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Phosphorus recovery from municipal and fertilizer wastewater: China's potential and perspective

Phosphorus recovery from municipal and fertiliser wastewater: China's potential and perspective

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HIGHLIGHTS:

- Review on current state of wastewater treatment plants and sludge treatment in China
- Assessment of discharged and recoverable P in Chinese wastewater
- A perspective on available technologies for P recovery according to specific conditions in China are presented
- Potentials and opportunities to recover and recycle phosphorus from wastewater were assessed
- Strategies and recommendations for future P-recovery in China
ABSTRACT

Phosphorus is a limited resource, which can neither be synthesized nor substituted in its essential functions as nutrient. Currently explored and economically feasible global reserves may be depleted within generations. China is the largest phosphate fertiliser producing and consuming country in the world. China's municipal wastewater contains up to 293,163 Mg/a of phosphorus (P) which equals approximately 5.5% of the chemical fertiliser phosphorus consumed in China. Phosphorus in wastewater can be seen not only as a source of pollution to be reduced, but also as a limited resource to be recovered. Based upon existing P-recovery technologies and the current wastewater infrastructure in China, three options for phosphorus recovery from sewage sludge, sludge ash and the fertiliser industry according to the specific conditions in China were analysed.

KEYWORDS

Phosphorus recovery, Municipal Wastewater, Fertiliser Industry, Sewage sludge, China
1. INTRODUCTION

Phosphorus is non-regenerable and non-replaceable limited resources (Asimov, 1959). Currently explored and economically feasible global reserves may be depleted within only a few generations (Childers et al., 2011). By 2050, the world’s population is estimated to reach 9.1 billion; in order to feed the growing population, agricultural production would need to increase by 70 percent overall and nearly 100 percent in developing countries (FAO, 2009). China is a big country with a large population and limited farmland area per capita with only 0.08 ha per capita compared with the world average of 0.2 ha per capita in 2012 according to the World Bank (WB, 2014). The production of sufficient food to feed the population is of vital importance for the country. In the year 2001, phosphorus was identified by the Ministry of Land and Resources of the People’s Republic of China (MLR, 2012) as one of the most important 20 minerals which, after 2010, cannot meet the development needs of the national economy.

According to statistics from the United States Geological Survey (USGS, 2015), China's phosphorus reserves are 3.7 billion Megagram (Mg), 5.52% of the global total volume. Based on current phosphate rock mine production with 100 million Mg in 2014 (USGS, 2015), Chinese phosphorus ore may run out within 37 years. It is a remarkable fact that there is only little high-grade phosphorus ore, but the country is rich in low-grade phosphorus ore. More than 80% is low grade phosphate rock and the average grade only reaches 17% of phosphorus pentoxide (P₂O₅) (Huang et al., 2014; Lu, 2004).

In Europe, phosphate rock is officially considered to be one of the 20 critical raw materials by the European Commission in 2014 (EC, 2014). The recovery of phosphorus has been repeatedly discussed due to the strong dependency above 90% on imports (De Ridder et al., 2012) and the food security of the growing population worldwide. Various phosphorus recovery technologies have been developed and tested in pilot or industrial scale. Among these technical options, phosphorus is mostly recovered by precipitation or crystallization processes in the form of HAP (hydroxyapatite, Ca₅(PO₄)₃OH) or struvite (MgNH₄PO₄·6H₂O). The recovered products can be utilized as fertiliser in agricultural or specific industry.

Consequently, closure of the anthropogenic phosphorus cycle through recovery and recycling of phosphorus from municipal wastewater and sludge, as well as from special industry wastewater, may help to avoid eutrophication, promote resource conservation and increase the value chain efficiency of this precious resource.

2. STATUS OF THE MUNICIPAL WASTEWATER INFRASTRUCTURE IN CHINA
2.1 The development of urban sewage treatment

In 1984, the first large-scale wastewater treatment plant (WWTP), the Tianjin Jizhuangzi wastewater treatment plant was built and put into operation with a treatment capacity of 260,000 m$^3$ (Fu et al., 2008). After 1990, with the rapid development of the economy, rapid urbanization and industrialization and the increasing environmental standards in China, the wastewater treatment infrastructure stepped into a rapid development period and improved the quantity of wastewater treatment facilities and also the effectiveness of treatment.

![Figure 1: Development of urban sewage treatment from 2005 to 2013 in China (MOHURD, 2016)](image)

Fig.1 shows the development of treatment capacity for urban sewage and the number of facilities from 2005 to 2013. During the past years, China's sewage treatment sector has experienced rapid development. In April 2015, the General Office of the State Council issued the “National Water Pollution Prevention and Treatment Action Plan of China” (MEP, 2015) to address nationwide water protection; the objective of municipal wastewater treatment is that by the end of 2020, the city and county municipal wastewater treatment rates should reach 95% and 85% respectively.

Although China’s urban wastewater treatment industry has seen much progress in terms of scale and number since the 1990s, the conditions of the municipal water networks and the treatment rate in rural areas still needs to be improved. In 2013, the wastewater treatment rate of the cities, counties, towns and villages are respectively 89%, 79%, 19%, 5% (MOHURD, 2016). The majority of wastewater generated in rural areas undergoes limited or discharge to water bodies without treatment. According to the corresponding population distribution in
different areas (MOHURD, 2016), 37% of the population is connected to wastewater treatment systems in China.

2.2 Wastewater Treatment Process

There are three major steps in state-of-the-art wastewater treatment schemes, i.e. primary physical treatment, secondary biological treatment and tertiary treatment (Halling-Sørensen and Jorgensen, 1993). Most Sewage treatment plants in China are centralized with biological wastewater treatment.

![Variety of different processes of municipal WWTPs in China](image)

**Figure 2: Variety of different processes of municipal WWTPs in China**

Fig. 2 shows the variety and distribution of different processes of WWTP in China. According to the statistics of the Ministry of Environmental Protection of the People's Republic of China (MEP, 2014) for 4,136 commissioned wastewater treatment plants in 2013, the most widely used technologies are the Oxidation Ditch Process with a share of 27%, the Anaerobic-Anoxic-Oxic (A²/O) process with a share of 26% and the Sequencing Batch Reactor (SBR) process with a share of 19%.

3% of super-large-scale (>30×10⁴ m³/d) and 13% of large-scale (10-30×10⁴ m³/d) WWTPs, were generally built in large and medium-sized cities. Most of these plants apply the A²/O process. The ratio of medium-scale (1-10×10⁴ m³/d) WWTPs was 75%. They were generally built in medium and small size cities and commonly apply the oxidation ditch and SBR processes (Jin et al., 2014).
2.3 Phosphorus removal in WWTPs

Two methods are currently being used around the world to remove phosphorus in wastewater: biological and chemical phosphorus removal and combination of both. In China, influent \( \text{NH}_4^-\text{N} \) ranges from 40 to 55 mg/L, and total phosphorus (TP) ranges from 4 to 9 mg/L (Jin et al., 2014). According to the “Discharge standard of pollutants for municipal wastewater treatment plant” (GB18918-2002), the primary A standard of total phosphorus concentration in WWTPs effluent built after 2005 should not exceed 0.5 mg/L. It is quite difficult to meet this requirement with biological phosphorus removal alone (Qiu and Ding, 2002). A potential reason for the low efficiency of enhanced biological phosphorus removal (EBPR) is the competition for carbon sources between denitrification and phosphorus release in sludge under an anoxic condition with respect to the sludge retention time (SRT) demand, the nitrate inhibition of phosphate release, which is not easily resolved (Chen et al., 2011; Peng et al., 2010; Qiu and Ting, 2014).

2.4 Sewage sludge treatment in China

In China, thickening, conditioning and dewatering are the three most applied methods for sludge treatment (Yang et al., 2015). There is no accurate official data of sludge disposal in China, rather conflicting sources with different estimates. According to (Yang et al., 2015), more than 84% of sludge is disposed by improper dumping. Regarding proper disposal, the most commonly used method is sanitary landfill (13%), followed by land application (2%), incineration (0.4%) and building materials (0.2%). Data from (Wang et al., 2015) indicates that, the most widely used disposal route was landflling with a ratio of 63%, followed by compost and agricultural use with the ratio of 14%, incineration with the ratio of 2%. The disposal route for around 22% of sludge was unknown. Many WWTPs in China did not report clearly the treatment and final disposal of their sludge (Jin et al., 2014). In general, the majority of sludge is often without stabilization or drying and disposed to sanitary landfill or dumping sites.

So far, anaerobic sludge digestion (AD) is not been widely used in China. Until 2010, only about 50 WWTPs adopted AD to stabilize sludge and some of them were not under stable operation or were even closed (Kong, 2012). The main problems for sludge digestion are the lack of an overall development plan on AD, the technical design parameters of sludge digestion not matching the specific local condition. On the other side, the utilization and efficiency of sludge digestion in China is not being high due to the low production of gas and the lower economic benefit. The technical reasons are the high sand content and less volatile organic compounds with 30–50% in the sludge (Dai et al., 2014). According to the overall
situation in China, thickening–anaerobic digestion–dewatering and following land application (Does not include agricultural use) can be considered as the main technical route of sludge treatment and disposal in the future. This route is favorable to large-scale and medium-scale WWTPs due to the limited land resources in the city and shortage in energy supply in economically developed regions (Yang et al., 2015).

3. MATERIALS AND METHODS

Phosphorus recovery and recycling options need to be ecologic, including social acceptance and economical and technical feasibility. Based on real operational data and samples from selected WWTPs in China and available technical solutions in the EU research and demonstration project P-REX (www.p-rex.eu), a systematic analysis of different options was conducted. The total concentration of phosphorus and nitrogen in sludge water, supernatants and centrates and were determined by spectrophotometry according to respective Chinese standards (GB11893-89) and (HJ636-2012). Ammonia nitrogen was determined with titration according to (GB7478-87).

For the determination of iron (Fe) and aluminium (Al) in sludge and sludge ash, samples were digested with nitric acid/hydrochloric acid according to the ASTM D3974-09 and measured in accordance with US EPA 6010/ICP-OES and US EPA 6020/ICP-MS. For the determination of phosphorus, samples were digested with sulphuric acid according to the APHA 4500P B, H.

4. POTENTIAL AND OPTIONS FOR PHOSPHORUS RECOVERY IN CHINA

In the year 2013, there was a total of 45.1 billion m³ (MOHURD, 2016) of municipal wastewater treated in counties and cities. The total phosphorus concentration in the WWTP influents ranged from 4 to 9 mg/L (Jin et al., 2014). Based on the average value of 6.5 mg/L, the phosphorus discharged to municipal wastewater in cities and counties added up to approximately 293,163 Mg in the year 2013. The quantity of this phosphorus in municipal wastewater in 2013 corresponds to 6% of the chemical fertiliser phosphorus (P) consumption of 5.3 teragram (Tg) (Li et al., 2015) in 2010 in China.

According to a statistical analysis of 98 WWTPs in China (Guo et al., 2009), the total P concentration in municipal sewage sludge varies significantly, from a low of 2.2 g/kg of sludge dry matter to 51.3 g/kg (Li et al., 2003) with a mean value of 22.2 ± 6.64 g/kg. The treatment plants with high P concentration in sludge are mostly located in phosphate mining areas or in highly developed areas, e.g. Yunnan or Hong Kong. With the dry sludge production of 7.55 million Mg in 2013 (MOHURD, 2016) and the content mean value for phosphorus, the total phosphorus that is contained in the current Chinese sewage sludge is
estimated to be 167,634 Mg/a, or in other words, 57% of the totally discharged phosphorus. This low rate of P in sludge might be due to the dilution in sanitary sewers by infiltration and inflow, which causes low phosphorus of influent as the average value of 6.5 mg/L.

Figure 3 Hot spots for P recovery in WWTP (Kabbe and Remy, 2013). 1. Direct agricultural utilization of dewatered sludge; 2a. Undrained sludge after anaerobic digestion; 2b. Sludge liquor after dewatering; 3. From Ash after undiluted incineration

At a municipal wastewater treatment plant, phosphorus can be recovered and recycled mainly from three locations (Fig. 3). The first is direct land utilization of sewage sludge, the second includes the dissolved P in the aqueous sludge phase prior to dewatering and sludge liquor after dewatering and the third is the recovery from mono-incineration ash.

The maximum recovery potential from the aqueous phase and sludge phase without extraction are respectively 25% and 20% with regard to the WWTP influent (Kabbe, 2015). For the recovery by sludge leaching (2a, 2b), a maximal P recovery rate of 70% can be achieved at high chemical and/or energy cost. Large amounts (70% - 85% of WWTP influent) of P can be recovered from mono-incineration ash (Egle et al., 2015; Niewersch et al., 2014). However, energy demand of ash treatment can vary depending on the process (ash leaching, thermo-chemical, metallurgic) and the potential integration of thermal processes into existing incineration facilities for efficient heat management (Remy, 2015).

P uptake from different P products of P recycling has been tested (Achat et al., 2014; Kataki et al., 2016; Römer, 2013; Wilken et al., 2015). Products from precipitation processes Mg compounds consistently showed a better P supply in relation to comparable Ca compounds. With struvite the same P uptake as triple super phosphate (TSP) was reached.
The traditional land utilization of sewage sludge in agriculture is being considered as one of the most economical ways for sludge disposal, but the presence of toxic heavy metals, organic contaminants and pathogens in the sewage sludge greatly limits its direct use as a fertiliser. According to a study of heavy metals in sewage sludge over China (Guo et al., 2014), the concentration of Cu, Zn, Cd, Hg, and Ni in alkaline soils, about 2%, 6%, 6%, 3%, 4% of the samples exceeded the limits set by “Discharge standard of pollutants for municipal wastewater treatment plant” of China (GB18918-2002). In acid soils the non-attainment rate of Cu, Pb, Zn, Cd, Hg, Cr and Ni were 7%, 1%, 10%, 27%, 20%, 2% and 12%, respectively. The main sources of the heavy metals may be derived from high-density industrial zones, non-ferrous metal ores and anthropogenic activities (Guo et al., 2014). The source control of wastewater, especially the industry wastewater, can help decrease the amount of heavy metals entering the sewer and ensuring the quality of sludge.

Agricultural soils are also significantly influenced by Cd, Hg and Pb derived from anthropogenic activities (Wei and Yang, 2010). The sewage sludge use on agricultural land is strictly limited. The amount, duration and quality of sludge applied to agriculture should meet the requirements of “Control standards for pollutants in sludges from agricultural use” (GB4284-84) and other existing relevant agricultural standards and regulations. Hence, cost-effective alternative strategies and technologies for phosphorus recovery for agriculture are needed.

5. RESULTS AND DISCUSSIONS

5.1 Option: Recovery in sludge

Dissolved phosphorus is recovered directly from the digested sludge. In the AirPrex® process, the struvite is crystallized within the wet sludge and can, therefore, prevent down-stream struvite scaling and, at the same time, improve the sludge dewater ability by 3–6 % dry matter content and save the polymer costs for sludge dewatering (Heinzmann and Lengemann, 2014).

Table 1: Anaerobic sludge digestion projects in China

<table>
<thead>
<tr>
<th>Name</th>
<th>Wastewater Treatment process</th>
<th>Sludge Treatment capacity (Mg DS/d)</th>
<th>Disposal</th>
<th>year of operation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing Gaobeidian</td>
<td>active sludge treatment process</td>
<td>160</td>
<td>-</td>
<td>1999</td>
<td>(Jiang, 2014)</td>
</tr>
<tr>
<td>Beijing Xiaohongmen</td>
<td>AAO process with biological phosphorus removal</td>
<td>160</td>
<td>land application</td>
<td>2009</td>
<td>(Chen, 2013; Zhang et al., 2014)</td>
</tr>
<tr>
<td>Chongqing Jiguanshi</td>
<td>reversed AAO process, combined biological and chemical phosphorus removal</td>
<td>90</td>
<td>co-incineration and land application</td>
<td>2009</td>
<td>(Zhang, 2009)</td>
</tr>
<tr>
<td>Location</td>
<td>Treatment Process</td>
<td>Phosphorus Recovery</td>
<td>Year</td>
<td>References</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>---------------------</td>
<td>------</td>
<td>------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Dalian Xiajiahe</td>
<td>Constant Waterlevel SBR with biological P-removal</td>
<td>land application</td>
<td>2009</td>
<td>(Dai et al., 2008; Yang et al., 2015)</td>
<td></td>
</tr>
<tr>
<td>Haikou Baishamen</td>
<td>activated sludge and biological aerated filter, chemical phosphor removal</td>
<td>agricultural use</td>
<td>2005</td>
<td>(Pan et al., 2006; Sun et al., 2008)</td>
<td></td>
</tr>
<tr>
<td>Qingdao Maidao</td>
<td>Enhanced clarification and lamella settling with biological aerated filter (BAF)</td>
<td>land application</td>
<td>2008</td>
<td>(Wang et al., 2012)</td>
<td></td>
</tr>
<tr>
<td>Shanghai Bailonggang</td>
<td>AAO process with chemically enhanced primary treatment</td>
<td>land application</td>
<td>2011</td>
<td>(Jiang et al., 2013)</td>
<td></td>
</tr>
<tr>
<td>Wuhan Sanjintan</td>
<td>modified A/O process with biological phosphorus removal</td>
<td>land application</td>
<td>2013</td>
<td>(Zhu, 2009)</td>
<td></td>
</tr>
<tr>
<td>Zhengzhou Wangxin</td>
<td>AAO process with biological phosphorus removal</td>
<td>-</td>
<td>2009</td>
<td>(Li et al., 2007)</td>
<td></td>
</tr>
<tr>
<td>Tianjing Jizhuangzi (Tianjing Jinnan sludge treatment plant)</td>
<td>AAO process with deep bed filtration, combined biological and chemical P-removal</td>
<td>land application</td>
<td>2015</td>
<td>(NCME, 2013)</td>
<td></td>
</tr>
</tbody>
</table>

In table 1 selected sewage sludge digestion projects in China are listed. These WWTPs are mostly operated with combined biological and chemical phosphorus removal. Among them, several plants have reported that struvite precipitation has been an problematic issue, e.g. Shanghai Bailonggang (Jiang et al., 2013), Haikou Baishamen (Pan et al., 2006). For most of these plants with anaerobic digestion, land application is the first choice for sewage disposal. This option is designed for a significantly more efficient for WWTPs with biological Phosphorus elimination (Bio-P) and sludge digestion. For the phosphorus that is fixed within the sludge, after chemical precipitation with ferrous or ferric, aluminum, direct struvite crystallization is not a suitable option for recovery. Hence, with the current sewage and wastewater treatment facilities in China, only a few WWTPs are adapted to this option, such as Dalian Xiajiahe, Wuhan Sanjintan Beijing Xiaohongmen WWTP etc. The current limits of this option for the WWTPs in China are the shortage of combined biological phosphorus removal and anaerobic sludge digestion.

**5.2 Option: Recovery from sludge water**

Phosphorus is recovered from the supernatants of the digested sludge after liquid-solid separation. In the Struvia™, Pearl®, and Airprex® process, an important component of these technologies are crystallization reactors. In these processes, struvite is precipitated by dosing MgCl₂ and increasing the pH by adding caustic soda (NaOH) or aeration.
Table 2: Parameters of sludge water in WWTP A in China (mean value) 

<table>
<thead>
<tr>
<th></th>
<th>Influent</th>
<th>Effluent</th>
<th>Supernatant Pre-thickener before digester</th>
<th>Supernatant Post-thickener after digester</th>
<th>Centrate after dewatering</th>
<th>Total returns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
</tr>
<tr>
<td><strong>Total nitrogen (TN)</strong></td>
<td>23.9</td>
<td>19.8</td>
<td>391</td>
<td>614</td>
<td>533</td>
<td>320</td>
</tr>
<tr>
<td><strong>NH₄-N</strong></td>
<td>19.0</td>
<td>15.6</td>
<td>325</td>
<td>489</td>
<td>398</td>
<td>249</td>
</tr>
<tr>
<td><strong>Total Phosphorus</strong></td>
<td>3.5</td>
<td>2.0</td>
<td>205</td>
<td>289</td>
<td>238</td>
<td>180</td>
</tr>
</tbody>
</table>

*The sludge water samples were taken from WWTP A in China from January to May 2014. The influent and effluent of the WWTP were analysed every two days. Other supernatants and centrates were analysed every second week.*

Municipal wastewater treatment plant A in south China has a capacity of 300,000 m³/d, and the wastewater is treated with activated sludge process and before discharge to the deep sea. After digestion, phosphate is released into the liquid phase, in which total phosphorus increases from 205 mg/L to 289 mg/L (Table 2). Under specific conditions, this phosphate reacts with magnesium and ammonium and buildup struvite in pipes and dewatering facilities, which needs to be cleaned every one or two weeks by high pressure water in this plant. The replacement of pipelines with external mechanical cleaning is also used to cope with the scaling problem in another WWTP in the east coast of China. The mechanical treatment is preferred due to economic reasons, i.e. the low cost of manpower, compared to the chemical treatment by anti crustation agents. In the Tianjing Chennan sludge treatment plant, a new project with recovery of phosphate from sludge water with AirPrex® process is under construction.

Regarding the high soluble phosphorus and ammonia concentration in centrates in such plants in China, techniques are available, to recover 80–90% of the dissolved phosphorus (Niewersch et al., 2014) in sludge water. The limits of this option are no more than 20% of a WWTP’s Phosphorus load can be recovered, and this only if enhanced biological P removal is applied, and its economic viability should be considered.
5.3 Option: Recovery from sludge water with sludge extraction

Phosphorus is recovered from the supernatant of the digested sludge after acidic leaching or thermal hydrolysis pre-treatment and followed by liquid-solid separation e.g. the Gifhorn, Stuttgart and Budenheim process.

Due to the additional increase of phosphorus dissolved in the sludge supernatant by acidic treatment, the processes with sludge extraction step are applicable for digested sludge from WWTPs with both EBPR and chemical P elimination. Hence, with the current sewage and wastewater treatment facilities in China, Shanghai Bailonggang, Haikou Baishamen and Tianjing Jinnan WWTP, among others, are technically suitable for this option. However, it was shown that with the current reagent strategies and investment costs, the struvite recovery process was not economically feasible for WWTPs with AD and P-physicochemical removal, only in the case of Bio-P removal WWTPs with AD (Garcia-Belinchón et al., 2013).

5.4 Option: Phosphorus recovery from sewage sludge ash

The P recovery from sewage sludge ash (SSA) is generally divided into two approaches: the wet-chemical (LeachPhos) and thermal processes (AshDec). Wet-chemical approaches consist of an acidic or alkaline digestion of SSA followed by a separation of P from dissolved (heavy) metals and organics. In Germany, 54.7% (Wiechmann et al., 2015) of the sludge is incinerated, and only about 3.45% (Fang et al., 2012) of sludge in China is treated by incineration. The quantity of recoverable phosphorus in sludge ash in China is not calculable due to the lack of reliable mono-incineration data.

Table 3: Analysis of selected parameters of composite sludge feed to incinerator and sludge ash in the Sludge Treatment Facility in Hong Kong, China

<table>
<thead>
<tr>
<th></th>
<th>Sludge</th>
<th>Sludge Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% Moisture Content (dried @103°C)</td>
<td>% P Dry Matter</td>
</tr>
<tr>
<td>Test on December 4th, 2014</td>
<td>69.3</td>
<td>0.925</td>
</tr>
<tr>
<td>Test on January 2nd, 2015</td>
<td>67.2</td>
<td>1.12</td>
</tr>
<tr>
<td>Mean</td>
<td>68.25</td>
<td>1.023</td>
</tr>
</tbody>
</table>

*The tested sludge and sludge ash samples were taken from incineration Sludge Treatment Facility in Hong Kong from December 2014 to January 2015.*

The Sludge Treatment Facility (STF) in Hong Kong is the world's largest sludge incineration facility with a capacity of 600 Mg of dry sludge per day. The facility adopts fluidized bed
incineration technology to decompose sewage sludge at 850°C. In Table 3, the selected parameters of composite sludge feed to incinerator and sludge ash are presented.

SSA in the STF of Hong Kong contains a phosphorus (P) concentration of around 4%, which, compared to the mean phosphorus content in Germany of 8.9% (Krüger and Adam, 2015) is only half of the content as in Germany. The concentrations of aluminum (Al) 3.3% and iron (Fe) 11.8% in Hongkong are similar to the mean value in Germany, 5.2% and 9.9% respectively (Krüger and Adam, 2014). For elementary white phosphorus $P_4$ production with the Thermphos process the molar ratio of Fe/P reaches about 0.6 in Hong Kong, which exceed the limit value of 0.2 (Petzet and Cornel, 2009). The high iron concentration in SSA increases the energy demand and reduces the output of $P_4$. Although with the current available technology approximately 2000 t P/a can be recovered in this plant, the relatively low phosphorus concentration should be considered to ensure the economic viability. The limitation of this option in China is the low P concentration in sludge ash compared to Europe.

6. PHOSPHATE FERTILISER INDUSTRY

Various industries produce wastewater that contains a high concentration of phosphorus. This includes fertiliser, semiconductor, phosphoric acid processing and swine wastewater (Hao et al., 2011). The mentioned processes (Struvia™, Crystallactor, Pearl®, AirPrex® etc.) for sludge water are also applicable to industrial wastewater containing a significant concentration of dissolved ortho-phosphate.

China is not only the largest phosphorus consumer but also the largest producer. There were 1,118 phosphate fertiliser enterprises in China in 2005 (Zhang et al., 2009), and in the plants, a significant amount of wastewater containing phosphate and fluoride is generated. The use of lime as a precipitating agent for fluoride and phosphate can be considered as the most common technique for wastewater from phosphate fertiliser plants (Grzmil and Wronkowski, 2006). But the large amount of phosphorus in the wastewater cannot be directly recycled in agriculture due to the low plant availability of fluoroapatite (Manahan, 1997; Ndala et al., 2010). A controlled phosphorus recovery with separate precipitation of fluorides and phosphates in a two-stage process would be an adapted option. It was found that, by acting on precipitation pH ranging from 2.6 to 3.7, a “selective” removal of 97–98% fluoride from phosphoric acid/hydrofluoric acid mixture was possible while that of phosphate did not exceed 6–8% (Gouider et al., 2009). It can also be observed that, using calcium, fluorides were mainly separated (pH 3) in the first stage, and phosphates (pH 8) were mainly separated in the second stage amounted to ca. 85–88% and ca. 63–73%, respectively. (Grzmil and Wronkowski, 2006).
Table 4: Different streams and compositions of wastewater in a fertiliser plant in China

<table>
<thead>
<tr>
<th></th>
<th>Wastewater flows (m³/h)</th>
<th>COD (mg/L)</th>
<th>NH₄-N (mg/L)</th>
<th>F (mg/L)</th>
<th>TP (mg/L)</th>
<th>SS (mg/L)</th>
<th>pH</th>
<th>TN (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia Wastewater</td>
<td>200</td>
<td>300</td>
<td>300</td>
<td>/</td>
<td>/</td>
<td>200</td>
<td>8</td>
<td>300</td>
</tr>
<tr>
<td>Phosphate fertiliser Wastewater</td>
<td>200</td>
<td>/</td>
<td>50</td>
<td>80</td>
<td>240</td>
<td>100</td>
<td>5</td>
<td>50</td>
</tr>
</tbody>
</table>

*a Data came from the operator of wastewater treatment plant*

Table 4 shows the different streams and compositions of wastewater in a big fertiliser plant in the East China. The WWTP has two major types of wastewater: respectively ammonia wastewater with 300 mg/L ammonia-nitrogen from synthetic ammonia production and phosphorus-containing wastewater with 240 mg/L total phosphorus from phosphate fertiliser production. The high concentration of both components in the wastewater provides a good possibility for producing magnesium ammonium phosphate. The excess ammonium in the wastewater, with a molar ratio (N:P) of more than 1, is also beneficial for struvite precipitation (Warmadewanthi and Liu 2009). For struvite formation in this fertiliser wastewater plant, an additional magnesium source is needed. A high calcium content in wastewater resulted in more calcium compounds rather than struvite in the precipitations (Hao et al., 2008). In this wastewater treatment plant approximately 1,800 t of struvite can be recovered annually by the technology currently available, and the product can be sold directly to customers. Unlike in Europe, China is abundant in phosphate fertiliser plants, which produce a large amount of wastewater with a high concentration of phosphate and ammonia. Wastewater treatment with P recovery can provide a promising prospect for future P recovery in an ecological and economically efficient way.

7. SUMMARY AND PERSPECTIVE

Growing urbanization in China caused a rising trend in domestic wastewater and sewage sludge discharges. The contained phosphorus is not yet recycled and ends up in water bodies or landfills.

An analysis of the potentials and limitations of existing P recovery technologies, taking into account their applicability to different types of WWTPs in China, shows that a huge amount of phosphorus is transferred to wastewater and sludge. However, some limitations should be taken into consideration, e.g. the existing WWTP infrastructure and sludge disposal routes.
From a long-term perspective, anaerobic digestion followed by land application can be considered as the main technical route of sludge disposal for large-scale and medium-scale WWTPs. In this way, a large part of the phosphorus will be recycled in lands, gardens or parks in China. However, the quality of biosolids for land application should be strictly controlled. On sloping land there is the risk of runoff reaching watercourses and causing water pollution. It is in this sense that a clean sludge also gives cleaner water. For the WWTPs with struvite incrustations the P recovery from sludge can be seen as the best option to solve this problem, instead of frequent mechanical cleaning. In most cases of recovery from sludge water, dissolution of P from solid sludge into the aqueous phase is needed. As special cases, sludge with an extremely high concentration of phosphorus potentially provides positive economics for the recovery of phosphorus, e.g. as in Yunnan and Hong Kong.

The average concentration of phosphorus in SSA in China is lower than that in Germany due to the high sand content in sludge and a lack of separation of rain water and municipal sewage. Therefore, the ash option is limited due to the low rate of mono-incineration and the low P concentration in SSA.

Therefore, the following suggestions for the future P recovery in China are:

- Increase wastewater collection and improve the phosphorus removal
- Promotion of sludge digestion and Bio-P and withdrawal from precipitation with iron salts
- A development strategy for a long-term perspective in sustainable P-recovery
- A legal framework governing recycling and the market for fertilisers
- Development of business models of companies utilizing P streams from wastewater
- Encouragement of research and promotion of a new treatment technology for P rich wastewater

8. Conclusion

There is no doubt that phosphorus is a finite resource. Although there is no “one-fits-all” option for phosphorus recovery and most of the P recovery technical options for municipal WWTPs face strong limitations in China, more efforts should be taken to increase both energy and resource efficiency. The recovery from industrial wastewater with a high concentration of phosphorus shows a higher potential than in municipal WWTPs due to easier market access and benefits to its operators. With an expected increasing percentage of municipal sewage sludge digestion and biological phosphorus removal, P recovery as struvite and recycling as fertiliser is recommended as one of the favorable options for P recycling.
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