Insight into chemical phosphate recovery from municipal wastewater

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Abstract

Phosphate plays an irreplaceable role in the production of fertilizers. However, its finite availability may not be enough to satisfy increasing demands for the fertilizer production worldwide. In this scenario, phosphate recovery can effectively alleviate this problem. Municipal wastewater has received high priority to recover phosphate because its quantity is considerable. Therefore, phosphate recovery from municipal wastewater can bring many benefits such as relieving the burden of increasing production of fertilizers and reduction in occurrence of eutrophication caused by the excessive concentration of phosphate in the released effluent. The chemical processes are the most widely applied in phosphate recovery in municipal wastewater treatment because they are highly stable and efficient, and simple to operate. This paper compares chemical technologies for phosphate recovery from municipal wastewater. As phosphate in the influent is transferred to the liquid and sludge phases, a technical overview of chemical phosphate recovery in both phases is presented with reference to mechanism, efficiency and the main governing parameters. Moreover, an analysis on their applications at plant-scale is also presented. The properties of recovered phosphate and its impact on crops and plants are also assessed with a discussion on the economic feasibility of the technologies.

Keywords: phosphate recovery, chemical process, anaerobic digester supernatant, sewage sludge, municipal wastewater, economic feasibility

Introduction

Phosphorus as a nutrient is essential to biological growth (Jalali and Jalali, 2016; Selbig, 2016; Thitanuwat et al., 2016). However, a high level of phosphate in the aquatic environment can lead to excessive proliferation of blue-green algae, for which dissolved oxygen will be largely consumed and fish and other aquatic life will die. This phenomenon is called eutrophication and it can endanger human life (Lu et al., 2016; Stapanian et al., 2016; Zoboli et al., 2016). To reduce the level of eutrophication, the maximum allowable concentration of P in effluent should decrease from 1-2 to 0.1 mg·P/L in municipal wastewater treatment, according to the Water Framework Directive in Europe (Shepherd et al., 2016) while the P concentration is required to be less than 0.025 mg·P/L in most aquatic environments. The latter measurement is based on Australian and New Zealand water quality guidelines (Anzecc, 2000). Since the world's population is increasing, more production of food and fertilizers is needed (van der Salm et al., 2016; Wu et al., 2016). However, the natural supplies of phosphate rock are non-renewable and it is predicted that deposits will be exhausted in 30-300 years (Mew, 2016; Reijnders, 2014); no material can substitute for the role of P in the production of fertilizers (TU DARMSTADT, 2007; Matsubae et al., 2016).

Normally, the objective of wastewater treatment is to remove phosphate rather than recover. However, researchers has increasingly recognized the importance of phosphate recovery from wastewater (Ahmed et al., 2015; Kumar and Pal, 2015; Nieminen, 2010) as wastewater provides rich sources for phosphate recovery (TNN, 2011). Recovering phosphate from wastewater can eliminate eutrophication to some extent and produce fertilizers as a supplementary source. Furthermore, the problem of global warming can also be alleviated through phosphate recovery (Bradford-Hartke et al., 2015). Some wastewater resources such as livestock wastes and manure have high concentrations of phosphate (Nancharaiah et al., 2016; Tao et al., 2016) while the amounts of such resources are limited. In comparison to them, municipal wastewater has the greatest potential for phosphate recovery (Mehta et al., 2015) because it has high quantities despite containing small concentrations of phosphate (Zhou et al., 2016). Specifically, it was reported that municipal wastewater flows contain rich phosphorus with about 60,000-70,000 t P/a in Germany (Adam, 2011). Hence, municipal wastewater is prioritised to recover phosphate.

In conventional municipal wastewater treatment, Tarayre et al. (2016) reported that approximately 90% of incoming P-load is concentrated in the sewage sludge. In this scenario, 11% of total P-load is incorporated into the sewage sludge through primary settlement while another 28% is incorporated into biomass and removed with the discharge of surplus sludge (Cornel and Schaum, 2009). Thus, the remaining 50% of incoming P load can be removed through other processes (e.g. adsorption and chemical precipitation). Consequently, phosphate in municipal wastewater treatment can be divided into liquid and sludge phases, and both of them can potentially recover phosphate (Nguyen et al., 2016).

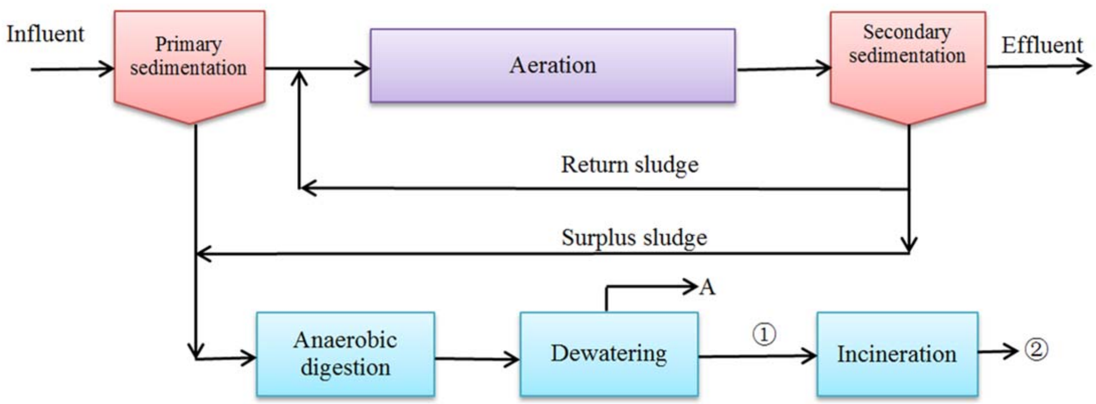

Figure. 1 Different potential locations for phosphate recovery in conventional municipal wastewater treatment (modified from Cornel and Schaum, 2009).

Four potential aspects of traditional sewage treatment can be utilized for phosphate recovery (Cornel and Schaum, 2009). As shown in Fig. 1, the liquid phase for phosphate recovery is sludge liquor (A) while the dewatered sewage sludge (1) and ash (2) are considered to constitute the sludge phase for the phosphate recovery (Bourioug et al., 2015; Egle et al., 2016; Li et al., 2016b). In addition, the sludge liquor is returned to the influent in the municipal wastewater treatment so as the P recovery from the sludge liquor can decrease the load of P by up to 20% (Evans, 2007). Through the incineration of sewage sludge (SS), sewage sludge ash (SSA) is achieved with the simultaneous removal of organic matter. In this process, although mercury is removed in its gaseous form because of its low boiling point, most of the heavy metals are enriched in SSA (Lederer and Rechberger, 2010). SS and SSA previously have been applied to agriculture as a fertilizer due to their high amounts of phosphate (Gong et al., 2015; Sartorius et al., 2011; Zhang et al., 2002). However, their application has been forbidden in some European countries such as Switzerland due to the fact they consist of pathogens, toxic matter and heavy metals (Schoumans et al., 2015). Compared to SS, SSA exhibits better plant availability of phosphate as a raw material for the production of fertilizers as no organic matter is retained in it. It is worth mentioning that the incineration process can only be utilized for SS which contains over 25% of dry solids and conducted in a fluidised sand bed reactor. The reactor is exposed to 800-900 °C with enough oxygen (Zhang et al., 2013) and this temperature range can make P thermally stable and non-volatile. Following the incineration, all the water in SS can be vaporized with the simultaneous removal of organic matter including organic pollutants in their gaseous form such as CO_2 and NO_x, resulting in the phosphate enrichment in SSA. However, the loss of carbon and nitrogen may also reduce the potential value of SSA while being applied as a supplementary source for fertilizer production.

The chemical phosphate recovery from municipal wastewater has been used widely because of its high stability and efficiency (Verstraete et al., 2009). The current state of the main chemical phosphate recovery techniques in municipal wastewater treatment are summarized in Table 1.

Table 1 Overview of main technologies for chemical phosphate recovery from municipal wastewater

Technology	Recovery spot	Main chemicals	P recovery	Lab-scale	Pilot-scale	Plant-scale
Chemical precipitation	Liquid phase	Mg/Ca materials	Over 80%	√	√	√
Adsorption	Liquid phase	Metal-based adsorbents	Over 90%	√	√	-
Wet-chemical process	Sludge phase	Acid/alkaline solution	Over 60%	√	√	√
Thermochemical process	Sludge phase	Chlorides	N/A	√	√	√

With reference to the chemical technique for P recovery from the liquid phase, chemical precipitation attracts more attention compared to adsorption. The possible reason for this is that phosphate recovered by the former process could be easily dewatered and then potentially reused as fertilizers (Chen et al., 2009). Moreover, the P recovery via adsorption needs downstream process such as desorption, thus complicating the recovery process. Nevertheless, adsorption is still important to develop a sustainable supply for phosphate and this process is based on the phosphate-specific adsorbents having good affinity for phosphate. As for P recovery from the sludge phase, wet-chemical process utilizes strong acid or alkali to extract P from SS/SSA. The P-rich supernatant should be then further treated by chemical precipitation/adsorption to obtain phosphate precipitates as the recovered product. At high temperature (over 800°C), thermochemical technology employs chlorides such as $NaCl_2$ and HCl to react with SS/SSA (Adam et al., 2009). In this scenario, the heavy metals can be removed from the sludge phase due to the formation of volatile heavy metal chlorides at such temperature range. For this reason, high purity of recovered phosphate can be achieved.

The view that phosphate recovery from municipal wastewater can supplement increasingly scarce sources of phosphate and reduce the dangers of discharging wastewater into the environment has been widely accepted (Loganathan et al., 2014). Hence, some papers have reviewed the process of phosphate recovery from municipal wastewater, especially focused on the chemical phosphate recovery due to its high stability and reliability. Among those review papers, few review papers compare the merits and drawbacks of the chemical technologies for the phosphate recovery and discuss their technical and economic feasibility. For this reason, this review paper focuses on the comparison of the chemical technologies for phosphate recovery including the technical and economic feasibility to minimize the gap of existing knowledge. Since phosphate in municipal wastewater is retained in the liquid and sludge phases as mentioned above, and the main objective here is to compare the different techniques of chemical phosphate recovery in the two phases. Certainly, the general information of the techniques such as their mechanisms and governing parameters is introduced. Furthermore, the full-scale applications of these methods are discussed to deepen the understandings of different processes. In addition to that, the technical and economic feasibility of the chemical phosphate recovery techniques are also assessed. Simultaneously, the effects of applications of the recovered phosphate on the plants and crops are also reported.

2. Chemical phosphate recovery from the liquid phase

2.1 Technology

2.1.1 Chemical precipitation

Chemical precipitation and adsorption are mainly utilized to recover phosphate from the liquid phase (Chen et al., 2009; Jones et al., 2015; Spears et al., 2013). Chemical precipitation for phosphate recovery means choosing the appropriate chemical as a precipitator which could be added before, after or during the conventional biological treatment of municipal wastewater. Phosphate recovered by this process could be easily dewatered and subsequently potentially reused as a fertilizer (Chen et al., 2009). Calcium and magnesium ions are commonly employed as precipitators to react with phosphate to form $Ca_5(OH)(PO_4)_3$ (hydroxyapatite= HAP) and $MgNH_4PO_4 \cdot 6H_2O$ (struvite= MAP), respectively, as shown in equations (1) and (2) (Desmidt et al., 2015):

$$5Ca^{2+} + 3PO_4^{2-} + OH^- \rightarrow Ca_5(OH)(PO_4)_3\downarrow \quad (1)$$

$$Mg^{2+} + PO_4^{3-} + NH_4^+ + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow \quad (2)$$

Of the recovered phosphate using different approaches, struvite could be directly applied in soil as a fertilizer while HAP could be recycled by the phosphate industry. However, iron and aluminium ions are normally prohibited from use as precipitators as the phosphate recovered via iron/aluminium precipitates is not suitable for application as a fertilizer (Petzet and Cornel, 2012). The possible reason is that phosphate is strongly bound in the recovered phosphate, thus generating little phosphate release. Thus, this scenario may increase the costs of waste disposal and be difficult for uptake by plants (Mehta et al., 2015; Petzet and Cornel, 2012). It is noteworthy that sometimes struvite/HAP is wet or coloured, so further processes such as dewatering, pelletizing and drying are needed to make it more commercially feasible as a fertilizer for the developing market. The formation of struvite and HAP only occurs when the concentrations of phosphate and magnesium/calcium ions outnumber the solubility product constants of the precipitates at fixed value of pH.

Influence of pH

The precipitator sources mainly derive from (hydr)oxides and salts of Mg and Ca (e.g. MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$, $MgCl_2$ and $CaCl_2$). The value of pH is an important parameter for chemical precipitation since it could influence the concentration of free NH_4^+ and PO_4^{3-} (Bi et al., 2014) and the solubility of precipitates (Huang et al., 2015), resulting in the variation of yield, size and purity of recovered phosphate. Moreover, chemical precipitation for phosphate recovery needs to adjust pH (> 8.0) for facilitating the formation of struvite and HAP. However, higher pH (> 10.0) may reduce the efficiency of phosphate recovery because: a) most of the ammonia may be converted into gaseous ammonia through volatilization at high pH and the formation of struvite is thereby affected; b) magnesium/calcium ions are depleted in the form of their hydroxides at such pH, thus the amount of the metal ions involving the precipitation between magnesium/calcium and phosphate may shrink; and c) the free concentration of Ca^{2+} would decline and the calcium phosphate is inhibited at high pH due to the fact that Ca^{2+} prefers CO_3^{2-} to PO_4^{3-} at such pH (Song et al., 2002). It is worth mentioning that ubiquitous calcium ions could react with phosphate ions to form precipitates such as HAP at high pH during chemical phosphate recovery via struvite (Hao et al., 2009). In this scenario, the purity of struvite is affected negatively despite the fact that the efficiency of phosphate recovery increases.

Influence of Chemical dose

The theoretical molar ratios of Mg: N: P and Ca: P are 1:1:1 and 1.7:1 for the formation of struvite and HAP, respectively. However, the experimental dose of magnesium is much larger than the theoretical value in the struvite precipitation because the soluble chemical oxygen demand and some organic substances could combine with magnesium ions and even react with them to form precipitates (Tong and Chen, 2007). Moreover, high concentrations of ammonia could significantly contribute to the formation of struvite due to: firstly, its pH buffering effects; and secondly, its role as a nitrogen supplier (Pastor et al., 2008; Stratful et al., 2004). Sometimes, K^+ can precipitate with Mg^{2+} and PO_4^{3-} to form insoluble $MgKPO_4$ (Huang et al., 2011), thus impairing the purity of struvite even though the adverse reaction could increase the P recovery efficiency. HAP has the highest supersaturation index among all the calcium phosphate precipitates (e.g. $CaHPO_4$, $Ca_3(PO_4)_2$, and $Ca_5(OH)(PO_4)_3$), so it can only be formed at the theoretical molar ratio of Ca/P 1.67 or above (Tran et al., 2014). Furthermore, P removal efficiency could be calculated through theoretical ratios of Ca/P, for which the molar ratios of Ca/P 1:1 and 1.5:1 result in 60% and 90% of total P being removed, respectively. The Ca/P 1.67:1 or above may cause 100% of P being removed when the calcium phosphate precipitates are assumed as HAP.

2.1.2 Adsorption

Phosphate recovery by adsorption shows its obvious advantages such as simple operation and design, and low costs (Loganathan et al., 2014). The process consists of two steps, the adsorption of phosphate and desorption of phosphate-load adsorbent. After desorption, the recovered phosphate is enriched in the ash or desorption solution, which can be utilized for direct land application. It is notable that the phosphate-rich solution after desorption can also be processed by chemical precipitation to form phosphate precipitates. Generally, metal-based adsorbents are mostly studied in the P adsorption due to their easy accessibility. However, aluminum and iron are not encouraged as materials for preparation of adsorbents. The possible reason for this is that Al^{3+} and Fe^{3+} could bind with P tightly, causing Al^{3+} to inflict damage on plants and soil organisms (Johnston and Richards, 2003). Phosphate adsorption on the metal-based adsorbents could be attributed to electrostatic attraction (Weng et al., 2008), ion exchange and surface precipitation (Li et al., 2013b). Besides, the mechanism of P adsorption on the metal-based adsorbents like calcium-based adsorbents may involve adsorption and precipitation (Moon et al., 2007). In this scenario the adsorption occurs first and the surface clusters are subsequently formed by the lateral interaction with P, contributing to crystal growth as nuclei (Oladoja et al., 2015).

Influence of pH

Most importantly, the adsorption of phosphate on the metal-based adsorbents is highly dependent on the value of pH. The possible reasons for this are: firstly, pH can greatly affect the surface charges of the adsorbent, through which the adsorption of phosphate can be controlled (Xie and Zhao, 2016; Yin et al., 2013); and secondly, the species of phosphate vary due to the changes in pH: H_3PO_4 (pH < 2.13), $H_2PO_4^-$ (pH = 2.13-7.20) and HPO_4^{2-} (pH = 7.20-12.33) (Dai et al., 2014). Hence, the P adsorption is inhibited at low pH (< 2.13) because H_3PO_4 as the predominant species of phosphate has no charges. Similarly, high pH causes the phosphate and adsorbents with high negative charges, for which the P adsorption is unfavorable (Loganathan et al., 2014). Moreover, OH^- could compete with phosphate ions for the adsorption sites at high pH and the P recovery is thereby inhibited. However, Fang et al. (2015) discovered that the pH range (4-10) has negligible effects on the adsorption capacity of Ca-Mg loaded biochar for P with fluctuation in 9.0 mg/g of the adsorbent.

Influence of adsorbent dose

Besides, Dai et al. (2014) demonstrated the increase in adsorbent from 0.5 to 4.0 g/L can cause the growth in the P removal efficiency from 31.63% to 99.55% because high adsorbent dose can provide more adequate vacant adsorption sites to phosphate ions. Consequently more phosphate ions are adsorbed. In addition, the main co-existing ions in municipal wastewater such as SO_4^{2-}, NO_3^- and Cl^- may inhibit P adsorption because the co-existing ions may compete for the vacant adsorption sites with phosphate ions and result in the greater coulomb repulsion forces (Dai et al., 2014; Li et al., 2016a; Zhang et al., 2016).

Influence of desorption

Apart from having good affinity for phosphate, the adsorbents should be easily desorbed and effectively regenerated several times. Generally, acids, alkalis and salts are used for desorbing phosphate from the adsorbents. Due to low cost, NaCl and KCl are used for the desorption of phosphate-load adsorbents as salts (Nguyen et al., 2015; Park et al., 2010). However, high salinity may be retained in the desorption solution, meaning that the phosphate recovery from the solution or direct land application of the solution may be ineffective (Johir et al., 2011). Some adsorbents may be dissolved or corroded by acids/alkalis and their structure may be changed by these chemicals (Cheng et al., 2009; Delaney et al., 2011). In this scenario, desorption by the addition of acids/alkalis is not suitable for further phosphate recovery.

1.2 Application at plant-scale

The overview of applications of chemical phosphate recovery from the liquid phase at plant-scale is summarized in Table 2.

Table 2 Overview of chemical phosphate recovery process from the liquid phase in municipal wastewater treatment plant

Plant-scale process	Chemicals	Recovered product	P Recovery	Type of reactor
NuReSys®	$MgCl_2$, NaOH	Struvite	80-85%	Continuous stirred tank reactor
Crystalactor®	$Ca(OH)_2$, NaOH, H_2SO_4, Sand	HAP	70-80%	Fluidized bed
AirPrex®	$MgCl_2$, Flocculent	Struvite	80-90%	Continuous stirred tank reactor
PHOSPAQ®	MgO	Struvite	70-95%	Continuous stirred tank reactor

The NuReSys® process (Moerman, 2012) which was first developed by the Belgian company Akwadok in 2006 uses mixed tanks for phosphate recovery via struvite. Apart from being applied in sewage treatment, the NuReSys® can also be utilized to a broader range of wastewater sources derived from manure treatment, dairy industry, etc. with about 80-85% of P being recovered. Besides, equipment relating to this technology can be easily installed and constructed between the existing anaerobic and aerobic/anoxic pools. In 2013, the NuReSys® process was utilized to treat digested sludge in municipal wastewater treatment and it can recover about 86.4% of phosphate. Fig. 2 presents the process of struvite precipitation from the anaerobic digestion supernatant (Moerman et al., 2009).

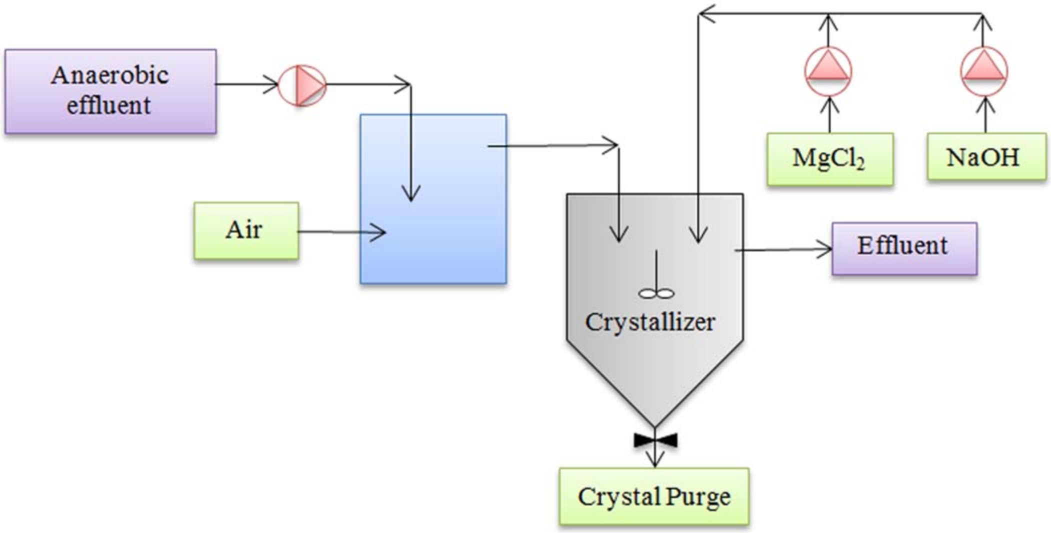

Figure. 2 Flow chart showing the NuReSys® process for phosphate recovery via struvite precipitation (modified from Moerman et al., 2009).

In the NuReSys® process, air stripping is employed to increase pH of influent and dissolve insoluble phosphate while $MgCl_2$ as the magnesium source is added to the crystallization reactor containing 29% of NaOH solution. The aim here is to increase pH in order to contribute to the formation of struvite. A simple blade impeller is placed in the crystallization tank and an advanced automated control algorithm is implemented to achieve the optimized pH (8-8.5), chemical dose and mixing intensity in the process. In this case the ideal crystal growth of struvite could be achieved and reactor scaling avoided simultaneously.

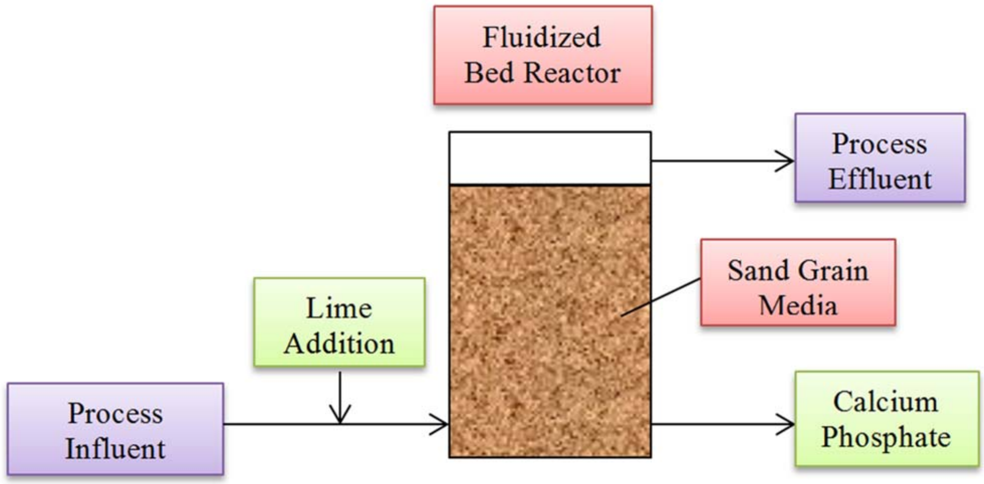

Figure. 3 Flow diagram demonstrating the Crystalactor® process for phosphate recovery via HAP (adapted from Desmidt et al., 2015).

Fig. 3 shows the Crystalactor® process (Van, 1990) to recover phosphate in a cylindrical fluidized bed reactor (Desmidt et al., 2015). The technology was originally developed by a Dutch company, DHV, in the early 1980s with the initial purpose of softening drinking and process water, which was subsequently applied to remove some compounds such as heavy metals at full-scale (Giesen and van der Moldeh, 1996). Before the influent containing phosphate flows to the Crystalactor®, P is collected in buffer tanks and carbonate is simultaneously removed from the feed water in a cascade stripper since the coexisting carbonate may compete with phosphate for calcium ions. As a result, the formation of HAP is detrimentally affected. The process influent flows through the reactor from the bottom up using a pump in the fluidized pellet bed. Besides, sand grains are utilized as seed material to grow HAP crystals in the reactor. Apart from serving as a calcium source, adding $Ca(OH)_2$ solution increases the level of pH to facilitate the formation of HAP and its dose is dependent on the value of pH. Moreover, the technology applied in P recovery at Geestmerambacht (Netherlands) could achieve

26-39 ton·P/year (Wilsenach and Loosdrecht, 2007) and 70-80% of P could be recovered in an appropriate process (Cornel and Schaum, 2009).

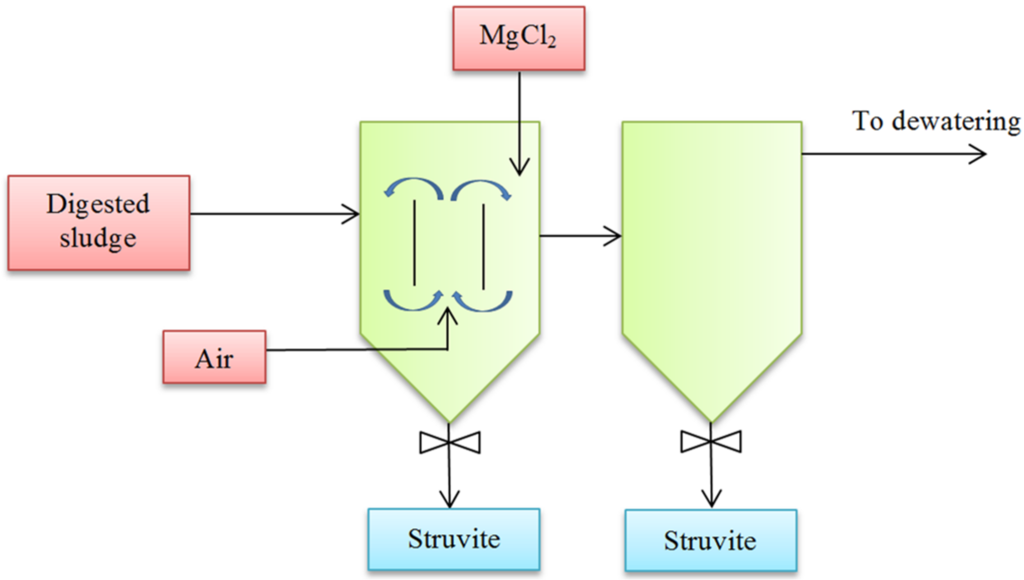

Figure. 4 Flow chart showing the AirPrex® process for phosphate recovery via struvite (modified from Heinzmann. B, 2009)

The AirPrex® process (cnp-Technology Water and Biosolids GmbH, 2015) to recover phosphate from digested sewage sludge has been developed by the Berliner Wasserbetriebe. As shown in Figure 4, the digested sludge flows through a cylindrical reactor, in which the aeration is supplied. $MgCl_2$ is added to the first reactor as the magnesium source for the struvite formation. The possible reason for aeration is: (i) air stripping can increase pH of digested sludge, which benefits the struvite formation; and (ii) the struvite crystals grow in the internal recycle in the first reactor and then sink to the bottom of the reactor when their size can separate from the recycle flow. It is worth mentioning that the smaller size of struvite crystals can settle in the second reactor. In the process, struvite is continuously moved out of the two tanks, after which the recovered struvite is washed and gently dried and its purity and market potential can be thereby improved. In this scenario, less organic-load is observed in the struvite. In the AirPrex® process, the production of sludge is reduced. The possible reasons for this are: firstly, the sludge water absorbing capacities is weakened due to aeration; and secondly, 90% of dissolved phosphate is recycled by struvite (Desmidt et al., 2015; Egle et al., 2016). Therefore, the costs involved in the sludge disposal and transport is decreased. The AirPrex® process has been applied in Germany and Netherlands with 80-90% of phosphate being recovered by struvite from digested sludge and the recovered struvite can be used as a commercial fertilizer (Desmidt et al., 2015).

The PHOSPAQ® process (PAQUES, 2006) was developed by Paques (Desmidt et al., 2015). It is utilized to recover phosphate via struvite in an aerated continuous stirred tank reactor. The aeration facilitates the increase in pH and mix of substances. MgO is preferred to be supplied as the magnesium source compared with $MgCl_2$ as it is cheaper and beneficial for increasing pH. The formation of struvite is optimized at pH range of 8.2-8.3 in the tank (Driessen, 2009). A special separator system is equipped in the tank for retaining struvite within the reactor. The bigger size of struvite crystals will sink to the bottom of the tank and then be harvested and dewatered while aeration may cause the accumulation of the smaller size of the crystals in the suspension, which results in further crystallization of struvite. The recovered struvite is removed from the bottom of the tank and then transferred to another container. In 2006, the PHOSPAQ® technology was employed at plant-scale in Olburgen (Netherlands) to recover phosphate from the mixed influent containing anaerobically treated effluent and reject water from indusial municipal wastewater treatment, respectively (Desmidt et al., 2015). In this scenario, 1.2 ton·of struvite could be achieved daily (Abma et al., 2010; Driessen, 2009).

In the four processes mentioned above, struvite and HAP are formed and sink to the bottom of the reactors making it possible for them to grow crystals. The crystals may need to be purged regularly from the reactors. In comparison to HAP, struvite can conserve nitrogen which is easy to volatilize. Moreover, N loss would reduce the potential value of recovered phosphate as a fertilizer and pose a risk to the environment (Kataki et al., 2016). This makes the process of P recovery via struvite (e.g. NuResys process®) more attractive. It is worth noting that the high operational cost and complexity of Crystalactor technology may inhibit its application (Desmidt et al., 2015).

2. Chemical phosphate recovery from the sludge phase

2.1 Technology

3.1.1 Wet-chemical treatment

Generally, phosphate fixed in the sludge phase (i.e. SS and SSA) exhibits low plant availability (Kahiluoto et al., 2015; Qin et al., 2015), so the wet-chemical approach and thermochemical treatment are the main technologies for phosphate recovery from the sludge phase (Appels et al., 2010). In wet-chemical technology phosphate bound in the SS/SSA is released by adding strong acids (e.g. HCl and H_2SO_4) or alkalis (e.g. NaOH) to the liquid phase. This process can simultaneously reduce the content of heavy metals, pathogens and other toxic substances in the supernatant. After phosphate is released to the liquid phase through the wet-chemical process, chemical precipitation and adsorption are mainly utilized to recover phosphate from the supernatant. Normally, phosphate extraction from the sludge phase by adding acids is more effective than simply adding alkalis.

The wet-chemical process is highly dependent on pH because pH can affect the efficiency of phosphate recovery and the species of P (Cokgor et al., 2009). However, Xie et al. (2011) believed that the species of P bound in SS derived from various wastewater treatment plants seem similar even if the P concentrations in SS are different. Furthermore, the properties of SSA can be affected by incineration temperature, so the temperature is also considered to be an important parameter in the wet-chemical process of SSA.

Acid leaching

Over 80% of P can be released from SS/SSA through acid leaching at low pH (< 2.0) (Donatello et al., 2010). The ratio of acid to SSA/SS can determine the amount of P released and acids needed. Normally, the required amount of strong acids is about 0.3-0.68 kg/SSA, which can result in 66.5-99.4% of P being dissolved (Petzet et al., 2012). Besides, the dissolution of metal compounds such as CaO and MgO will also react with acids and thus increase the depletion of acids. It is worth noting that H_2SO_4 is prioritized for use in the wet-chemical process as an acid due to its low cost and easy accessibility (Donatello and Cheeseman, 2013). Moreover, if the phosphate-rich leachate is processed by struvite precipitation for phosphate recovery, H_2SO_4 can react with Ca^{2+} to reduce its disturbance of the process. However, Cohen (2009) found that H_2SO_4 cannot release P from SSA effectively. In addition, phosphoric acid (~52% H_3PO_4) as industrial grade can be used to dissolve phosphate bound in SSA in a rotary kiln. This scenario could enhance the enrichment of phosphate and create a product which is similar to triplesuperphosphate (Weigand et al., 2013):

$$Ca_4Mg_5(PO_4)_6 + 12H_3PO_4 + 2H_2O \rightarrow 4Ca(H_2PO_4)_2 + 5Mg(H_2PO4)_2 + 12H_2O \quad (3)$$

Heavy metals or their compounds may simultaneously release from the sludge phase at low pH (< 2.0). The amount and type of dissolved heavy metals depend on: firstly, the composition of SS/SSA; and secondly, the concentration and type of added acids. Although concentrations of dissolved metal ions can be reduced at pH range of 3-4, this range can also decrease the released amount of P from the sludge and subsequent P recovery is thereby compromised. For this reason many technologies such as ion exchange (Donatello et al., 2010) and nano filtration (Niewersch et al., 2009) are applied to remove heavy metals from the P-rich leachate so that they are less restrictive of phosphate recovery. It is remarkable here that phosphate bound in SSA in the form of aluminum/iron phosphate is unsuitable as a supplementary source for fertilizer production.

Alkali leaching

Alkali leaching could directly separate P from heavy metals in SS/SSA because most heavy metals cannot dissolve in alkaline solutions. However, this scenario may cause precipitation of some metal ions such as Mg^{2+} and Ca^{2+}. Furthermore, if Al-salts are used for P removal in wastewater treatment plants, Al-P can be released from SS/SSA in the alkaline extraction process due to the amphiprotic property of Al. The release efficiency of phosphate increases at high pH (Li et al., 2013a) because the sludge cells can be disintegrated only at pH > 11 and then release phosphate to the liquid phase (Becerra et al., 2010). However, Li et al. (2012) found the level of pH of the alkaline extraction supernatant is still at 12 even after 24 h, which may severely affect subsequent phosphate recovery via chemical precipitation. The wastewater treatment plant in Gifu (Japan) utilizes alkali leaching for phosphate recovery, achieving about 60-70% of total P recovered from SSA (Takaoka et al., 2010). In addition, NaOH is the preferred alkali leachate in most cases due to producing more P dissolved (Torres and Lloréns, 2008).

3.1.2 Thermochemical treatment

In the thermochemical treatment process, chloride additives such as NaCl, KCl, $MgCl_2$ and $CaCl_2$ are mixed with SS/SSA at high temperatures (800-1000 °C) (Adam et al., 2009). In this scenario, most of the heavy metals could be removed due to the formation of volatile heavy metal chlorides which can be captured in the flue gas with further processing to clean them (Herzel et al., 2016). For example, Zn in SSA could be removed through the addition of $CaCl_2$:

$$2HCl + ZnO \rightarrow H_2O + ZnCl_2 \qquad (4)$$

$$2Cl_2 + 2ZnO \rightarrow O_2 + 2ZnCl_2 \qquad (5)$$

Humid reaction atmosphere may easily result in the formation of either HCl or Cl_2 and then volatile Zn can react with them to form $ZnCl_2$ which is easily removed with the emission of flue gas due to its low evaporation temperature. Most heavy metals can be removed from the sludge phase via the thermochemical process, but some heavy metals (e.g. As and Ni) are still retained in the sludge phase (Nowak et al., 2013). The heavy metals in the flue gas could be treated by the filter while $MgCO_3$ and $NaHCO_3$ are utilized to adsorb chloride and remove SO_2, respectively. In addition, Na_2SO_4 could replace the chlorides as an additive to treat SS/SSA for the formation of $NaCaPO_4$ (Vogel et al., 2016).

Mattenberger et al. (2008) reported that the thermochemical treatment of SSA with 5-15% of KCl or $MgCl_2$ can result in the highly efficient removal of heavy metals such as Pb, Cd and Cu. SSA treated by thermochemical means with $MgCl_2$ can be only effectively applied in acidic soils as a fertilizer (Nanzer et al., 2014) and the product satisfies the stringent requirement of German fertiliser standards (Adam et al., 2009). It is highlighted that higher temperatures facilitate better plant availability of P in the treated SSA (Donatello and Cheeseman, 2013).

2.2 Application at plant-scale

The chemical phosphate recovery process from the sludge phase at full-scale is summarized in Table 3.

Table 3 Overview of chemical phosphate recovery process from the sludge phase at plant-scale in municipal wastewater treatment

Plant-scale process	Chemicals	Recovered product	P Recovery	Type of reactor
Seaborne®	H_2SO_4, Na_2S, NaOH, MgO, flocculent	Struvite	> 90%	Continuous stirred tank reactor
AshDec®	$MgCl_2$, $CaCl_2$	Multi-nutrient fertilizers including P, nitrogen and potassium	N/A	Furnace

The Seaborne® process was put into operation at pilot-scale in 2000 in Owschlag (Germany) (Schulz et al., 2001) and the first large-scale installation of the process occurred in the wastewater treatment plant located in Gifhorn (Germany) with capacity for about 1,000 tons of dry SS per year. This process aims to treat SS and recover P and N in the form of struvite with the simultaneous removal of heavy metals and clean of digester gas. Fig. 5 presents the Seaborne® process as a wet-chemical approach to recover phosphate from the sludge phase (Müller et al., 2005).

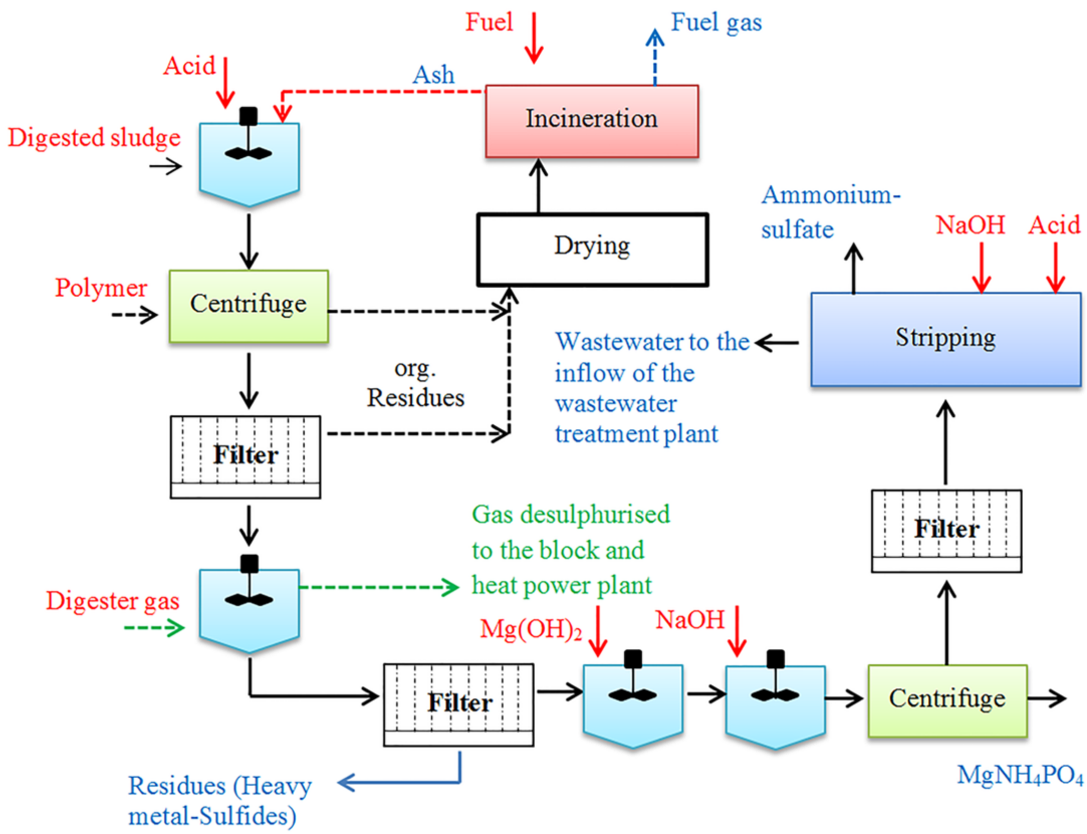

Figure. 5 Diagram of the Seaborne® process (adapted from Müller et al., 2005).

In this Seaborne® process, pH of digested sewage sludge is first adjusted to 4 through adding strong acids such as H_2SO_4 with the simultaneous dissolution of phosphate, organic matter and partial heavy metals. At this pH level, the amount of heavy metals dissolved can be reduced even if the phosphate release may to some extent be inhibited. The organic substances can be selectively removed through dewatering and incineration of the sludge and then SSA (i.e. incinerated SS) is returned to the initial stage of the Seaborne® process. If the digester gas containing H_2S is supplied to react with heavy metals, the removal of heavy metals can be achieved through precipitation and the precipitates are separated by a belt filter. Simultaneously, desulphurising of the digester gas occurs. After that, $Mg(OH)_2$ is added as a magnesium source to react with P and ammonium to form struvite while NaOH is used to increase pH. The recovered phosphate is centrifuged for separation from the liquid phase.

Furthermore, the centrate containing surplus ammonia is washed by H_2SO_4 in an air stripping column, leading to the removal of ammonia in the form of di-ammonium sulphate, while the treated wastewater is returned to the influent. However, the precipitation of calcium carbonate may occur in the column head with the simultaneous conversion of nitrogen to ammonia due to rising pH. For this reason, additional costs are needed to clean the top part of the column regularly. Besides, the colloidal size of the heavy metal precipitates may inhibit their separation from the liquid phase in the belt filter (Müller et al., 2005).

The AshDec® process is utilized as a thermochemical treatment to recover phosphate from SSA in a rotary kiln. This process was conducted in the European project named "SUSAN-Sustainable and Safe Re-use of Municipal sewage Sludge for Nutrient Recovery". It operated from 2005 to 2008 and involved treating 4000 kg·SSA/h in an Austrian plant in Leoben (ASHDEC, 2008).

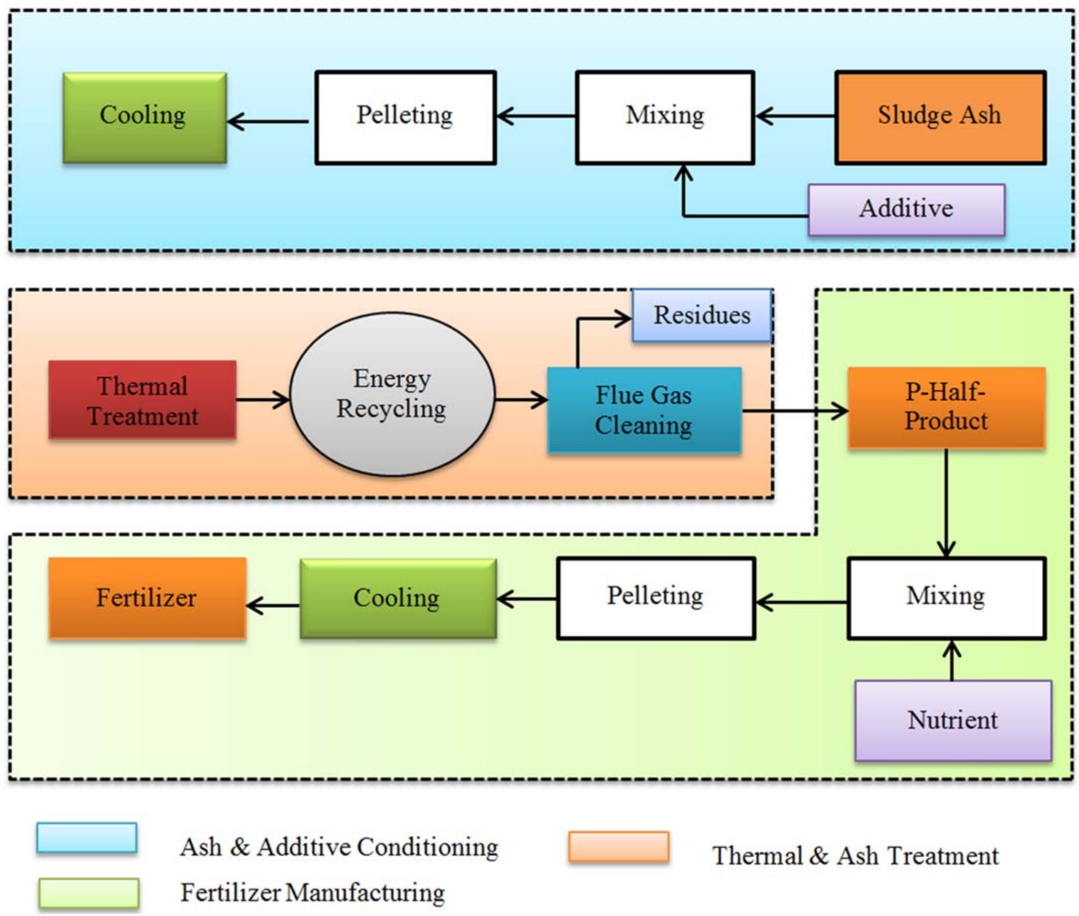

Figure. 6 Diagram of the AshDec® process (adapted from ASHDEC, 2008).

Firstly, SSA mixes with $MgCl_2$ or $CaCl_2$ and the mixture is compacted in a pellet press and then exposed to a temperature range of 850-1000 °C for a minimum reaction time of 20 min in a thermal reactor. The dose of chloride additives is highly dependent on the composition and weight of SSA. In this scenario, most of the heavy metals such as As, Zn and Pb can be removed in the form of their respective gaseous chlorides by reacting with the additives. The hot kiln off gas could be used to heat SSA for recycling and saving energy. Subsequently, 98% of SSA can be achieved in the form of P-rich granules, which is followed by the addition of nutrients such as nitrogen and potassium and multi-nutrient fertilizers are thereby produced. Although the AshDec® process can produce the fertilizer which meets the requirements of EU fertilizer standards, it has to consume large amounts of energy for increasing plant availability of phosphate. Hence, this process is costly and complex. Nevertheless, this process can recover the desired phosphate without moisture content, thus further improving the process of phosphate recovery.

Both of the Seaborne® and AshDec® processes require specific equipment to treat SS and SSA. Doing so will make the phosphate recovery process more complicated and increase the costs involved. It is evident that by-products are both observed in these two processes such as acid sludge in the Seaborne® process and heavy metal chlorides in the AshDec® process. Consequently an additional process is needed to dispose of these unwanted products and this drives up operational costs. Compared to the Seaborne® process, the AshDec® process seems simpler because it can directly remove heavy metals and achieve the recovered phosphate while the former process has to use more complicated technology such as ion exchange to separate heavy metals from phosphate in the supernatant. Furthermore chemical precipitation is necessary to recover phosphate from the supernatant. The AshDec® process has to consume more energy compared to the Seaborne® process since it needs heat to separate phosphate from heavy metals (Egle et al., 2016).

3. Comparison of phosphate recovery in the liquid and sludge phases

3.1 Technology

Table 4 Advantages and disadvantages of different chemical phosphate processes

Chemical phosphate recovery process	Advantage	Disadvantage
Chemical precipitation	High efficiency Simple operation Running stability	High depletion of chemicals Large chemical sludge produced
Adsorption	Easy controllability Simple operation and design	High requirement for adsorbents Needs downstream process (e.g. desorption)
Wet-chemical process	Less organic-load High efficiency	High consumption of chemicals and energy Needs downstream process and specific equipments
Thermochemical process	High purity of recovered phosphate	High consumption of energy Needs specific equipments

As shown in Table 4, the obvious advantage of chemical precipitation and adsorption for chemical phosphate recovery is its simple operation, yet the high consumption of chemicals and separation of recovered phosphate from other recovered products remain serious challenges that may inhibit their application. These processes may also produce large volumes of chemical sludge (Zhang et al., 2014) and thus pose an operational burden and danger to the environment. Phosphate recovery via adsorption has high requirements for adsorbents such as good affinity for phosphate and wide applicability. The P recovery through adsorption needs a downstream process such as desorption. If a phosphate-load adsorbent is desorbed by the addition of acids, alkalis and salts, the phosphate is then transferred to the supernatant and a further process such as chemical precipitation is necessary. Hence, adsorption requires more processes compared to chemical precipitation for phosphate recovery from the liquid phase. Moreover, recovering phosphate from the liquid phase could be applied at nearly all sewage treatment plants as it may not need complex or additional equipment.

Obviously, phosphate recovery from the sludge phase is more complicated compared to that from the liquid phase due to the complex composition of SS/SSA. Some by-products such as volatile (heavy) metals and acidic sludge may be produced in the phosphate recovery process from the sludge phase, and subsequent processes are needed to reduce their risks to the environment. Furthermore the wet-chemical process for phosphate recovery may deplete many chemicals while thermochemical treatment may consume more energy, so both processes seem to result in high operational costs. Fermentation of the sewage sludge and acid-resistant equipment are needed while applying the wet-chemical process for phosphate recovery. However, it is not economic when implemented at small plant-scale. Similarly, thermochemical treatment needs corrosion-resistant equipment due to the high concentration of volatile Cl^- compounds in the flue gas (Fraissler et al., 2009). Phosphate recovered via the wet-chemical approach is purer than that by the thermochemical treatment due to residual ash existing in the recovered product in the latter process. Compared to thermochemical treatment, wet-chemical treatment may produce by-products such as acidic sludge and high levels of heavy metals of supernatant, which may limit its application for phosphate recovery. Besides, SSA is achieved through the incineration of SS, so recovering phosphate from that source must cost much more than from other sources.

3.2 Application of recovered phosphate

The low solubility of struvite with 0.0018 g/mL at 25 °C in water could lead to a slow phosphate release rate (Bridger et al., 1962) and struvite shows higher dissolution rates compared to those derived from conventional phosphate rock (Roncal-Herrero and Oelkers, 2011). Although struvite may consist of heavy metals such as Cd, Cu and Cr, and organic pollutants (Kataki et al., 2016), the amounts of impurity in struvite are less than those in commercial phosphates (Forrest et al., 2008; Latifian et al., 2012). It is worth noting that struvite has the same fertilizer potential as triple superphosphate at the broader pH range of soil (neutral and acidity), based on a 2-year pot experiment with maize (Cabeza et al., 2011). The accumulation of Mg will be detected in soil while applying struvite as a fertilizer over a long period of time, but the coexisting Mg could enhance the P intake by crops because of synergistic outcomes (González-Ponce et al., 2009). However, some plants treated by struvite have produced smaller yields than those with chemical fertilizers due to the poor availability of phosphate in struvite (Ackerman et al., 2013; Ganrot et al., 2007). For this reason, it is recommended to use struvite to supplement chemical fertilizers.

Moreover, the adsorbents synthesised by metal(s) and biochar show enormous advantages for phosphate recovery (de Rozari et al., 2016; Fang et al., 2015; Yao et al., 2013b). The possible explanation for this is that the adsorbents can restore the soil ecosystems due to biomass derived carbon (Case et al., 2014) and also be used as a fertilizer in agriculture (Yao et al., 2013a). Moreover, the organic matter in these adsorbents could be removed if the P-load adsorbent is desorbed by calcination (Xie et al., 2015). However, Fang et al. (2015) used Ca-Mg/biochar to recover P from an alkalescent solution and found the adsorbent after desorption may be more applicable in an acid soil as a fertilizer. In addition, the P recovered via calcium phosphate could only be efficient in acid soils (Tarayre et al., 2016).

Hirota et al. (2010) discovered that using thermochemical treatment for phosphate recovery could generate a raw material which contains similar level of P to the phosphate rock. In their study, Vogel et al. (2010) believed that thermochemical treatment for SSA can produce a raw material for fertilizer production. However, approximately 10% of input chloride additives are detected in the recovered phosphate after thermochemical treatment and this may inhibit the application of recovered phosphate in soils where the concentration of chlorine is strictly controlled (Adam et al., 2007). Adam et al. (2009) indicated that higher solubility of P in citric acid (2%) means better plant availability of P in SSA. They also found that the solubility of P rose from 25-40% to 97% after thermochemical treatment with $MgCl_2$ at 1000 °C. It is noteworthy that SSA treated by $MgCl_2$ exhibits more efficiency when applied as a fertilizer than that treated by $CaCl_2$ (Nanzer et al., 2014).

3.3 Economic feasibility

In municipal wastewater treatment, chemical phosphate recovery from the sludge phase normally needs more capital than that from the liquid phase. It is reported that recovering P from the liquid phase costs €6-10 (≈ US$6.72-11.2)/kg·P while the total costs of P recovery through wet-chemical process is €9-16 (≈ US$10.07-17.91)/kg·P (Egle et al., 2016). This is because the former process has to convert phosphate bound in the sludge phase to the liquid phase through the wet-chemical approach or to increase the bioavailability of phosphate via thermochemical treatment. Hence, more consumption of chemicals and/or energy is observed with specific equipment and downstream processes utilized when recovering phosphate from the sludge phase. The investment in specific equipment accounts for a great deal of total costs (Egle et al., 2016). Moreover, the process of phosphate recovery from the sludge phase may produce unwanted by-products such as acidic sludge and supernatant-containing rich heavy metals. Recovering phosphate from the liquid phase can also decrease the back-flow of phosphate and the operational costs for treating municipal wastewater can be therefore lowered. Moreover, the P recovery can save €2-3 (≈ US$2.24-3.36)/kg·P of operational costs compared with the P removal (Dockhorn, 2009).

The costs of chemical precipitation and adsorption for chemical phosphate recovery mainly include the depletion of chemicals for reaction and energy for mixing (Sakthivel et al., 2012). The total costs for the phosphate recovery via chemical precipitation could be reduced by using: a) CO_2 stripping for increasing pH instead of NaOH solution; and b) $Mg(OH)_2$ as a magnesium source instead of $MgCl_2$ (Jaffer et al., 2002). Huang et al. (2015) used magnesium and calcium materials as precipitators to recover phosphate. In their study, they analysed the production costs in term of depletion of chemicals and energy. Specially, using $CaCl_2$ and $MgCl_2$ as the precipitator for P recovery costs US$1.56 and 0.82/kg·$P_{Total}$, respectively, while applying air stripping for increasing pH. However, when NaOH solution is utilized to increase pH, the total costs for the P recovery via $CaCl_2$ and $MgCl_2$ is increased to US$1.85 and 0.95/kg·$P_{Total}$. It also shows that adding NaOH solution to increase pH is less economical than air stripping, which is reverse to the study of Jaffer et al. (2002). This is mainly because the feed water in the two studies came from different wastewater sources. In addition, US$0.38/kg·$P_{Total}$ for P recovery can be obtained while applying MgO as the precipitator with air stripping. Kumar and Pal (2015) also reported that the seawater containing high concentration of magnesium ions can be economical to supply Mg^{2+} if the location of phosphate recovery is near a coastal area, because the consumption of Mg^{2+} accounts for 75% of total costs involved in the struvite formation. The P recovery via struvite from municipal wastewater can minimize the sludge production and reduce the operational costs by AUD$1.13 (≈ US$0.86)/kg·struvite (Shu et al., 2006). Jeanmaire and Evans (2001) stated that recovering phosphate from municipal wastewater can save costs with UK 100 pounds (≈ US$124.33)/ton·P.

Referring to the wet-chemical process, some specific microorganisms can produce sulphuric acid to dissolve P fixed in the sludge phase with 90% of P recovered (Chi et al., 2006). This may reduce the depletion of chemicals despite the fact that the stability and reliability of the biological community are big challenges for the process. Besides, the thermochemical treatment can utilize the methane gas as a supplementary energy source while a heat exchanger can be used to effectively save the thermal energy derived from the process. If SSA can be directly transported from the incinerator to the subsequent thermochemical treatment, less energy might be consumed. Alternatively, the incinerator can be located near the plant to save the costs of transferring SSA. In addition, acid extraction for P bound in the sludge phase can produce phosphoric acid which has a high market value. Using CO_2 is a promising method instead of mineral acids since the former can reduce the depletion of chemicals, but more studies are needed to ascertain this. Furthermore, renewable energy such as solar energy can be utilized for the sustainable operation of chemical phosphate recovery system and to keep operational costs down.

Currently, the use of rock phosphate for fertilizer production is more economical than the application of recovered P (Hukari et al., 2016; Molinos-Senante et al., 2011). The possible reason is that the prices of raw phosphate rock and triple superphosphate are €0.6-1.2 (≈ US$0.67-1.34) and €1.2-2.2 (≈ US$1.34-2.46)/kg·P (Desmidt et al., 2015) while the market price of struvite is €2.6 (≈ US$2.91)/kg·P (Dockhorn, 2009). Besides, the totals costs of P recovery is highly dependent on the technology, ranging from €2.2 to 8.8 (≈ US$2.46 to 9.85)/kg·P (Schaum, 2007). In this study, the total costs are less than that reported by Egle et al. (2016) as the two references are published in different years and the costs such as labor costs increase from 2007 to 2016. Nevertheless, it can still be concluded that phosphate recovered by chemical methods needs more costs compared to the commercial phosphate. However, phosphate recovery from municipal wastewater is a need due to worldwide demand for increasing amounts of fertilizer and the environmental benefits such as alleviation of eutrophication (Molinos-Senante et al., 2011). In addition, the scaling speed can be reduced while the dewaterability of treated sludge can be enhanced through phosphate recovery (Bradford-Hartke et al., 2015; Zhang and Chen, 2009), for which operational issues such as pipe clogging can be addressed (Marchi et al., 2015).

4. Future perspectives

Phosphate recovery from municipal wastewater could supplement the demand of phosphate and ensure a more sustainable way of human life. Successful chemical phosphate recovery needs to avoid phosphate loss and more effort is required to find a sustainable way of reusing recovered phosphate.

Chemical precipitation and adsorption for phosphate recovery from the liquid phase are highly stable and efficient, but the existing foreign ions and high consumption of chemicals may compromise their application. In addition, the concentration of phosphate in influent of municipal wastewater treatment is normally less than 10 mg/L and the economic feasibility of chemical phosphate recovery may thereby be inhibited (Yuan et al., 2012). For example, Dockhorn (2009) studied the economic feasibility including the operational and maintenance costs of P recovery from digested sludge and found that when the phosphate concentrations are 50 and 800 mg/L, the recovery costs are €2800 and 520 (≈ US$3135.16 and 582.24)/ton·struvite, respectively. Similarly, Mehta et al. (2015) also considered that the phosphate accumulation is needed before the P recovery implemented in the municipal wastewater treatment. Hence, the high P concentration can save costs in the chemical phosphate recovery process. As membranes have selective high-rejection for ions, a phosphate-rich stream could be created. For this reason, the combination of chemical precipitation/adsorption and membrane technology can be employed to recover P from sewage even though the membrane fouling and high costs of membrane synthesis may affect the application. Among the different types of membrane, the forward osmotic (FO) process is the mostly studied as it can highly reject the phosphate and inorganic ions such as NH_4^+, Mg^{2+} and Ca^2 with low potentiality of membrane fouling and energy consumed (Luo et al., 2016). In addition, FO can be used for pre-concentrating municipal wastewater (Ansari et al., 2016a) despite the fact that the regeneration of the draw solution still remains a challenge for the use of FO. Ansari et al. (2016b) recently utilized the seawater as the draw solute in the FO process and found that the seawater can not only provide the driving force, but also supplement the essential metal ions such as Mg^{2+} and Ca^{2+} for the P recovery via chemical precipitation due to the reverse draw flux. In this scenario, 92% of P is recovered by this hybrid system (FO process integrated with chemical precipitation). Moreover, a FO-membrane distillation (MD) hybrid system integrated with struvite precipitation can recover P from digested sludge centrate with simultaneous recovery of fresh water (Xie et al., 2014). Moreover, biological process such as enhanced biological phosphorus removal (EBPR) system can also recover P by concentrating phosphate in the surplus sludge through polyphosphate-accumulating organisms (PAOs) under alternating anaerobic and aerobic/anoxic conditions (Yuan et al., 2012). In this scenario, phosphate recovery is achieved via the discharge of surplus sludge, but the direct land application of P-rich surplus sludge has been forbidden in some European countries such as Switzerland (Schoumans et al., 2015). Due to this, Yan et al. (2015) applied EBPR system integrated with chemical precipitation at full-scale and this hybrid system can recover 74.5% of total P. However, the stability and reliability are big challenges for EBPR system. It is worth noting that chemical precipitation can integrate with the combination of membrane technology and biological process for the P recovery. To examine this concept, Luo et al. (2016) used the osmotic membrane bioreactor (OMBR) with microfiltration extraction to concentrate phosphate and then recovered P via calcium phosphate with high efficiency. In addition, the chemical phosphate recovery process can be integrated with bioelectrochemical systems such as microbial fuel cells (MFC) and microbial electrolysis cells (MEC), in which the phosphate recovery can be enhanced while energy can also be recovered (Ahmed et al., 2015).

Although chemical phosphate recovery process integrated with the EBPR system has some drawbacks mentioned above, the hybrid system is still a promising method to create a purer recovered phosphate and improve the economic feasibility (Kumar and Pal, 2015; Vraale and Jenssen, 2005). To develop the hybrid system, more research on their efficiency and economic feasibility are necessary. Further, the recovered phosphate should be investigated for its composition and agricultural applications. The application of recovered phosphate in agriculture should also consider the type of soil and plant as well as the weather conditions.

For the chemical phosphate recovery from the sludge phase, more depletion of chemicals energy and downstream processes may limit its application. However, the disturbance of the interfering substances such as organic matter can be minimized in this scenario. Although the binding strength of P in SSA is greater than that in SS, phosphate recovery from SSA still has higher potential. The possible reasons for this are: a) the incineration of SS could remove organic matter including organic pollutants; b) most wastewater treatment plants have to incinerate SS, so the incineration process will not increase additional costs in the phosphate recovery process; and c) if SSA is treated by thermochemical treatment, the majority of volatile heavy metals could be removed. Thus only negligible amounts of waste are retained in the recovered phosphate and the costs of the application of recovered solid as a fertilizer are reduced. The process of phosphate recovery from SSA needs more research on reusing energy and application of treated SSA in soils.

5. Conclusion

As the phosphate rock is finite and increasingly consumed due to the increasing requirement of the fertilizer production, the chemical phosphate recovery has been employed in municipal wastewater treatment from liquid and sludge phases. The main reasons are: (i) the chemical techniques for the phosphate recovery have high stability and reliability; and (ii) municipal wastewater with high quantity can be used as a supplementary source for phosphate recovery despite containing low content of P. The chemical technologies for phosphate recovery have been applied at plant-scale with good performance. In comparison to chemical P recovery from the liquid phase, recovering P from the sludge phase needs more depletion of chemicals and energy and specific equipment, thus increasing the total costs in this process. Although the recovered phosphate as fertilizers is less economical than the commercial fertilizers in the agriculture, it can still be a supplementary resource of fertilizers. The low content of P in municipal wastewater may reduce the economic feasibility of the P recovery and thus compromise the applications at full-scale. To address this concern, chemical phosphate recovery can be integrated with biological system (e.g. EBPR system), membrane technology or their combination to maximize the economic feasibility. Further studies are needed to assess the viability of this hybrid system and then make its application more accessible.

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