in swine manure in N:P ratios ranging from 1:1 to 2:1, while the N:P ratios needed by crops are between 3:1 to 15:1 [36, 37]. Therefore, when manure, especially swine manure, is applied to supply the crops demand for N, it results in the overdose of P. P-based application of manure is proposed as a new practice; however, this practice will not only result in under-application of N in most cases, but also will require more land to apply the same volume of manure [38, 39]. Over-application of P leads to its accumulation in soils; in turn, soils with high levels of P have been linked to environmental problems such as eutrophication of water bodies [40]. The land application of manure, especially swine manure, is considered an important contributor of P entering surface waters. Finally, once commercial chemical P fertilizer and manure are applied to soil, a large portion of soluble inorganic P is rapidly converted into insoluble forms by adsorption to the surface of soil particles, reacting with soil cations (such as calcium, iron, and aluminum), or immobilized into organic P by microorganisms in soil [41, 42]. Although the total P content in soil (average 0.05% w/w) is sufficient for plant growth, only 0.1% of the total P in soil is available to plants [43]. Overall, phosphorus separation from animal manure and digestate is a critical step in the sustainable utilization of the nutrient and in the healthy development of livestock industry. Some common phosphorus separation methods for liquid manure and digestate are discussed in the following sections.

2. Coagulation

2.1. Chemical coagulation/flocculation

Many commercialized processes for phosphorus removal from wastewater use chemical coagulation/flocculation methods by dosing divalent or trivalent metal cations (e.g.,

$[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$, abbreviated as Al^{3+} and Fe^{3+} for convenience) via chemicals such as ferric chloride, ferric sulfate, aluminum sulfate, alum $[KAl(SO_4)_2 \cdot 12H_2O]$ and poly-aluminum chloride [44]. Coagulation process removes not only phosphorus in the form of phosphate, but also dissolved organic matter, colloids and particulates which are prone to be coagulated [45]. Coagulation is different from crystal precipitation process (crystallization) in which by adding lime or magnesium compounds to wastewater precipitates of calcium phosphate (e.g., hydroxyapatite) or struvite are formed and gravitationally separated from liquid fraction [8]. But when multivalent metal cations of coagulants are added, only a portion of phosphate is precipitated with these ions to serve to the phosphate removal from liquid. Further information about precipitation is described in the section of "Struvite precipitation" in this chapter. It is suggested by some authors that the real mechanisms in the coagulation/ flocculation are complex, and it may include effects induced by other processes such as hydrolysis, complexation, crystallization, precipitation, adsorption (Figure 1), reduction-oxidation, other types of interactions (e.g., ligand competition) among different ions, etc. It is not surprising that a study with emphasis on theoretical aspect of a process may have little indication of the real significance in experimental observations [46].

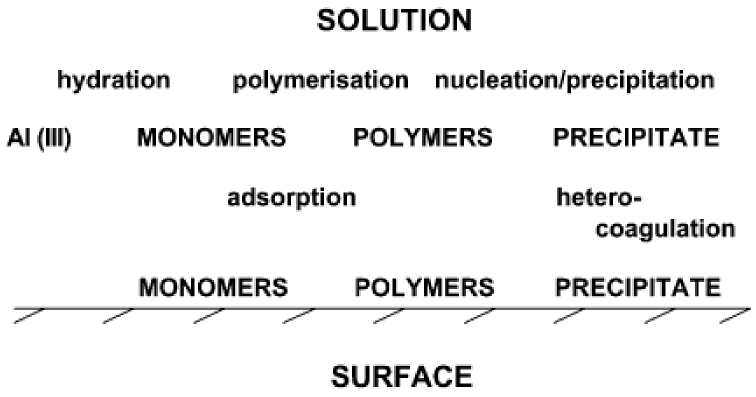

Figure 1. Schematic illustration of the charge neutralization by aluminum species [45].

The stability of colloidal system in wastewater is maintained principally by two ways: the coverage of the negative charge on particulate surface so that a repelling electrostatic force counteracts with van der Waals force and separates particulates from each other; and the hydration of the surface layers of colloids [46]. Destabilization of colloidal systems is the first step for coagulation. The efficacy of aluminum and iron coagulants principally originates from their ability to form multi-charged poly-nuclear complexes that enhance their adsorption capability [46]. Hydrated metal ions (Al^{3+} and Fe^{3+}) with one or more hydroxyl ions are observed to substantially improve absorptivity and coagulation, but it is not clear through what mechanisms the hydrolysis and the poly-nuclear complexation improve adsorption (sweep flocculation) [45, 46]. The above processes for aluminum species are illustrated in Figure 1, while ferric species follow a similar way. The formation of insoluble amorphous metal hydroxide precipitate also provides an important way as adsorbents for phosphate to attach [44, 47]. Generally, the hydrolyzed cations generated from dosed chemicals (applied in solid or solution forms depending on the chemicals used) will provide positive charges in bulk liquid and neutralize the surface charge of colloids, causing an increased attraction among colloids and destabilizing the colloidal system. The destabilized particles are followed by flocculation process through metal hydroxo complexes to form larger agglomerates, eventually forming larger particles of flocs. This mechanism can be especially useful because it is well accepted that the majority of manure phosphorus already exists in the colloidal form rather than dissolved phosphate anions, so crystallization of phosphate salts may be unnecessary prior to coagulation. Precipitation of insoluble phosphate salts, e.g., $FePO_4$ and $Fe_5(PO_4)_2(OH)_9$ when ferric is added, is another significant factor contributing to phosphate removal [48]. When chemical dosing is high, insoluble metal hydroxides are precipitated from liquid, which will also enmesh particulate materials by a sweep action. After flocculation the wastewater can be directly subjected to some physical separation processes, such as floating, gravitational sedimentation, screw press, or filtration.

Both Fe^{3+} and Al^{3+} salts (sulfate and chloride salts in solid or solution form) are widely used for coagulation for phosphorus removal, and the dose in liquid manure should reach 2 to 3 for the molar ratio of metal to phosphorus in order to achieve over 95% removal. Aluminum salts usually outperform iron salts at anaerobic condition because part of ferric is reduced to ferrous which is less effective in coagulation. A study evaluated the phosphorus removal by adding iron salts to simulated cattle manure (dissolving back dry solids in water): ferric salts were found much more effective than ferrous salts, and ferric chloride was more effective than ferric sulfate. Adding calcium oxide (CaO) removed additional amount of phosphorus [49]. Ferric chloride, ferric sulfate, aluminum chloride, and aluminum sulfate were assessed in jar test for phosphorus removal from liquid dairy manure [50]. Compared to the removal efficiency of 50% by natural sedimentation, 100 mg-Fe/L by ferric chloride slightly reduced the removal by 2%. Further increase of Fe (ferric chloride) to 200 mg/L, 300 mg/L, 400 mg/L, 500 mg/L, and 600 mg/L achieved removal efficiencies of 71%, 82%, 89%, 89%, and 92%, respectively. Ferric sulfate addition achieved very close removal efficiency for phosphorus, and removal efficiency was slightly improved from 82% to 88% when ferric was increased from 300 mg/L to 600 mg/L. Aluminum chloride obtained much better phosphorus removal: 80%, 85%, and 99% efficiency at 100, 200, and 300 mg-Al/L. Aluminum sulfate was comparable to the chloride salt: 60%, 75%, 89%, 95% and 100% removals were achieved at 59, 119, 179, 239, and 300 mg-Al/L [50]. 200 mg/L of flocculant (polyacrylamide) dosing with ferric (300 mg/L) and aluminum (180 mg/L) achieved over 98% of phosphorus removal. The total cost of P removal (84%) and transportation of 5 mile was calculated to be \$4.09/m^3 (\$0.02/gal). More data based on liquid cattle/dairy manure expressed in molar units are presented in Table 1.

Another study compared the coagulation/flocculation performance in terms of phosphorus removal from liquid swine manure by coagulants/flocculants of $FeCl_3$, $FeCl_2$, $FeClSO_4$, poly aluminum chloride (PAC), and sodium aluminate solutions [54]. The manure was liquid/solid separated and treated by activated sludge in a reactor for 30 days. The resulting total phosphorus was 322 mg/L. The ranges for the chemical dosing (mmol-metal/L) and removal efficiencies were listed as follows: $FeCl_3$, 3.3 to 16.3, 39% to 95%; $FeCl_2$, 2.1 to 10.6, 17% to 78%; $FeClSO_4$, 3.3 to 16.7, 26% to 91%; poly aluminum chloride (PAC), 4.5 to 23, 23% to 91%; and sodium aluminate, 5.7 to 28.7, 14% to 34%. $FeCl_3$ had the best performance of 95% removal, and the corresponding molar ratio of Fe to total-P was 1.57. Based on extrapolated data, in order to achieve total phosphorus down to the 2 mg/L from 322 mg/L, 27 mmol/L of $FeCl_3$ should be dosed to manure, corresponding to a molar ratio of 2.6 [54]. Performance variance in different studies (Table 1) indicates that further investigation is needed for optimal phosphorus removal and a reduced chemical cost.

Coagulant	**Fe/Al dose**	**Total solids**	**Initial total P**	**Final total P**	**Ratio of Fe/Al to total P**	**Reference**
	mmol/L	%	mg/L	mg/L	Molar ratio	
$FeCl_3$	5.0	1	104	12.6	1.5	[51]
$Fe_2(SO4)_3$	4.4	1	104	16.4	1.3	[51]
$FeCl_3$	5.4	0.9	110	19.8	1.5	[50]
$FeCl_3$	10.7	0.9	110	8.8	3.0	[50]
$Fe_2(SO4)_3$	5.4	0.9	110	19.8	1.5	[50]
$Fe_2(SO4)_3$	10.7	0.9	110	13.2	3.0	[50]
$AlCl_3$	3.7	0.9	110	22.0	1.0	[50]
$AlCl_3$	11.1	0.9	110	1.1	3.1	[50]
$Al_2(SO4)_3$	6.6	0.9	110	12.1	1.9	[50]
$Al_2(SO4)_3$	11.1	0.9	110	0.0	3.1	[50]
$Al_2(SO4)_3$	8.0	1.6	106	8.4	2.3	[52]
$FeCl_3$	16.0	1.6	106	29.6	4.7	[52]
$Al_2(SO4)_3$	5.9	1.1	143	25.0	1.3	[53]
$Al_2(SO4)_3$	11.7	1.1	143	4.4	2.5	[53]
$FeCl_3$	3.4	1.1	143	25.9	0.7	[53]
$FeCl_3$	6.7	1.1	143	16.0	1.5	[53]

Table 1. Performance of chemical coagulation on total phosphorus removal from liquid dairy manure

2.2. Electrochemical Coagulation (electrocoagulation; EC)

Electrochemical coagulation (EC) is an alternative to chemical coagulation. The main mechanism responsible for coagulation is similar in electrocoagulation and chemical dosing, except the self-generation of metal cations by anode oxidation. The electrocoagulation offers some advantages over chemical dosing: it has simple equipment requirement and can be readily automated; reduces the chemical cost by using cheaper materials; gas bubbling provides gentle mixing that promotes coagulation and helps form bigger flocs; and gas bubbling carries some particles up to the top of liquid in a way of flotation, which may be easily separated. So electrocoagulation is not only an alternative to the conventional way, but also a promising method due to its effectiveness and low cost [55, 56], which has been used for phosphate removal from drinking water [57], turbidity reduction [58], and wastewater remediation [59, 60].

The application and performance of EC for animal manure treatment has been reported in several recent publications [61-63]. EC was explored to remove solids from digested and screw pressed manure [62]. Before the pre-processed manure entered the EC system, the screw pressed digestate contained 4.2% TS and 3.0% VS. The EC effluent had a decreased TS and VS to 0.89% and 0.28%, corresponding to a removal efficiency of 79% and 89%, respectively. A parallel EC yielded a comparable results in effluent, with only 0.62% TS and 0.13% VS. Electrode materials, configurations, operating conditions, and phosphorus removal were not reported in the literature. Another field EC test reported total and dissolved phosphorus removal from lagoon effluent which was chemically pretreated and centrifuged before entering EC unit [61]. The dissolved and total phosphorus was reduced from 0.15 and 7 mg/L to 0.01 and 2.1 mg/L respectively, with limited description of the EC reactor configuration and operating conditions in the literature [61]. The preprocessing of lagoon effluent may generate effluent that did not reveal the total capability of EC for P removal. 304 stainless steel was used as EC electrodes for dairy manure treatment [63] with 1 A (at a voltage of about 6 V) for 500 mL manure. Within the first 30 min, 83% TP was removed but the ensuing current application seemed not to substantially improve removal efficiency. TSS removal reached 88% after 20 min EC operation. In a continuous mode, 53% to 78% TP was removed at current density of 3 A to 5.5 A after 30 min operation. Based on these results, EC can be a method to treat liquid discharge from dairy farm, but more studies must be conducted before its field application in order to articulate the interfering factors, appropriate electrode materials and configuration, and operating conditions.

3. Struvite precipitation

The crystallization technology was originally developed primarily because of the more stringent phosphorus removal requirements to further decrease the phosphorus (P) level of effluent in wastewater treatment plants and produce more valuable and sustainable end-products, such as struvite (magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$) and calcium phosphate (e.g., hydroxyapatite, $Ca_5(PO_4)_3OH$) [17]. Struvite is a mineral crystalline substance consisting of equal molar magnesium, ammonium, and phosphate, and it can potentially be an excellent slow-release fertilizer that has numerous potential uses in agriculture and horticulture. Its precipitation reaction can be expressed as Eq. (1):

$$Mg^{2+} + NH_4^{+} + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^{+} \tag{1}$$

Precipitation of struvite often occurs in wastewater when ammonium, phosphate, and magnesium ions exceed the struvite solubility limit. The solubility product constant of struvite is $10^{-13.26}$ [64]. Struvite precipitation from digested manure has attracted tremendous attention recently as a method of P removal and recovery [65-68], although the reusability of this precipitated phosphate salt is debatable [66, 69], especially when it is applied to the soil with higher pH due to the low solubility of the struvite in the alkaline conditions [70]. Manure sources to apply this technology include calf manure [71], swine wastewater [72-80], poultry manure wastewater [81], and dairy manure [82-85]. Struvite precipitation can be separated into two stages: nucleation and growth. Nucleation occurs when constituent ions combine to form crystal embryos. Then, they quickly form a larger nucleus of crystals and crystal growth continues until equilibrium is reached [86]. Struvite precipitation is influenced by type of reactors, pH, temperature, Mg:P ratio, chemicals added, reaction time and the presence of other ions in solution such as calcium.

3.1. Crystallizer

Several types of crystallizer have been developed to remove phosphorus from manure wastewater by struvite precipitation. Bowers and Westerman [87] developed a cone-shaped fluidized-bed for struvite precipitation from swine wastewater. This design provided a high ratio of crystal surface area to reactor volume and it struvite seed to promote the growth of struvite crystals within the reactor. Field tests with pH adjustment and magnesium amendment demonstrated dissolved reactive phosphorus (DRP) removal efficiencies ranging from 70% to 82%, and total phosphorus (TP) reductions ranging from 63% to 80% [88]. However, high content of solids in the influent slurry could lead to washout of fine bed particles, resulting in lower phosphorus removal. The solids also could interfere with the bed particles and inhibit the struvite crystal growth. Shepherd et al. [89] developed a bench-scale continuous flow air sparged tank reactor (ASTR) for struvite precipitation in swine manure slurries. This system used air sparging for both pH adjustment and mixing, and used a peristaltic pump to continuously inject $MgCl_2$ for struvite precipitation. The bench-scale ASTR system provided DRP reductions of 78% and 95% in swine manure slurry collected from a shallow under floor pit collection system and from a concrete storage tank with a permeable cover, respectively. However, separation of precipitated struvite for TP reduction was not achieved with an up-flow clarifier operated in continuous flow mode. Then, they tested the performance of a pilot-scale ASTR-hydrocyclone system [90]. The pilot-scale ASTR-hydrocyclone system provided a 92% reduction of DRP in manure slurry from a swine finishing facility concrete storage tank and a 91% reduction of DRP in manure slurry collected from a swine finishing facility deep-pit under floor collection system. The pilot-scale ASTR-hydrocyclone system removed 18% of TP in swine manure from a concrete storage tank and 9% to 14% of TP in swine manure slurry from a deep-pit under floor collection system. The low TP recovery was attributed to the hydrocyclones inability to provide effective struvite separation as operated. Although ASTR was simple in design, fabrication, and operation, economics analysis indicated that this ASTR-hydrocyclone system in swine finisher manure slurries was not currently economically viable. The third design presented the reactor for removing and recovering phosphorus from swine wastewater with dual functions of crystallization through aeration and separation of formed struvite by settling [78]. The swine wastewater was fed to the aeration column of the reactor continuously. Air was aerated to diffuser units via a stainless steel air tube. The crystals formed in the aeration column were settled and withdrawn from the bottom of the reactor. The maximum yield of struvite was 171 g/m^3 swine wastewater, and the purity of the recovered struvite was approximately 95% without washing [79].

3.2. Effect of pH

pH is an important role for struvite production because struvite plays slightly soluble under neutral and alkalinic conditions but readily soluble in acid [91]. At 25°C, the solubility of struvite is 0.018 g/100 mL in water, and increases to 0.033 g/100 mL in 0.001N HCl and 0.178 g/100 mL in 0.01N HCl [92]. Therefore, optimized struvite precipitation in manure slurries generally requires increasing the slurry pH. The minimal pH required for effective precipitation of struvite from anaerobically digested cattle manure effluents is about 8 and the operation pH should be controlled between 8.5 and 9.5 [83]. Miles and Ellis [76] reported that the optimum pH was about 9.5 for struvite precipitation in anaerobically digested piggery wastes. The experiments using anaerobic swine lagoon liquid for struvite precipitation showed that that the minimum concentrations of DRP occurred between pH 8.9 and 9.25 at all Mg:P ratios [77]. Burns et al. [74] also found that 96%-98% of the DRP was removed from swine manure slurries at a pH of 8.6 with a 10-minute reaction time and $MgCl_2$ addition. However, a higher operation pH concurrently increases the caustic consumption and the cost of neutralizing the final treated effluents, even though it promotes better phosphate removal efficiency. Air sparging to elevate pH may be an advantageous approach for P recovery at larger scales because it would avoid liabilities from alkali additions [84]. Suzuki et al. [93] confirmed that aeration was effective for elevating the pH of swine wastewater to 8.5, and 65% removal of orthophosphate was achieved.

3.3. Effect of magnesium salts

The $Mg^{2+}/PO_4^{3-}/NH_4^+$ molar ratio is 1:1:1 in struvite based on the molecular formula ($MgNH_4PO_4 \cdot 6H_2O$). The concentration of soluble P in animal manure is normally much higher than that of magnesium ion but much lower than ammonium nitrogen, which results in that magnesium ion becomes the limiting constituent for struvite precipitation from manure. Without magnesium addition, only 20–30% of soluble phosphorus was removed from centrifuged digested cattle manure effluent at pH 7.8–9.0 as both struvite and calcium phosphates due to the low levels of the initial Mg^{2+} and Ca^{2+} in the effluent [83]. In order to increase phosphate removal efficiency through struvite precipitation, more Mg^{2+} would be needed. Phosphate removal efficiency greater than 80% was achieved when the molar ratio of Mg^{2+}/PO_4^{3-} in swine wastewater was between 1.1 and 1.6 [74, 77]. However, the requirement of higher Mg^{2+}/PO_4^{3-} molar ratio was also observed by other studies [83]. The phosphate removal efficiency just increased to 50% at a Mg^{2+}/PO_4^{3-} molar ratio larger than 5 and reached 73% at a Mg^{2+}/PO_4^{3-} molar ratio up to 22:1. Struvite formation could be hindered by high Ca^{2+} concentration, ionic strength, alkalinity, suspended solids content, or a combination of these [85, 93]. Huchzermeier and Tao [85] reported that Ca^{2+} inhibited the struvite formation by blocking active struvite growth sites and competing for orthophosphate to form calcium phosphates. They also found that calcium can be effectively removed from anaerobically digested dairy manure through precipitation of calcium carbonate at pH 9 to 10 while retaining magnesium and orthophosphate.

Technically, many magnesium sources that produce Mg^{2+} ions can be used for the struvite precipitation process. $MgCl_2$, $MgSO_4$, MgO, $Mg(OH)_2$ and other low-cost sources of magnesium, such as bittern and seawater, were tried as magnesium amendment for struvite precipitation [83, 94, 95]. Magnesium chloride ($MgCl_2 \cdot 6H_2O$) was considered a good source of Mg^{2+} for struvite formation and reduced the reaction time that was required to dissolve Mg^{2+} into solution for struvite formation [73]. Burns et al. [74] indicated that $MgCl_2$ can force the precipitation of P from swine manure. Zeng and Li [83] also found that $MgCl_2$ and $MgSO_4$ provided the higher P removal efficiency, likely due to their highly water-soluble property. The advantage of using $MgCl_2$ is its faster dissolution in water and hence a shorter reaction time. However, it decreases pH because it is slightly acidic. A pH of 8.5 or greater would be required for effective struvite precipitation [96]. Use of MgO or $Mg(OH)_2$ can supply Mg^{2+} and raise solution pH, and they are normally less expensive than $MgCl_2$ and $MgSO_4$. Although MgO and $Mg(OH)_2$ are both poorly soluble in water, MgO is still a good magnesium source for struvite precipitation and it was better than $Mg(OH)_2$ for struvite precipitation from digested swine wastes after they incurred insolubility problems with $Mg(OH)_2$ [76]. For struvite precipitation from digested cattle manure, MgO was slightly worse than $MgCl_2$ and $MgSO_4$ but much better than $Mg(OH)_2$ and $MgCO_3$. Due to its insolubility, $MgCO_3$ was the least effective for struvite precipitation from manure among the salts used [83]. A fine particle size and vigorous agitation of the reaction solution were needed when using MgO or $Mg(OH)_2$ for struvite precipitation.

3.4. Hydroxyapatite precipitation

Except struvite, small amount of other phosphate precipitates are also formed, which include K-struvite ($KMgPO_4 \cdot 6H_2O$), calcium phosphates, and magnesium phosphates. Zeng and Li [83] reported that less than 1.5% K-struvite was formed in precipitated solids although the original digested cattle manure effluent contains a high level of potassium. Burns et al. [74] detected brushite ($CaPO_3(OH) \cdot 2H_2O$) in precipitates from struvite precipitation of swine manure slurries due to the Ca^{2+} in the slurries. Magnesium phosphates possibly as $MgHPO_4 \cdot 3H_2O$ (newberyite), $Mg_3(PO4)_2 \cdot 8H_2O$ (bobierrite), and $Mg_3(PO_4)_2 \cdot 22H_2O$ were formed [83].

As a matter of fact, phosphorus removal in high Ca^{2+} content wastewater also can be achieved by direct precipitation of calcium phosphate (hydroxyapatite, $Ca_5(PO_4)_3OH$). For sludge side streams of wastewater treatment plant, phosphorus removal efficiencies by hydroxyapatite crystallization ranged from 75% to 85% with additional artificial crystal seed material, consisting of calcium silicate hydrate (tobermorite crystals, manufactured by mixing siliceous and calcareous raw materials, pelletizing, and autoclaving) [97]. However, few studies have been done to remove phosphorus via hydroxyapatite crystallization from manure slurries. When Harris and coworkers [84] recovered phosphorus from flushed dairy manure wastewater by precipitation, they found that phosphorus can be recovered from flushed dairy manure wastewater not only in the form of struvite, but also calcium phosphate. Presence or formation of carbonates inhibits hydroxyapatite formation and solution pH value, again, is a key factor influencing the precipitation process. Addition of $MgSO_4$ can suppress carbonate precipitation and enhance Ca phosphate precipitation at elevated pH (>9) [84].

3.5. Commercialization and application of struvite precipitation

Struvite precipitation is currently the most commercially adopted technology for phosphorus recovery from wastewater as fertilizer. Modification on waste streams' constituents or operating conditions, such as chemical dosing, temperature elevation, air stripping and reactor innovation, is made to improve struvite crystallization and precipitation, and therefore, to increase P removal and recovery efficiency. Based on internet search, we found that there are numeral commercially available processes which have been developed and marketed. These processes include AirPrex™ developed by Berlin Water (Wassmannsdorf, Germany), NuReSys® by Akwadok Company (Waregem, Belgium), Pearl® with WASSTRIP (patent pending) by Ostara Nutrient Recovery Technologies Inc. (Vancouver, Canada), Crystalactor® by Royal HaskoningDHV Company (Amersfoort, the Netherlands), PHOSNIX by Unitika Ltd (Osaka, Japan), and Quich Wash™ by Renewable Nutrients LLC (Raleigh, NC). Struvite precipitation technology dominates the market compared to other types of technologies such as incineration, enzyme hydrolysis, critical point oxidation, and adsorption.

Phosphorus recovery from raw manure or anaerobically digested manure via struvite precipitation has been widely studied, and high phosphorus removal efficiencies were both obtained from the two kinds of manure. However, just few researches investigated the effect of anaerobic digestion on struvite precipitation. Moody et al. (2009) found that anaerobic digestion of swine slurry increased orthophosphate (PO_4^{3-}) in solution by 25% (from 1.26 g/L to 1.59 g/L), but the amount of Mg^{2+} increased by 254% (from 88.3 mg/L to 313.3 mg/L), which indicated that anaerobic digestion have no significant effect on reactive phosphate releasing, but it significantly increased the amount of available Mg^{2+}. Increasing the solution Mg^{2+} concentration means less amendment of magnesium salt and low cost. In addition, PO_4^{3-} removal efficiency of struvite precipitation was increased by 36% with anaerobic digestion pretreatment.

4. Enhanced Biological Phosphorus Removal (EBPR)

Biological nutrient process (BNP) refers to modified activated sludge processes where contaminants, biochemical oxygen demand (BOD), nitrogen and phosphorus can be simultaneously removed from the bulk wastewater and accumulated to the waste sludge [98]. In this method, phosphorus removal is usually realized by enhanced biological phosphorus removal process (EBPR), a process that recirculates activated sludge in alternating anaerobic and aerobic conditions and enriches or selects the microbial strains synthesizing polyphosphate (polyphosphate accumulating organisms, PAO). It has been applied to municipal wastewater treatment, but is also acknowledged that in large-scale applications the process experiences reactor upset and failure from time to time due to environmental or biological reasons such as nitrate overloading, high rainfall, and microbial competition [99]. Selecting and maintaining suitable operational conditions to avoid reactor upset can be important to the process. One limitation for EBPR is the insufficient carbon source in wastewater, or relatively low soluble COD-to-phosphorus ratio so PAOs does not sequester enough PHAs or energy for phosphorus accumulation. Manure before or even after anaerobic digestion usually contains a high level of organic compounds and a large portion of it is readily biodegradable such as acetate, propionate and butyrate. So manure can at least be a good substrate for providing carbon source for PAOs; in other words, EBPR can be an alternative method for phosphorus removal from liquid manure [100]. Some of the previous studies using animal manure in fact achieved good results in phosphorus removal via EBPR. Note that EBPR process usually is not the final step closing the phosphorus removal but a pretreatment method, although phosphorus is concentrated in sludge. The reason is that poly-phosphate in the sludge tends to be hydrolyzed, released and leaked to liquid phase. There are several other processes that can be used to further treat the EBPR sludge and phosphorus-accumulated media, e.g., coagulation and crystallization.

4.1. Microbiology and mechanisms

EBPR has been used in wastewater treatment plants for a long period of time, and most fundamental studies were based on activated/recycled sludge from these treatment plants. Briefly, the anaerobic/aerobic cycling selects and enriches PAOs, and PAOs take up phosphate from wastewater at the aerobic stage (process diagram illustrated in Figure 2). In the PAOs well developed sludge, acetate and other short-chain fatty acids are taken up at the anaerobic stage by PAO cells and transferred to acetyl-CoA with ATP consumption from poly-P hydrolysis. This process is accompanied with release of cations such as K^+ and Mg^{2+} as well as $H_2PO_4^-$ to wastewater. After several steps of transformation and polymerization, acetyl-CoA is transformed to poly-β-hydroxyalkanoates (PHAs), mainly poly-β-hydroxybutyrate (PHB) and poly-β-hydroxyvalerate (PHV). The reducing power for acetyl-CoA transformation at anaerobic condition comes from NADH in the degradation of internal carbohydrate, via full [102] or split TCA cycles [103], but also found via the EMP pathway (a glycolysis pathway) from consumption of internal carbohydrates mainly glycogen [104]. As said before, hydrolysis of poly-P may also contribute energy source as ATP at the anaerobic stage, for acetate transport across cell membranes. Multiple of these pathways may co-exist depending on sludge sources and environmental conditions, which needs clarification by future studies [99]. At aerobic condition, the degradation of PHAs leads to the generation of acetyl-CoA and propionyl-CoA, both of which enter TCA cycle as carbon and energy source for biomass growth, phosphate uptake and poly-P generation, and glycogen generation.

Another important microbial composition of activated sludge is glycogen-accumulating organisms (GAOs). GAOs consume external carbon source at anaerobic stage, but at aerobic stage they do not uptake phosphate from environment and there is no poly-P accumulation occurring; instead, carbon and energy from PHAs hydrolysis is mostly used for biomass growth and glycogen synthesis. Therefore, there is a substrate competition between PAOs and GAOs for acetate and other short-chain fatty acids utilization. This relationship dominates the performance of phosphate removal in EBPR process [99], and is affected by environmental

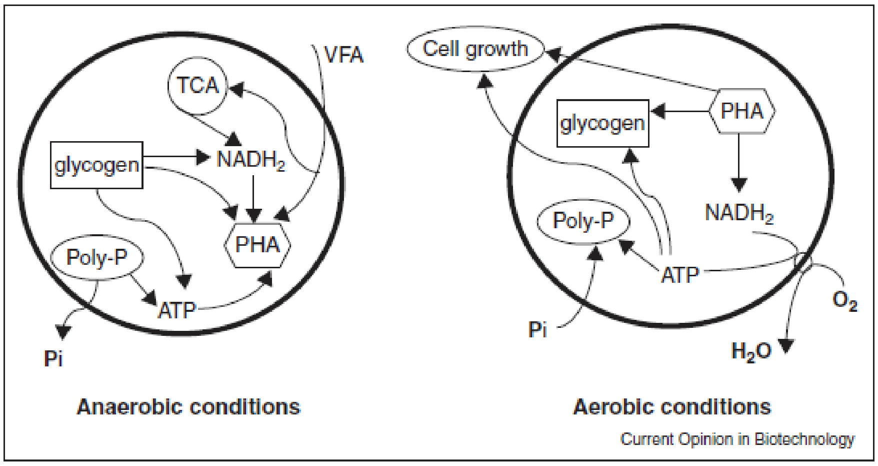

Figure 2. Schematic diagrams of the anaerobic and aerobic PAO metabolism in EBPR process [101].

conditions for selective advantages between two groups, such as types and concentrations of carbon sources, organic loading rate, nutrients level and their ratio to carbon sources, pH, temperature, etc. Generally speaking, at the ambient pH range (6 to 8), a relatively higher pH is found advantages for phosphate removal and for PAOs selection over GAOs. At the ambient temperature range (5 to 35 ^{o}C), a lower temperature is favored by PAOs over GAOs for phosphate removal. Relative abundance of PAOs over GAOs may be increased by a relative lower dissolved oxygen levels (1.5 to 3 mg/L) at the aerobic stage [99].

Phosphate uptake is also possible by denitrifying PAOs which use nitrate as electron acceptor in the anoxic condition, corresponding to oxygen in the aerobic condition. This pathway is promising because it removes both nitrogen and phosphate and it reduces sludge production due to less energy release compared to aerobic condition [99]. There is no exclusive relationship between the concepts of general PAOs and denitrifying PAOs. Multiple commercial processes have been established for the combined biological nitrogen and phosphate removal in wastewater treatment plants, such as A_2O, modified-UCT, five-stage Bardenpho, and DE-PHANOX with either pre- or post-denitrification [99].

4.2. EBPR with animal manure as substrate

At the anaerobic stage, VFAs are substrates for PHAs regeneration inside PAOs cells, and the accumulated PHAs can be degraded for biomass growth and phosphate uptake at the aerobic stage. However, municipal wastewater contains only a small amount of VFAs, which reduces the suitability of EBPR process. Acetate may be added to wastewater but it increases overall chemical cost. So supplementing agro-food wastewater can be a good option, because it is considered waste and cost-effective. EBPR potential test, which evaluates the phosphorus release from activated sludge in certain medium composition in batch mode, was developed for assessing the feasibility of implementing EBPR for a substrate [105, 106]. Based on this test, it was found that tomato processing and milk bottling industry wastewater had short-term enhancement for EBPR, while wastewater from cheese industry, slaughter houses, beet sugar processing, and winery processing didn't show improvement [107].

The spatial requirement on condition variation (anaerobic/aerobic) in conventional flow systems for EBPR can be transformed to temporal variation by using sequencing batch reactors (SBRs) [108, 109]. This approach is widely adopted for treating liquid manure (liquid swine and dairy manure) [110, 111] because it saves space and operating cost over the conventional alternate flow systems, thus suitable for use in animal farms. SBRs consist several phases in its operation, typically including feeding, anaerobic, aerobic, settling, and withdrawal. Operating conditions such as medium composition, ORP, HRT, SRT, length of a cycle, length of each phase, pH, and temperature will have an impact on SBR performance. Surplus phosphorus uptake from swine manure and poly-P accumulation in biomass was observed in liquid swine manure treatment in SBRs, with 93% of COD removal, 88%-93% of total nitrogen removal and 95% of phosphate removal [112]. With non-diluted swine wastewater that initially contained 1500 mg-N/L of ammonium and 144 mg-P/L of phosphate, a removal efficiency of 99.7% for nitrogen and 97.3% for phosphate was achieved in SBR operated with 3 cycles/day at temperature of 30 ^{o}C, SRT of 1 day and HRT of 11 days [110]. Subjecting the digested manure to EBPR may encounter lack of VFAs at the anaerobic stage of EBPR, so non-digested liquid swine manure can be supplemented to AD effluent as additional carbon source. This combined substrate achieved good nutrient removal by EBPR in SBR, 99.8% of nitrogen and 97.8% of phosphate removal from an initial content of 900 mg/L of ammonia and 90 mg/L of phosphate [111]. A 16 L SBR was constructed for treating liquid dairy manure by EBPR [113], and with 6-fold dilution, 98% of phosphate removal (from 33 mg/L to 0.5 mg/L of phosphate) was obtained, while the removal was dropped to 70% with 5-fold dilution. It was suggested by the authors that the higher strength dairy manure contained inhibitory components to EBPR, and high content of acetate was thought as the major reason but was not conclusive. Another study fed EBPR SBR with dairy industry wastewater, and phosphate concentration was decreased from 29.8 - 43.6 mg/L to less than 1 mg/L, demonstrating a highly effective phosphate removal [114]. The EBPR sludge showed a high proportion (31.4% to 38.3%) of *Rhodociclus*-related bacteria, an indicator of PAOs population, in the total microbial cell counts, and phosphorus accounted for 5.4% to 10.1% of the MLVSS [114]. Another SBR study reported 59% of phosphate removal with an initial phosphate level of 37.4 mg/L in dairy manure, generating sludge with 2.6% of phosphorus in the MLVSS [115].

5. Phytoremediation

Phytoremediation could be a low-cost clean up technology for wastewater treatment and also for the P removal, as the green algae and plants offer the finest eco-friendly option for environment remediation. The major hitch with the phytoremediation is the slow growth rate of the plant species and its survival capacity in the non-ideal environment. But, algae and aquatic plants offer a realistic time frame for the nutrient recovery from eutrophic water and other contaminated waters rather than the P removal from the soils, and also require less than one-tenth of the area to recover phosphorus compared to terrestrial crops [116]. The characteristic advantages of the system has made the algal ponds and macrophyte wetlands more popular for environmental applications including herbicides [117], heavy metals [118] and antibiotics [119] removal, and is already been explored widely for varieties of wastewater types including animal manure [120]. Anaerobic treatment of manure results in digestate which requires further treatment before discharge, especially for the removal of P and N. Growing microalgae or macrophytes on the anaerobic effluent could be a commendable option considering the valuable byproducts and process efficiency.

5.1. Algae for phosphorous recovery

Anaerobically treated swine manure has proved to be good medium for algae growth [120-122]. Microalgae with its rapid growth potential, better adaptation to various ecological habitats and as an important feedstock for third generation biofuel, can be a best suited strain to grow in the waste waters for its valuable biomass and the nutrient recovery. It is reported that the major bottleneck to commercialization of algal fuels is the supply of N and P nutrients [123, 124]. Many recent research focuses on a suitable nutrient management strategy to use wastewater (industrial, municipal, dairy, food wastewater and digested dairy manure) as a nutrient supplement for cultivation of oil-rich green microalgae growth and recycling of nutrients [121, 122, 125-127]. The anaerobic digested effluent after decomposing organic waste to produce biogas has been used to grow algae for nutrient recovery. The effluent has relatively lower carbon levels for algae because of microbial utilization during anaerobic digestion [121]. Pretreatment steps like dilution to avoid inhibition and sterilization to prevent the contamination may be required for certain algae systems [121]. Raw and anaerobically digested swine manure has been treated widely by (1) suspended algae in (i) high rate pond systems [128-131], (ii) mixed algae systems [132] and (iii) mixed algae-bacterial systems [133] or (2) by immobilized algae [120], e.g., algal turf scrubber units [134-136]. The harvested algae can be a good high-grade protein supplement for animal feed and also can be used as a slow-release fertilizer [136] which can be directly sprayed as suspension in farm land or stored for future use [137].

Different species of freshwater micaralgae have been tested for nutrient removal from municipal wastewater and manure. The nutrient removal capacity of a *Chlorella sp.* from a highly concentrated municipal wastewater stream generated from activated sludge thickening process (raw and autoclaved medium) was tested by Li and coworkers [125]. After 14-day batch culture, algae could remove ammonia, total nitrogen, total phosphorus, and chemical oxygen demand (COD) by 93.9%, 89.1%, 80.9%, and 90.8%, from raw medium respectively. It was concluded that the system could be successfully scaled up, and continuously operated at 50% daily harvesting rate, providing a net biomass productivity of 0.92 g-algae/(L day) [6]. The immobilized and free cell cultures of two nanoplanktonic algal species, *Scenedesmus intermedius Chod.* and *Nannochloris sp.* isolated from different sources of pig manure was used to study the growth rate, phosphorus and nitrogen uptake from anaerobically treated manure [120]. P and N uptake rates for *S. intermedius* were 0.014 and 0.012 mg P h^{-1} and 0.022 and 0.009 mg N h^{-1} for free and immobilized cells respectively; and rates for *Nannochloris sp.* were 0.006

and 0.009 mg P h^{-1} and 0.011 and 0.006 mg N h^{-1} for free and immobilized cells. It was observed that the isolated species were more efficient in nutrient recovery than the commercially available strains [120], as the isolated strains were better acclimatized to the prevailing conditions. The anaerobically digested swine manure from a farm digester was used to culture *Chlorophyceae*, *Chlorella sp.*, *Scenedesmus obliquus,* and a cyanobacterium, *Phormidium bohneri*, to evaluate the inorganic nitrogen and orthophosphate removal efficiency. *Chlorella sp.* performed well in batch cultures wheres *P. bohneri* in semi-continuous conditions [138]. Benthic freshwater algae was also used to recover nutrients from dairy manure [134] in algae growth chambers operated in semi-batch mode by continuously recycling wastewater and adding manure inputs daily. It was found that, when compared to a conventional corn/rye rotation, such benthic algae production rates would require 26% of the land area requirements for equivalent N uptake rates and 23% of the land area requirements on a P uptake basis [134]. Besides microalgae species, some filamentous fungal species also showed some potential to combine with AD to remove and recover the phosphorus [139].

Harvesting microalgae from treated wastewater is cost intensive, therefore becoming the key to remove and recover the phosphorus. The attached algae cultures for the nutrient removal from the manure waste water was evaluated [140]. It was found that, depending on different culture conditions, the attached algal culture removed 61–79% total N and 62–93% total P from dairy manure. Overall, the attached algal culture removed 62–90% of total phosphorus, 62–87% of soluble phosphorus, and 43–80% of orthophosphate from dairy manure. The economic assessment of algal turf scrubber technology for treatment of dairy manure effluent showed that economic balance would become more favorable if values from algae as a byproduct and nutrient trading credits can be realized [141].

5.2. Macrophytes for phosphorous recovery

Aquatic macrophytes are the conspicuous plants that dominate wetlands, shallow lakes, and streams, playing a vital role in healthy ecosystems. Total nitrogen and total phosphorous removal in treatment wetlands can range from 3–98% to 31–99% respectively [142, 143] with an average removal of about 50% [144]. Studies have showed that vascular aquatic plants have acceptable animal feed qualities, ability to remove nutrients from water, and high production rates [145]. Macrophytes constitute a diverse assemblage of taxonomic groups and are often separated into four categories based on their habit of growth: floating unattached, floating attached, submersed, and emergent [146]. Macroscopic flora includes the aquatic angiosperms (flowering plants), pteridophytes (ferns), and bryophytes (mosses, hornworts, and liverworts). Macrophytes based nutrient removal technology has the merits of (1) high productivity of several large-leaf floating plants; (2) high nutritive value of floating plants relative to many emergent species; and (3) ease of stocking and harvesting [147]. Also, the harvested floating macrophytes biomass can potentially be used for composting, soil amendments, anaerobic digestion with methane production, being processed for animal feed, and could be mixed with separated manure solids to increase the amount of nutrients available for exporting off the farm [148]. The biomass can be a good resource of starch, and utilized for the production of value-added products such as fuel ethanol [149]. For example, *Spirodela polyrrhiza* grown on anaerobically treated swine wastewater had a starch content of 45.8% (dry weight) and enzymatic hydrolysis of the duckweed biomass yielded a hydrolysate with a reducing sugar content corresponding to 50.9% of the original dry duckweed biomass, yielding 25.8% ethanol (dry weight) after fermentation by yeast [150]. Duckweed (*Lemnaceae*) has been widely used to recover the nutrients from pig effluents, because of its tolerance to high nutrient levels and preferred absorption of ammonium [149, 151], and can also grow all seasons in areas with warm climates and doubles its biomass within two days under the optimal conditions [152]. Screened duckweed strains, *Lemnaceae* that grew well on the anaerobically treated swine wastewater in laboratory and greenhouse experiments were tested for nutrient recovery under field conditions. Under nutrient abundant conditions in waste water, duckweed takes the nutrients for its growth and store the nutrients in its tissue for future nutrient limited conditions for a significant period of time, and the nutrient reserve in duckweed biomass has been found the key to the kinetics of duckweed growth [153]. Plants take up nutrients while growing and if not harvested, decompose in wetlands returning nutrients to the ecosystems.

6. Conclusions and future remarks

With the increasing size of livestock farms, especially in the area where livestock raising is highly concentrated, the surplus digested manure applied on soil increases P concentration in agricultural runoff, causing environmental problems like eutrophication. Phosphorus removal and recovery from digested manure reveals its importance in livestock raising area. Coagulation and electrocoagulation methods have been used for P removal from either digested or undigested animal manure. Compared to the municipal wastewater treatment, the dosing of multivalent cations is more intensive for manure treatment, e.g., the molar ratio of metal to P is mostly more than 3. This can be a result of the presence of high solids content and high level of carbonate/bicarbonate, which may consume additional portion of the added metal coagulants. Aluminum salts work better than the ferric counterparts in the anaerobic condition of manure media. Electrocoagulation avoids the direct chemical dosing by releasing metal ions through sacrificing metal anode, so is less chemically intensive but consumes additional electric energy. Struvite precipitation is the most commercially available method to recover the phosphorus from manure as fertilizer. The anaerobic digestion of manure seems to be beneficial to the struvite precipitation while more detailed studies are needed. The key issue related to this process is the bioavailability of phosphate in these precipitates, including struvite and hydroxyapatite, to the plant growth. Animal manure contains high level of carbon source in the form of VFAs which can be the ultimate reducing power for PAOs. Therefore, manure can be treated with EBPR process without additional carbon dosing. The high level of ammonium may be simultaneously removed by enriching denitrifying PAOs community with suitable process design. An integrated process combining anaerobic digester and algae cultivation / macrophyte growth can also be an eco-friendly and sustainable process to reduce nutrient loss to environment and to produce valuable biomass.

Overall, these currently available methods for phosphorus removal and recovery are primarily designed for industrial and municipal wastewater treatment, where there is incentive related to the operations. However, the phosphorus removal from the manure is economically challenging because the end products of phosphorus recovery do not justify the cost of the removal process. It is beneficial to combine the AD process with the phosphorus removal and recovery so that the overall techno-economic feasibility of the process can be significantly improved.

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