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Review

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

Kuangxin Zhou[1,2,*], *Matthias Barjenbruch*[2], *Christian Kabbe*[1], *Goulven Inial*[3], *Christian Remy*[1]

1. *Berlin Centre of Competence for Water, Berlin 10709, Germany*
2. *Department of Urban Water Management, Technical University of Berlin, Berlin 13355, Germany*
3. *Research & Innovation Asia, Veolia Environment, Beijing 10004, China*

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ABSTRACT

Phosphorus (P) 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 fertilizer producing and consuming country in the world. China's municipal wastewater contains up to 293,163 Mg year of phosphorus, which equals approximately 5.5% of the chemical fertilizer 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 phosphorus-recovery technologies and the current wastewater infrastructure in China, three options for phosphorus recovery from sewage sludge, sludge ash and the fertilizer industry were analyzed according to the specific conditions in China.

Introduction

Phosphorus (P) is a non-regenerable and non-replaceable limited resource (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% overall and nearly 100% 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 in 2012 compared with the world average of 0.2 ha per capita, according to the World Bank (2014). The production of sufficient food to feed the population is of vital importance to the country. In the year 2001, P 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 P reserves are 3.7 billion Megagrams, 5.52% of the global total volume. Based on the current phosphate rock mine production of 100 million Mg in 2014 (USGS, 2015), Chinese P ore may run out within 37 years. It is a remarkable fact that there is only a small amount of high-grade phosphorus ore, but the country is rich in low-grade phosphorus ore. More than 80% is low grade

* *Corresponding author.* E-mail: Kuangxin.zhou@kompetenz-wasser.de (Kuangxin Zhou).

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phosphate rock and the average grade only reaches 17% of the phosphorus content of phosphorus pentoxide (P_2O_5) (Huang et al., 2014; Lu, 2004).

In Europe, phosphate rock was 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 on imports, above 90%, (De Ridder et al., 2012) and the food security needs of the growing population worldwide. Various P recovery technologies have been developed and tested at pilot or industrial scale. Among these technical options, P is mostly recovered by precipitation or crystallization processes in the form of HAP (hydroxyapatite, $Ca_5(PO_4)_3OH$) or struvite ($MgNH_4PO_4 \cdot 6H_2O$). The recovered products can be utilized as fertilizer in agriculture or in specific industries.

Consequently, closure of the anthropogenic P cycle through recovery and recycling of P 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.

1. Status of the municipal wastewater infrastructure in China

1.1. *The development of urban sewage treatment*

In 1984, as 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.

Fig. 1 shows the development of treatment capacity for urban sewage and the number of facilities from 2005 to 2013. During the past several 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 need to be improved. In 2013, the wastewater treatment rate of the cities, counties, towns and villages was respectively 89%, 79%, 19%, and 5% (MOHURD, 2016). The majority of wastewater generated in rural areas undergoes limited treatment 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.

1.2. *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.

Fig. 2 shows the variety and distribution of different processes in WWTP in China. According to the statistics of the Ministry of Environmental Protection of the People's Republic of China (MEP, 2014) for 4136 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 (A^2/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 × 10^4 m^3/day) and 13% of large-scale (10 × 10^4–30 × 10^4 m^3/day) WWTPs were generally built in large and medium-sized cities. Most of these plants apply the A^2/O process. The percentage of medium-scale (1 × 10^4–10 × 10^4 m^3/day) 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).

1.3. *Phosphorus removal in WWTPs*

Two methods are currently being used around the world to remove P in wastewater: biological and chemical P removal and combinations of both. In China, influent NH_4-N ranges from 40 to 55 mg/L, and total P 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 P concentration in WWTPs effluent built after 2005 should not exceed 0.5 mg/L. It is quite difficult to meet this requirement with biological P removal alone (Qiu and Ding, 2002). A potential reason for the low efficiency of enhanced biological phosphorus removal is the competition for carbon sources between denitrification and P release in sludge under an anoxic condition with respect to the sludge retention time demand, and the nitrate inhibition of phosphate release, which is not easily resolved (Chen et al., 2011; Peng et al., 2010; Qiu and Ting, 2014).

1.4. *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 are no accurate official data on 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 use in building materials (0.2%). Data from Wang et al. (2015) indicates that the most widely used disposal route was landfilling with a ratio of 63%, followed by composting and agricultural use with the ratio of 14%, and incineration with the ratio of 2%. The disposal route for around 22% of sludge was unknown. Many WWTPs in China did not report clearly on the treatment and final disposal of their sludge (Jin et al., 2014). In general, the majority of sludge is often disposed to

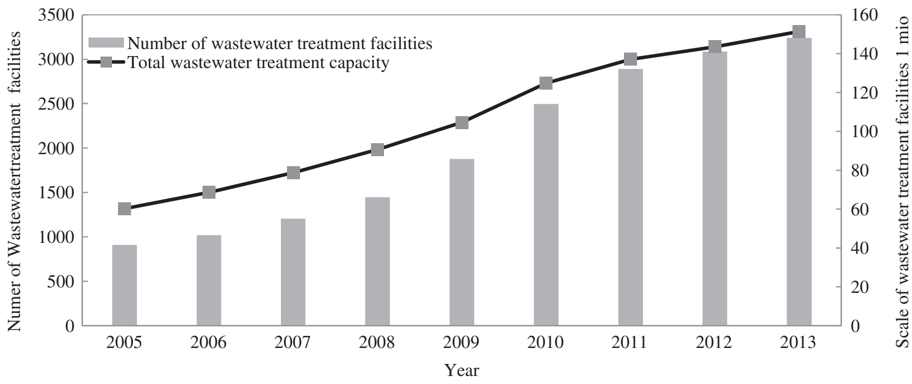

Fig. 1 – Development of urban sewage treatment from 2005 to 2014 in China (MOHURD, 2016).

sanitary landfill or dumping sites without stabilization or drying.

So far, anaerobic sludge digestion (AD) is not 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 for AD, and the technical design parameters of sludge digestion not matching the specific local conditions. On the other side, the utilization and efficiency of sludge digestion in China is not high due to the low production of gas and the lower economic benefit. The technical reasons are the high sand content and lower amounts of volatile organic compounds in the sludge (Dai et al., 2014). According to the overall situation in China, thickening–anaerobic digestion–dewatering and subsequent land application (does not include agricultural use) can be considered as the main technical route for sludge treatment and disposal in the future. This route is favorable for large-scale and medium-scale WWTPs due to the limited land resources in the city and shortage of energy supply in economically developed regions (Yang et al., 2015).

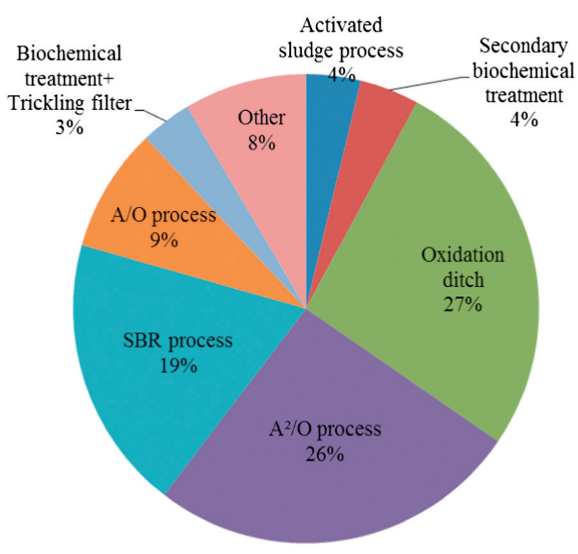

Fig. 2 – Variety of different processes of municipal wastewater treatment plants in China.

2. Materials and methods

P recovery and recycling options need to be ecologically sound, taking into consideration both social acceptance and economical and technical feasibility. Based on real operational data and samples from selected WWTPs in China and available technical solutions from the EU research and demonstration project P-REX (www.p-rex.eu), a systematic analysis of different options was conducted.

The total concentrations of P and nitrogen in sludge water, supernatants and concentrates were determined by spectrophotometry according to the respective Chinese standards (GB11893-1989) and (HJ636-2012). Ammonia nitrogen was determined by titration according to (GB7478-1987).

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

3. Potential and options for phosphorus recovery in China

In the year 2013, there was a total of 45.1 billion m^3 (MOHURD, 2016) of municipal wastewater treated in counties and cities. The total P 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 P discharged to municipal wastewater in cities and counties added up to approximately 293,163 Mg in the year 2013. The quantity of this P in municipal wastewater in 2013 corresponds to 6% of the chemical fertilizer 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 a high of 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 mean content value for P, the total P contained in the current Chinese sewage sludge is estimated to be 167,634 Mg/year, or in other words, 57% of the total discharged P. This low rate of P in sludge might be due to dilution in sanitary sewers by infiltration and inflow, which causes low P in the influent with the average value of 6.5 mg/L.

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

The maximum recovery potential from the aqueous phase and sludge phase without extraction is respectively 25% and 20% with regard to the WWTP influent (Kabbe, 2015). For recovery by sludge leaching (2a, 2b in Fig. 3), 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, the energy demand of ash treatment can vary depending on the process (ash leaching, thermo-chemical, metallurgical) 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). Regarding products from precipitation processes, Mg compounds consistently showed better P supply in relation to comparable Ca compounds. With struvite, the same P uptake as triple super phosphate was reached.

The traditional land utilization of sewage sludge in agriculture is considered 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 fertilizer. According to a study of heavy metals in sewage sludge over China (Guo et al., 2014), regarding the concentrations of Cu, Zn, Cd, Hg, and Ni in alkaline soils, about 2%, 6%, 6%, 3%, and 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 rates for 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 industrial wastewater, can help decrease the amount of heavy metals entering the sewer and ensure the quality of sludge.

Agricultural soils are also significantly influenced by Cd, Hg and Pb derived from anthropogenic activities (Wei and Yang, 2010). 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" (GB4284-1984) and other existing relevant agricultural standards and regulations. Hence, cost-effective alternative strategies and technologies for P recovery for agriculture are needed.

4. Results and discussion

4.1. Option: recovery in sludge

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

In Table 1, selected sewage sludge digestion projects in China are listed. These WWTPs are mostly operated with combined biological and chemical P removal. Among them, several plants have reported that struvite precipitation has been an problematic issue, *e.g.*, Shanghai Bailonggang (Jiang et al., 2013) and Haikou Baishamen (Pan et al., 2006). For most of these plants using anaerobic digestion, land application is the first choice for sewage disposal.

This option is significantly more efficient for WWTPs with biological P elimination and sludge digestion. For the P that is fixed within the sludge, after chemical precipitation with ferrous or ferric salts or 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.

4.2. Option: recovery from sludge water

P is recovered from the supernatants of the digested sludge after liquid–solid separation. In the Struvia™, Pearl®, and AirPrex® processes, an important component of these technologies are crystallization reactors. In these processes, struvite is precipitated by dosing with $MgCl_2$ and increasing the pH by adding NaOH or aeration.

Municipal wastewater treatment plant A in south China has a capacity of 300,000 m^3/day, and the wastewater is treated with an activated sludge process before discharge to the deep sea. After digestion, P is released into the liquid phase, in which total P increases from 205 to 289 mg/L (Table 2). Under specific conditions, this phosphate reacts with magnesium and ammonium, creating buildup of 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 chemical treatment by anti-crustration agents. In the Tianjing Chennan sludge treatment plant, a new project with recovery of phosphate from sludge water with the AirPrex® process is under construction.

Regarding the high soluble P and ammonia concentration in concentrates in such plants in China, techniques are available to recover 80%–90% of the dissolved P (Niewersch et al., 2014) in sludge water. The limits of this option are that no more than 20%

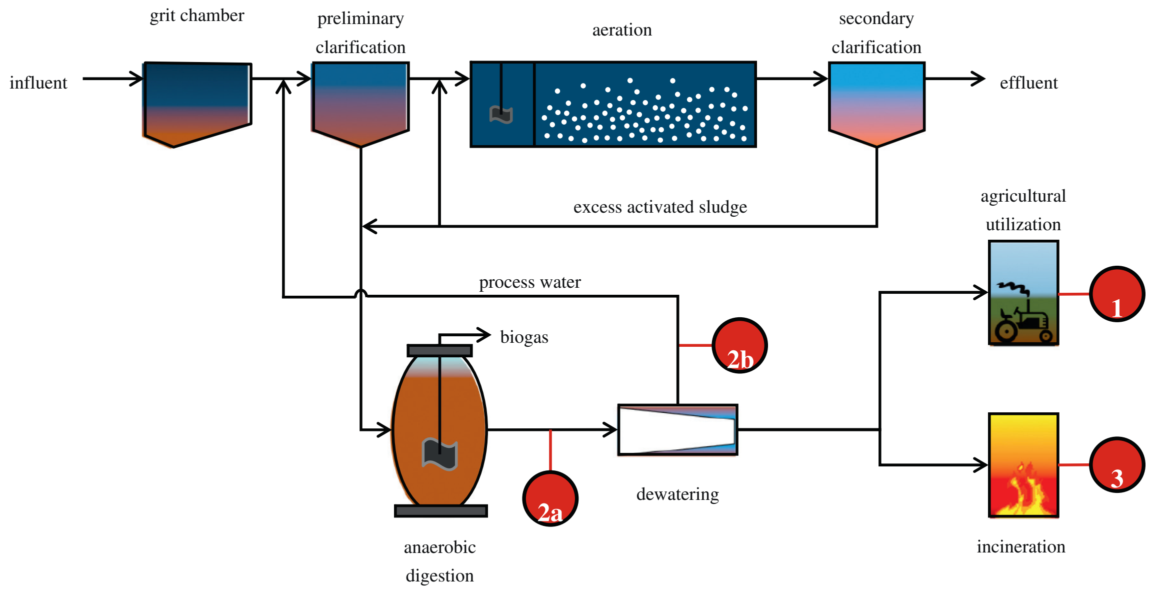

Fig. 3 – Hot spots for P recovery in wastewater treatment plant (Kabbe and Remy, 2013). 1. Direct agricultural utilization of dewatered sludge; 2a. undrained sludge after anaerobic digestion; 2b. sludge liquor after dewatering; 3. from ash after undiluted incineration.

of a WWTP's P load can be recovered, and this only if enhanced biological P removal is applied, thus its economic viability should be considered.

4.3. *Option: recovery from sludge water with sludge extraction*

P 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 P dissolved in the sludge supernatant caused by acidic treatment, the processes with a sludge extraction step are applicable for digested sludge from WWTPs with both enhanced biological P removal and chemical P elimination. Hence, with the current sewage and wastewater treatment facilities in China, Shanghai Bailonggang, Haikou

Table 1 – Anaerobic sludge digestion projects in China.

Sewage sludge digestion projects	Wastewater treatment process	Sludge treatment capacity (Mg DS/day)	Disposal	Year of operation	Reference
Beijing Gaobeidian	Active sludge treatment process	160	–	1999	Jiang (2014)
Beijing Xiaohongmen	AAO process with biological phosphorus removal	160	Land application	2009	Chen (2013), Zhang et al. (2014)
Chongqing Jiguanshi	Reversed AAO process, combined biological and chemical phosphorus removal	90	Co-incineration and land application	2009	Zhang (2009)
Dalian Xiajiahe	Constant waterlevel SBR with biological P-removal	120	Land application	2009	Dai et al. (2008), Yang et al. (2015)
Haikou Baishamen	Activated sludge and biological aerated filter, chemical phosphor removal	100	Agricultural use	2005	Pan et al. (2006), Sun et al. (2008)
Qingdao Maidao	Enhanced clarification and lamella settling with biological aerated filter	21.8	Land application	2008	Wang et al. (2012)
Shanghai Bailonggang	AAO process with chemically enhanced primary treatment	204	Land application	2011	Jiang et al. (2013)
Wuhan Sanjintan	Modified A/O process with biological phosphorus removal	40	Land application	2013	Zhu (2009)
Zhengzhou Wangxin	AAO process with biological phosphorus removal	66	–	2009	Li et al. (2007)
Tianjing Jizhuangzi (Tianjing Jinnan sludge treatment plant)	AAO process with deep bed filtration, combined biological and chemical P-removal	160	Land application	2015	NCME (2013)

DS: dry sludge; AAO: anaerobic–anoxic–oxic; SBR: sequencing batch reactor; A/O: anoxic–oxic.

Table 2 – Parameters of sludge water in wastewater treatment plant A in China (mean value)[a].

	Influent	Effluent	Supernatant pre-thickener before digester	Supernatant post-thickener after digester	Centrate after dewatering	Total returns
Total nitrogen (mg/L)	23.9	19.8	391	614	533	320
NH_4-N (mg/L)	19.0	15.6	325	489	398	249
Total P (mg/L)	3.5	2.0	205	289	238	180

[a] The sludge water samples were taken from wastewater treatment plant A in China from January to May 2014. The influent and effluent of the wastewater treatment plant were analyzed every two days. Other supernatants and centrates were analyzed every second week.

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 biological P elimination removal WWTPs with AD (Garcia-Belinchón et al., 2013).

4.4. *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 (AshDec) processes. 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 P in sludge ash in China is not calculable due to the lack of reliable mono-incineration data.

The Sludge Treatment Facility 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 the composite sludge feed to the incinerator and sludge ash are presented.

SSA in the Sludge Treatment Facility of Hong Kong contains a P concentration of around 4%, which, compared to the mean P content in Germany of 8.9% (Krüger and Adam, 2015) is only half the content in Germany. The concentrations of Al 3.3% and Fe 11.8% in Hong Kong are similar to the mean values in Germany, 5.2% and 9.9% respectively (Krüger and Adam, 2014). For elemental white phosphorus (P_4) production with the Thermphos process, the molar ratio of Fe/P reaches about 0.6 in Hong Kong, which exceeds the limiting 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 tons P/year can be recovered in this plant, the relatively low phosphorus concentration should be considered to ensure economic viability. The limitation of this option in China is the low P concentration in sludge ash compared to Europe.

5. Phosphate fertilizer industry

Various industries produce wastewater that contains a high concentration of P. This includes fertilizer, 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 P consumer but also the largest producer. There were 1118 phosphate fertilizer 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 fertilizer plants (Grzmil and Wronkowski, 2006); but the large amount of P in the wastewater cannot be directly recycled in agriculture due to the low plant availability of fluorapatite (Manahan, 1997; Ndala et al., 2010). A controlled P recovery with separate precipitation of fluorides and phosphates in a two-stage process would be a useful adapted option. It was found that, by adjusting the precipitation to 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).

Table 3 – Analysis of selected parameters of composite sludge feed to incinerator and sludge ash in the sludge treatment facility in Hong Kong, China[a].

	Sludge				sludge ash			
	Moisture content (dried at 103°C)	P (dry matter)	Al	Fe	Moisture content (dried at 103°)	P (dry matter)	Al	Fe
Test on December 4th, 2014	69.3%	0.925%	0.577%	3.1%	0.1%	2.74%	2.74%	10.9%
Test on January 2nd, 2015	67.2%	1.12%	0.78%	2.85%	2.1%	5.25%	3.8%	12.7%
Mean	68.25%	1.023%	0.679%	2.975%	1.1%	3.995%	3.27%	11.8%

[a] The tested sludge and sludge ash samples were taken from incineration sludge treatment facility in Hong Kong from December 2014 to January 2015.

Table 4 – Different streams and compositions of wastewater in a fertilizer plant in China [a].

	Wastewater flows (m^3/hr)	COD (mg/L)	NH_4-N (mg/L)	F^- (mg/L)	TP (mg/L)	SS (mg/L)	pH	TN (mg/L)
Ammonia wastewater	200	300	300	/	/	200	8	300
Phosphate fertilizer wastewater	200	/	50	80	240	100	5	50

COD: chemical oxygen demand; TP: total phosphorus; SS: suspended solids; TN: total nitrogen.
[a] Data came from the operator of wastewater treatment plant.

It was also 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, amounting to ca. 85%–88% and ca. 63–73%, respectively. (Grzmil and Wronkowski, 2006).

Table 4 shows the different streams and compositions of wastewater in a big fertilizer plant in East China. The WWTP has two major types of wastewater: respectively ammonia wastewater with 300 mg/L ammonia-nitrogen from synthetic ammonia production and P-containing wastewater with 240 mg/L total P from phosphate fertilizer 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 of N:P of more than 1, is also beneficial for struvite precipitation. For struvite formation in this fertilizer wastewater plant, an additional magnesium source is needed. The high calcium content in wastewater resulted in more calcium compounds rather than struvite in the precipitates (Hao et al., 2008). In this wastewater treatment plant, approximately 1800 tons of struvite can be recovered annually by the technology currently available, and the product can be sold directly to customers. Unlike in Europe, China has an abundance of phosphate fertilizer 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.

6. Summery and perspective

Growing urbanization in China has caused a rising trend in domestic wastewater and sewage sludge discharges. The contained P 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 P 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 P 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. In special cases, sludge with an extremely high concentration of P potentially provides positive economics for the recovery of P, *e.g.*, in Yunnan and Hong Kong.

The average concentration of P 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: (1) Increase wastewater collection and improve the P removal; (2) promote sludge digestion and biological P elimination and reduce the precipitation with iron salts; (3) develop the strategy for a long-term perspective in sustainable P-recovery; (4) build up the legal framework governing recycling and the market for fertilizers, (5) develop the business models for companies utilizing P streams from wastewater; and (6) encourage the research and promote a new treatment technology for P rich wastewater

7. Conclusions

There is no doubt that phosphorus is a finite resource. Although there is no "one-size-fits-all" option for P 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 P shows 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 P removal, P recovery as struvite and recycling as fertilizer is recommended as one of the favorable options for P recycling.

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REFERENCES

Achat, D.L., Sperandio, M., Daumer, M.-L., Santellani, A.-C., Prud'Homme, L., Akhtar, M., Morel, C., 2014. Plant-availability of phosphorus recycled from pig manures and dairy effluents as assessed by isotopic labeling techniques. Geoderma 232, 24–33.

Asimov, I., 1959. Life's bottleneck. The Magazine of Fantasy and Science Fiction, pp. 31–40.

Chen, Y., 2013. Key points of the process selection and design of the sludge anaerobic digestion in wastewater treatment plant. Water Waste Eng. 39, 41–44.

Chen, Y., Peng, C., Wang, J., Ye, L., Zhang, L., Peng, Y., 2011. Effect of nitrate recycling ratio on simultaneous biological nutrient removal in a novel anaerobic/anoxic/oxic (A2/O)-biological aerated filter (BAF) system. Bioresour. Technol. 102, 5722–5727.

Childers, D.L., Corman, J., Edwards, M., Elser, J.J., 2011. Sustainability challenges of phosphorus and food: solutions from closing the human phosphorus cycle. Bioscience 61, 117–124.

Dai, W., Zhan, J., Mou, J., Liu, D., Liu, Y., 2008. The application of CWSBR process in Xiajiahe WWTP. Water Waste Eng. 34, 38–41.

Dai, X., Zhao, Y., Sha, C., Dai, L., Dong, B., 2014. Investigation on the status and causes of sludge sand content of wastewater treatment plants in China. Water Waste Eng. 21.

De Ridder, M., De Jong, S., Polchar, J., Lingemann, S., 2012. Risks and Opportunities in the Global Phosphate Rock Market: Robust Strategies in Times of Uncertainty. Hague Centre for Strategic Studies.

EC, 2014. 20 Critical Raw Materials — Major Challenge for EU Industry, 26 May. 2014 ed. European Commission.

Egle, L., Rechberger, H., Zessner, M., 2015. Overview and description of technologies for recovering phosphorus from municipal wastewater. Resour. Conserv. Recycl. 105, 325–346 (Part B).

Fang, P., Cen, C., Tang, Z., Tang, Z., 2012. Air pollutants emission and their control from sludge incineration: a review. Environ. Sci. Technol. 1.

FAO, 2009. Can technology deliver on the yield challenge to 2050? How to feed the world in 2050. Food and Agriculture Organization of the United Nations, Rome.

Fu, T., Chang, M., Zhong, L., 2008. Reform of China's Urban Water Sector. IWA Publishing, p. 26.

Garcia-Belinchón, C., Rieck, T., Bouchy, L., Galí, A., Rougé, P., Fàbregas, C., 2013. Struvite recovery: pilot-scale results and economic assessment of different scenarios. Water Pract. Technol. 8.

GB11893-89, Water quality—determination of total phosphorus-ammonium molybdate spectrophotometric method. Ministry of environmental protechtion of the People's Republic of China, Beijing.

GB18918-2002, Discharge standard of pollutants for municipal wastewater treatment plant. Ministry of environmental protection of the People's Republic of China, Beijing.

GB4284-84, Control standards for pollutants in sludges from agricultural use. Ministry of environmental protection of the People's Republic of China, Beijing.

GB7478-87, Water quality — determination of ammonium — distillation and titration method. Ministry of environmental protection of the People's Republic of China, Beijing.

Gouider, M., Feki, M., Sayadi, S., 2009. Separative recovery with lime of phosphate and fluoride from an acidic effluent containing H_3PO_4, HF and/or H_2SiF_6. J. Hazard. Mater. 170, 962–968.

Grzmil, B., Wronkowski, J., 2006. Removal of phosphates and fluorides from industrial wastewater. Desalination 189, 261–268.

Guo, G.i., Chen, T., Yang, J., Zheng, G., Gao, D., 2014. Regional distribution characteristics and variation of heavery metals in sewage sludge of China. Acta Sci. Circumst. 34, 2455–2461.

Guo, G.i., Yang, J., Chen, T.i., Zheng, G., Gao, D., Song, B., Du, W., 2009. Concentrations and variation of organic matter and nutrients in municipal sludge of China. China Water Wastewater 25, 120–121.

Halling-Sørensen, B., Jorgensen, S.E., 1993. 2. Biological nitrification and denitrification. In: Halling-Sorensen, B., Jorgensen S, E. (Eds.), Studies in Environmental Science. Elsevier, pp. 43–53.

Hao, X., Wang, C., Jin, W., 2011. Overview of Phosphorus and Phosphorus Crisis Recovery Technology Global Change and Earth System Science Series. Higher Education Publishing, China.

Hao, X.D., Wang, C.C., Lan, L., van Loosdrecht, M.C.M., 2008. Struvite formation, analytical methods and effects of pH and Ca(2+). Water Sci. Technol. 58, 1687–1692.

Heinzmann, B., Lengemann, A., 2014. Stand der Phosphorrückgewinnung in Berlin- Von wissenschaftlichen Untersuchungen zur großtechnischen Anwendung. Internationales Symposium "Re-Water Braunschweig", Braunschweig, Germany (in German).

HJ636-2012, Water quality—determination of total nitrogen-alkaline potassium persulfate digestion UV spectrophotometric method. Ministry of environmental protechtion of the People's Republic of China, China.

Huang, L., Mao, X.-y., Wang, J., Chen, X., Wang, G.-h., Liao, Z.-w., 2014. The effect and mechanism of improved efficiency of physicochemical pro-release treatment for low grade phosphate rock. J. Soil Sci. Plant Nutr. 14, 316–331.

Jiang, Q., 2014. Recovery operation of sludge anaerobic digestion system at Gaobeidian WWTP. China Water Wastewater 30.

Jiang, L., Yang, C., Hu, Q., Li, Z., Guo, Z., 2013. Operation analysis of sludge anaerobic digestion system at Bailonggang wastewater treatment plant. China Water Wastewater 29.

Jin, L., Zhang, G., Tian, H., 2014. Current state of sewage treatment in China. Water Res. 66, 85–98.

Kabbe, C., 2015. P-REX introduction: hot spots for P recovery from municipal wastewater. Final International P-REX Workshop, Amsterdam.

Kabbe, C., Remy, C., 2013. Sustainable sewage sludge management fostering phosphorus recovery in Europe, 4. Internationale Symposium "Re-Water Braunschweig". Braunschweig, Germany. Nov 6–7.

Kataki, S., West, H., Clarke, M., Baruah, D.C., 2016. Phosphorus recovery as struvite: Recent concerns for use of seed,alternative Mg source, nitrogen conservation and fertilizer potential. Resour. Conserv. Recycl. 107, 142–156.

Kong, X., 2012. The interpretation of policies on bioenergy from municipal waste in urban area, in: center of Science and Technology of Construction M (Ed.).

Krüger, O., Adam, C., 2014. Monitoring von Klärschlammmonoverbrennungsaschen hinsichtlich ihrer Zusammensetzung zur Ermittlung ihrer Rohstoffrückgewinnungspotentiale und zur Erstellung von Referenzmaterial für die Überwachungsanalytik. Fachgebiet III 2.5 Überwachungsverfahren, Abwasserentsorgung, Dessau, Germany (in German).

Krüger, O., Adam, C., 2015. Recovery potential of German sewage sludge ash. Waste Manag. 45, 400–406.

Li, Y., Chen, T., Luo, W., Huang, Q., Wu, J., 2003. Contents of organic matter and major nutrients and the ecological effect

related to land application of sewage sludge in China. Acta Ecol. Sin. 23, 2464–2474.
Li, X., Li, G., Guo, S., Yan, B., 2007. Design and operation of sludge digestion in Wangxinzhuang Wastewater Treatment Plant in Zhengzhou. Water Waste Eng. 33, 13–14.
Li, H., Liu, J., Li, G., Shen, J., Bergström, L., Zhang, F., 2015. Past, present, and future use of phosphorus in Chinese agriculture and its influence on phosphorus losses. Ambio 44, 274–285.
Lu, R., 2004. Phosphorus resource of China and phosphate fertilizer production and consumption Soils. 36 (1), 1–4.
Manahan, S.E., 1997. Nitogen, Phosphorus, and Potassium in Soils, Environmental Science and Technology. Press LLC, United States of America, pp. 358–361.
MEP, 2014. List of National Commissioning Urban Sewage Treatment Facilities in 2013. Ministry of Environmental Protection of the People's Republic of China (MEP) (Available at: http://www.mep.gov.cn/gkml/hbb/bgg/201404/t20140415_270550.htm, (in Chinese). Date accessed: 01 March 2016).
MEP, 2015. Notice of the State Council on Issuing the National Water Pollution Prevention and Treatment Action Plan of China Ministry of Environmental Protection of the Government of the People's Republic of China, Beijing (in Chinese).
MLR, 2012. Evolution of the Phosphate Rock Industry in Hunan. Ministry of Land and Resources of the People's Republic of China (MLR) (Available at: http://www.mlr.gov.cn/kczygl/zhgl/201204/t20120411_1082843.htm, (in Chinese). Date accessed: 21 March 2016).
MOHURD, 2016. China Urban–Rural Construction Statistical Yearbook 2013. Ministry of Housing and Urban–Rural Development (Available at: http://www.mohurd.gov.cn/xytj/tjzljsxytjgb/index.html (in Chinese). Date accessed: 21 March 2016).
NCME, 2013. Environmental Impact Assessment of Jinnan Sludge Treatment. North China Municipal Engineering Design & Research Institut, Tianjing, p. 40.
Ndala, S.m., Claassens, A., Makaringe, P., Dube, B., 2010. Citro-acidulation of Rock phosphates for rapid conversation of fluorapatite to hydroxyapatite. In: Zhang, P., Swager, K., Filho L, L., El-Shall, H. (Eds.), Beneficiation of Phosphates: Technology Advance and Adoption. Society for Ming, Metallurgy & Exploration, USA, pp. 197–203.
Niewersch, C., Stemann, J., Ewert, W., Hermanussen, O., Kabbe, C., Mêlè, C., Paillard, H., Stössel, E., 2014. Description of sludge related processes, sustainable sewage sludge management fostering phosphorus recovery and energy efficiency, P-REX Deliverable D5.1. (Available at:) http://p-rex.eu/index.php?id=11 (Date accessed: 21 Februar 2016).
Pan, B., Lu, Z., Sun, C., 2006. Operational analysis of sludge digestion in wastewater treatment plant in Haikou City. China Water Wastewater 22, 91–94.
Peng, Z., Peng, Y., Gui, L., Liu, X., 2010. Competition for single carbon source between denitrification and phosphorus release in sludge under anoxic condition. Chin. J. Chem. Eng. 18, 472–477.
Petzet, S., Cornel, P., 2009. P-recovery from sewage sludge and sewage sludge ashes. Presentation in BALTIC 21. Berlin, Germany, Sep 28–30.
Qiu, S., Ding, T., 2002. Explore the biological treatment of urban sewage effluent total phosphorus compliance issues. China Water Wastewater 18, 23–25.
Qiu, G., Ting, Y.-P., 2014. Direct phosphorus recovery from municipal wastewater via osmotic membrane bioreactor (OMBR) for wastewater treatment. Bioresour. Technol. 170, 221–229.
Remy, C., 2015. Deliverable D 9.2 life cycle assessment of selected processes for P recovery from sewage sludge, sludge liquor, or ash, sustainable sewage sludge management fostering phosphorus recovery and energy efficiency (P-REX). (Available at:) http://p-rex.eu/index.php?id=11 (Date accessed: 21 Februar 2016).
Römer, W., 2013. Phosphor-Düngewirkung von P-Recyclingprodukten. Korrespondenz Abwasser, Abfall 60, 202–215 (in German).
Sun, C., Shi, Z., Shen, Z., 2008. Analysis of sludge disposal techniques in municipal sewage plants of Hainan. J. Hainan Norm.Univ. 21, 303–306.
USGS, 2015. Phosphate Rock: World Mine Production and Reserves, Mineral Commodity Summaries, America.
Wang, F., Li, H., Chen, X., 2012. Mesophilic sludge digestion and heat and power co-generation in Qingdao Maidao WWTP. China Water Wastewater 28, 49–51.
Wang, X., Zhao, B., Zhang, A., Sha, Z., 2015. The present situation and research progress of treatment of sludge from city sewage treatment plant. Tianjin Daxue Xuebao 30.
Wei, B., Yang, L., 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem. J. 94, 99–107.
Wiechmann, B., Dienemann, C., Kabbe, C., Brandt, S., Vogel, I., Roskosch, A., 2015. Sewage Sludge Management in Germany, Bonn.
Wilken, V., Zapka, O., Muskolus, A., 2015. Product quality: fertilizing efficiency, results of pot and field tests. Final International Workshop Proceedings — P-REX Consortium, Amsterdam.
World Bank, 2014. World Development Indicators: Rural Environment and Land Use.
Yang, G., Zhang, G., Wang, H., 2015. Current state of sludge production, management, treatment and disposal in China. Water Res. 78, 60–73.
Zhang, X., 2009. The run and praetice of sludge anaerobic digestion treatment for the sewage treatment plant of Jiguanshi. Autom. Instrum. 115–119.
Zhang, W., Qi, D., Wu, S., Dong, J., Zhao, W., 2014. Effect of different pretreatment methods on sewage sludge anaerobic digestion. Trans. Chin. Soc. Agric. Mach. 45, 187–198.
Zhang, F., Zhang, W., Ma, W., 2009. China's Phosphorus (P) Fertilizer Industry: Development and Outlook, The Chemical Fertilizer Industry in China: A Review and its Outlook International Fertilizer Industry Association.
Zhu, Y., 2009. Design of the sludge digestion system of Sanjintan wastewater treatment plant in Wuhan City. Water Waste Eng. 35, 40–43.