Species, Fractions and Nutritional Value of Phosphorus in the Typical Biological Treatment Process of Sludge

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Abstract

Sludge treatment is an important part of wastewater treatment and the recovery and utilization of phosphorus from wastewater treatment plant (WWTP) is a challenge for sludge treatment and product disposal. In this paper, eight Chinese typical sludge treatment projects were selected to analyze the species and fractions, and characterization of phosphorus during the sludge treatment process. Furthermore, the nutritional value of phosphorus in the sludge treatment process and the land resource utilization value of phosphorus in the sludge treatment product were discussed. The results showed that the insufficient release of phosphorus to supernatant during anaerobic digestion (AD) of sludge is an important factor restricting phosphorus recovery. Phosphorus in sludge aerobic composting treatment products is mainly in the solid phase, and the concentration effect is beneficial for the phosphorus recovery potential. Phosphorus in sludge treatment products mainly exists in the form of non-apatite inorganic phosphorus, which indicates that improving the bioavailability of phosphorus in sludge treatment products is the key to realizing the nutritional value of the sludge products.

Keywords: sludge treatment, phosphorus, species and fractions, nutritional value

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Introduction

Phosphorus is a necessary nutrient element to sustain life. As a non-renewable mineral resource, it has important strategic significance for ecosystem maintenance and food production [1]. However, the mining of phosphate rock has been accelerated all over the world, and the consumption of phosphate fertilizer has increased from $3.2 \times 10^8$ t to $4.6 \times 10^8$ t since 2000 [2]. It is predicted that phosphorus resources in most countries will be nearly exhausted in the next 100 years [3]. China is now the largest consumer of phosphate fertilizer, while the phosphate production is likely to peak sometime between 2035 and 2045 [4, 5], and this could cause depletion of phosphate reserve by 2045. So it’s urgent to increase the utilization rate and recovery rate of phosphorus resources.

WWTPs are important sources for phosphorus recovery. Every year, about $1.3 \times 10^8$ t of phosphorus enters the wastewater treatment system in the world, and most of the phosphorus in wastewater is transferred to sludge phase through the activated sludge and sedimentation [6, 7]. According to the data of Statistical Yearbook of Urban and Rural Construction in 2020, China would produce 11.62 million tons of dry sludge in 2020 [8]. Given the total phosphorus content of sludge of 2%, the annual phosphorus output from sludge in China is about $2.3 \times 10^5$ tons.

The resource utilization of phosphorus in sludge from WWTPs has been a hot topic in sludge treatment industry in recent years. Germany promulgated a new sludge regulation in 2017, which stipulated that large-scale WWTPs should adopt phosphorus recovery technology for sludge with phosphorus content above 20 mg/g [9], which has certain reference value in policy formulation for China and countries lacking phosphorus resources. The overall goal of sludge treatment and disposal in China’s “14th Five-Year Plan for Urban Sewage Treatment and Resource Utilization” is to achieve the harmless treatment of sludge in an all-round way, and significantly improve the resource utilization level [10]. The recycling of phosphorus resources is the concrete embodiment of the resource utilization of sludge treatment products. AD and aerobic composting of sludge are the two most important technologies for harmless and stabilization treatment of sludge, and the nutritional value of phosphorus in sludge treatment process is the focus of attention in the future. Many studies have discussed the mechanisms of phosphorus release and recovery during sludge treatment [11-14], but there is a lack of systematic analysis on the nutritional value of phosphorus according to the actual operation status of typical sludge biological treatment facilities in China. In this paper, two typical sludge biological treatment process in China, namely AD and aerobic composting were chosen to analyze the migration and species changes of phosphorus in the sludge treatment process, and discuss the nutritional value of phosphorus in sludge products. The results of this paper are helpful for the design of sludge treatment projects aiming for the recovery and utilization of phosphorus in China.

Materials and Methods

Materials

In this paper, the sludge treatment projects of 8 WWTPs from different regions in China were chosen as the research objects. The treatment capacity (based on water content of 80%) and process of sludge treatment are shown in Table 1. Samples of sludge were taken from each treatment unit of sludge project, and sludge filtrate was taken from the dewatering unit.

Pre-Treatment

The raw sludge, process sludge and end-product sludge treated by AD and aerobic composting were freeze-dried for more than 48 hours until the sludge samples were completely dried, then ground through a 60-mesh sieve (0.25 mm). The oversize samples (mainly the large impurities in the sludge) were discarded, and the undersize collected and stored in a dry and low-temperature environment.

<table>
<thead>
<tr>
<th>Location</th>
<th>Label</th>
<th>Capacity</th>
<th>Technology process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing</td>
<td>A</td>
<td>900 m$^3$/d</td>
<td>Thermal hydrolysis+Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Beijing</td>
<td>B</td>
<td>600 m$^3$/d</td>
<td>Thermal hydrolysis+Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Beijing</td>
<td>C</td>
<td>814 m$^3$/d</td>
<td>Thermal hydrolysis+Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Zhongshan</td>
<td>D</td>
<td>300 m$^3$/d</td>
<td>Thermal hydrolysis+Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Zhengzhou</td>
<td>E</td>
<td>800 m$^3$/d</td>
<td>Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Shanghai</td>
<td>F</td>
<td>1000 m$^3$/d</td>
<td>Mesophilic anaerobic digestion+Plate-frame press dewatering</td>
</tr>
<tr>
<td>Kunming</td>
<td>G</td>
<td>200 m$^3$/d</td>
<td>Centrifuge dewatering+Membrane covered aerobic fermentation</td>
</tr>
<tr>
<td>Shanghai</td>
<td>H</td>
<td>200 m$^3$/d</td>
<td>Centrifuge dewatering+Membrane covered aerobic fermentation</td>
</tr>
</tbody>
</table>
Species, Fractions and Nutritional Value...

The supernatant of the sludge was obtained by centrifugation. The sludge sample was centrifuged at 5000 rpm for 20 minutes, and the supernatant was put in the refrigerator for cold storage.

Analytical Methods

Determination of Total Phosphorus Content in Liquid

The concentration of total phosphorus in the sludge supernatant was determined by the national standard method “Determination of total phosphorus-Ammonium molybdate spectrophotometric method” (GB 11893-89) [15].

Speciation Analysis of Phosphorus

Phosphorus forms in sludge solids were analyzed by standards in measurement and testing (SMT) developed by Council of Europe. This method mainly uses hydrochloric acid and sodium hydroxide solutions with different concentrations to extract phosphorus, and five phosphorus forms can be obtained, namely total phosphorus (TP), inorganic phosphorus (IP), organic phosphorus (OP), non-apatite inorganic phosphorus (NAIP) and apatite phosphorus (AP) [16].

XRD Analysis

In order to analyze the composition of phosphorus-containing inorganic phase in sludge solids, the crystal structure characteristics of sludge samples were determined by D8-Advance Diffractometer (Bruker Optics, Germany), and the 2θ range was 20°-60°, in 0.02° steps, counting by 4 s per step. The radiation was Cu Kα at wavelength of 0.1541 nm (40 kV).

Bioavailability Test of Phosphorus

The bioavailability of phosphorus refers to the phosphorus that can either be directly utilized by plants in soil or absorbed and utilized after biochemical transformation. According to the current “Determination of Available Phosphorus Content in Compound Fertilizers” standard in China, 2% citric acid solution is generally used to extract phosphorus to determine the availability of phosphorus [17]. In this study, 1g of sludge powder sample was placed in a 250 mL conical flask, and 100ml of 2% citric acid solution was added, and then shaken in a constant temperature water bath oscillator at 65°C for 1h, and then stood for 1h. A certain amount of extract was diluted and the phosphorus concentration was determined, and the bioavailability of phosphorus in sludge sample was calculated. The calculation formula is as follows:

\[ P_{CA} = P_{EX} \times r \times 100 \times 10^{-4} \times 100\% \]  

where \( P_{CA} \) is the bioavailability of phosphorus in sludge samples (%), \( P_{EX} \) is the phosphorus concentration after dilution of the extract (mg/L), and \( r \) is the dilution multiple of the extract.

Carbon Offset Emission

Phosphorus of sludge treatment end-product can be applied as a substitute for fertilizer. Thus, when sludge land used, it can reduce CO₂ emissions from the production of chemical fertilizers. The offset CO₂ emission from sludge land application could be calculated by the following equation:

\[ OE = P_{bio} \times S_p \times EF_{pf} \]  

where \( OE \) is the offset CO₂ emission by fertilizer substitution from the land application (kg CO₂-eq/ton DS), \( S_p \) is the phosphorus content of sludge (kg P/ton DS), \( EF_{pf} \) is the emission factor for phosphorus fertilizer production (t CO₂/t P₂O₅).

Results and Discussion

Mechanism of Phosphorus Transform during Sludge Biological Treatment

In the process of sludge treatment, phosphorus has different characteristics. Among them, the sludge aerobic composting project adopts the membrane-covered two-stage composting process, and the auxiliary materials such as sawdust and leaf are mixed with dewatered sludge at a volume of about 1:1 for composting. Generally, there is no leachate discharge in the actual operation process, so the phosphorus in the sludge is always distributed in the heap, and the resource utilization of phosphorus can generally be realized through the land use of composting products. The total phosphorus in AD process and dewatering sludge products was analyzed, as shown in Fig. 1.

The sludge treatment of WWTP A, B, C, and D, adopt the process of thermal hydrolysis+AD. Prior to thermal hydrolysis, the sludge was pre-dewatered, and the total phosphorus content in the filtrate was between 16.4 mg/L and 31.4 mg/L. After thermal hydrolysis at high temperature, the total phosphorus content in the supernatant showed an increasing trend, which is mainly due to bacterial cell wall breakage and dissolution of phosphorus-containing organic matter in bacterial cells [18]. After AD treatment, the total phosphorus content in the supernatant of sludge also improved and continued to increase, ranging from 58.3 mg/L to 79.7 mg/L. This is because in anaerobic environment, sludge cells decomposed and the phosphorus release effect of sludge increased the total phosphorus concentration in the supernatant. After chemical conditioning, the sludge was dewatered. During the dewatering process, the phosphorus in the supernatant...
was combined with Fe, Al and Ca metal ions, and the content of total phosphorus in the dewatered filtrate dropped sharply to as low as 6.3 mg/L. The phosphorus content in the sludge was consistent with the total phosphorus content in the supernatant. After high-temperature thermal hydrolysis and AD, the phosphorus content in the sludge increased, mainly due to the degradation of organic matter, and the concentration effect of phosphorus in the solid. However, after sludge dewatering, the total phosphorus content in the solid decreased from 30.9 mg/g to 27.4 mg/g on average, which is mainly because the addition of chemical conditioning agents has a “dilution effect” on phosphorus in the solid.

The sludge treatment process of WWTP E and F are the conventional AD. As can be seen from Fig. 1(e,f), the total phosphorus content in the sludge supernatant also increased after the conventional AD treatment, with an average increase of 6.7%, which is obviously smaller than that of the AD process with high-temperature thermal hydrolysis pretreatment (with an average increase of 16.0%). After sludge dewatering, the total phosphorus content in the supernatant decreased from 27.9 mg/L to 13.3 mg/L, which was mainly related to the dilution effect of adding sludge dewatering agents.

In the case of WWTP A in Beijing, the distribution of phosphorus in sludge treatment system was analyzed. It can be seen from Table 2 that at pre-dewatering stage, about 99.7% of the total phosphorus remained in the solid phase of sludge and the TP content in liquid phase was only 29.5 mg/L. After the sludge was hydrolyzed by high temperature, the share of the total amount of phosphorus in the solid decreased to 98.2%, which indicated that the high temperature hydrolysis promoted the migration of phosphorus from the solid phase to the liquid phase in the sludge system. After AD, the share of total phosphorus in solid came to 96.9%, meaning the phosphorus in sludge kept migrating from solid phase to liquid phase, but the phosphorus release effect of sludge was not as good as that of thermal hydrolysis. Total phosphorus in the liquid phase increased from 50.6 mg/L to 58.4 mg/L. After the sludge was

Fig. 1. Distribution of TP in solid and liquid phases during the sludge treatment process in WWTP A(a), B(b), C(c), D(d), E(e), F(f).
dewatered, the phosphorus concentration in the dewatered filtrate was only 6.3 mg/L and the share of total phosphorus in the liquid phase returned to initial treatment stage value of 0.3%. Therefore, from the point of view of phosphorus recovery, it is advisable to recover phosphorus from the liquid phase of AD of sludge before dewatering. However, due to the limitation of the current technology, the total phosphorus content in the supernatant generally does not exceed 100 mg/L, and it is difficult to achieve the synchronous recovery of nitrogen and phosphorus compared with the concentration of ammonium and nitrogen in the supernatant of 1500–2000 mg/L. Therefore, the next step is advised to strengthen the research on facilitating phosphorus release in AD of sludge.

Analysis of Phosphorus Speciation Transformation in Sludge Stabilization Process

The occurrence form of phosphorus determines its bioavailability. Bio-available phosphorus includes phosphorus that can be used immediately and phosphorus that is transformed into available form through natural physical, chemical and biological reaction processes [19]. Zhu et al. [20] has reported that phosphorus combined with oxides of Fe, Mn, Al and their hydroxides, namely NAIP, can be used by organism; However, phosphorus combined with calcium oxide, namely AP, is difficult to be biologically utilized [21]. It is considered that most organophosphorus, namely OP, can be biologically utilized after hydrolysis [22]. Therefore, from the morphological point of view, we can roughly take the amount of NAIP and OP as the evaluation index of the potential bioavailability of phosphorus in sludge.

Fig. 2 showed the forms and compositions of phosphorus in thermal hydrolysis +AD and aerobic composting sludge, and Fig. 3 depicted the fractions of phosphorus forms in the above sludge treatment processes. The results of three WWTPs showed that IP was the main phosphorus in all types of sludge, accounting for more than 74.7% of total phosphorus. Among inorganic phosphorus, NAIP was the main component, which is mainly because the phosphorus

<table>
<thead>
<tr>
<th>Treatment unit</th>
<th>TP content in solid phase (mg/g)</th>
<th>TP in solid phase (%)</th>
<th>TP content in liquid phase (mg/L)</th>
<th>TP in liquid phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-dewatering</td>
<td>22.4</td>
<td>99.7</td>
<td>29.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal hydrolysis</td>
<td>24.8</td>
<td>98.2</td>
<td>50.6</td>
<td>1.8</td>
</tr>
<tr>
<td>AD</td>
<td>34.5</td>
<td>96.9</td>
<td>58.4</td>
<td>3.1</td>
</tr>
<tr>
<td>Dewatering</td>
<td>29.5</td>
<td>99.7</td>
<td>6.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 2. Distribution of TP in sludge anaerobic digestion treatment process.

Fig. 2. Phosphorus content of different speciation in WWTP A, thermal hydrolysis+AD a), WWTP E, AD b), WWTP G, aerobic composting c).
removal from wastewater is generally achieved by chemical methods such as adding iron salt and aluminum salt. Comparing WWTP A and E, it can be found that the average proportion of inorganic phosphorus in sludge by thermal hydrolysis+AD (87.2%) was larger than that of conventional sludge AD (82.1%), which indicated that thermal hydrolysis promotes the release of organic phosphorus and its conversion into inorganic phosphorus. However, among inorganic phosphorus, the average proportion of NAIP in sludge treated by thermal hydrolysis and AD (62.70%) was smaller than that of conventional sludge treated by AD (72.4%), which indicated that the inorganic phosphorus in sludge was transformed into AP by thermal hydrolysis. Fang et al. [23] studied the change of phosphorus forms in sludge during hydrothermal treatment, and proved that hydrothermal treatment promoted the change of phosphorus forms in sludge from aluminum phosphate (Al-P) and iron phosphate (Fe-P) to calcium phosphate (Ca-P), which was consistent with the results presented in this study.

For AD and aerobic composting of sludge, except organic phosphorus, the content of other forms of phosphorus increased first and then decreased, which was mainly due to the loss of organic matter in the process of thermal hydrolysis and AD. There were two reasons for the decrease of phosphorus content after mechanical dehydration. One was that TS was increased by sludge conditioning, and the other was that most phosphorus in liquid phase was taken away by sludge dehydration filtrate.

In this study, the end-products of sludge biological treatment were analyzed by XRD. Fig. 4 showed that the phosphorus in sludge was mainly in the form of orthophosphate, mostly combined with metal ions such as Fe, Al, Mg, Ca, etc., which was consistent with the results of fractional extraction of phosphorus by SMT in this study. Silica sand is a common mineral component in sludge products. The phosphorus in the product rarely existed in the form of HPO$_4$ and H$_2$PO$_4$ superphosphate, which has poor water solubility and slow-release characteristics, so it is not easy to cause eutrophication of water body during land use.

Analysis of Phosphorus Nutritional Value in Sludge Treatment End-Product

In terms of revealing the land use and nutritional value of sludge treatment end-products, some scholars have analyzed the role of organic components in sludge stabilization products, especially humic acid, in soil improvement [24]. As an important nutrient element, the nutritional value of phosphorus is mainly reflected in the nutrients that can be used for plant growth. The results of this study have shown that the content and form distribution of phosphorus in biologically treated solid products have their own characteristics.

As can be seen from Table 3, after the sludge of WWTP in this study was stabilized, the phosphorus content was concentrated due to the degradation of organic matter, and the concentration times was between 1.1 and 1.5. According to the sludge regulations of Germany, in theory, phosphorus content greater than 20mg/g has high nutritional value. In fact, the utilization of phosphorus in sludge products is of high complexity. It is necessary to consider the bioavailability of
phosphorus and avoid the heavy metal pollution caused by sludge products.

Table 4 listed the bioavailability of phosphorus from different types of sludge in two WWTPs. The bioavailability has certain quick effect and can be quickly utilized by plants. Although Ping et al. [25] pointed out that citric acid can effectively promote the release of phosphorus combined with Fe and Al, the content of available phosphorus measured in this paper is higher than that reported in Germany. However neutral ammonium citrate is used as the extracting solution in German fertilizer standards. According to German industrial standard [26], the proportion of phosphorus soluble in neutral ammonium citrate in sludge is the key index to evaluate the bioavailability of phosphorus in sludge. Relevant research reported that 47.0% of phosphorus of composting sludge in China [27] is bioavailable and 25.0% of phosphorus of composting sludge in Poland [28]. As for the incinerated sludge ash, about 33.9% of phosphorus in Poland [29] and 26.0% in Germany [30] is bioavailable. The big bioavailability difference was found between 25.0% and 55.2%.

Table 3. Total phosphorus content before and after biological sludge treatment (mg/g).

<table>
<thead>
<tr>
<th>WWTP</th>
<th>Before treatment</th>
<th>After treatment</th>
<th>Concentration times</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>22.4</td>
<td>29.5</td>
<td>1.3</td>
</tr>
<tr>
<td>B</td>
<td>18.5</td>
<td>28.3</td>
<td>1.5</td>
</tr>
<tr>
<td>C</td>
<td>18.7</td>
<td>27.9</td>
<td>1.5</td>
</tr>
<tr>
<td>D</td>
<td>21.2</td>
<td>23.8</td>
<td>1.1</td>
</tr>
<tr>
<td>E</td>
<td>16.5</td>
<td>17.9</td>
<td>1.1</td>
</tr>
<tr>
<td>F</td>
<td>15.6</td>
<td>22.9</td>
<td>1.5</td>
</tr>
<tr>
<td>G</td>
<td>16.6</td>
<td>19.2</td>
<td>1.2</td>
</tr>
<tr>
<td>H</td>
<td>13.9</td>
<td>16.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 4. Bioavailability of phosphorus in sludge treatment end-products as fertilizer.

<table>
<thead>
<tr>
<th>Sludge treatment</th>
<th>Sludge type</th>
<th>WWTP A</th>
<th>WWTP B</th>
<th>Literature data</th>
<th>Literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Digested sludge</td>
<td>Dewatered digested sludge</td>
<td>Composting sludge [27]</td>
<td>Incinerated sludge ash [29]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.4%</td>
<td>41.1%</td>
<td>47.0%</td>
<td>33.9%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.2%</td>
<td>52.3%</td>
<td>25.0%</td>
<td>26.0%</td>
</tr>
</tbody>
</table>

Fig. 4. XRD pattern of sludge treatment end-products from thermal hydrolysis+anaerobic digestion a), anaerobic digestion b), aerobic composting c).
which may be caused by different chemicals added in chemical phosphorus removal from wastewater and sludge treatment and different bioavailability measuring method. When applied as fertilizer, appropriate treatment should be taken to increase the bioavailability of phosphorus, and at the same time, heavy metals contained in sludge should be removed. Moreover, the evaluation methods of bioavailability of phosphorus in sludge solid products need to be further studied and unified. Under the background of advocating carbon neutrality in China, the resource value of phosphorus in sludge stabilization products can also be extended to carbon emission reduction. Some studies at home and abroad believe that [31-33], the land use of sludge stabilization products can also be extended to carbon emission reduction. It has been reported that the comprehensive carbon emission coefficient of phosphate fertilizer products in China is 0.63 t CO₂/t P₂O₅ [34]. Assuming that the phosphorus content in sludge stabilized products is 4%, of which about 50% is equivalent to that of phosphate fertilizer, the emission reduction will be about 2.8t CO₂ per 100 t sludge stabilized products (calculated as dry sludge). Therefore, the land resource utilization of phosphorus from sludge stabilized products has great carbon emission reduction value.

Conclusions

The recovery and utilization of phosphorus resources should be focused on through the whole process of sludge treatment and disposal. In the process of AD of sludge in China, the release of phosphorus from solid phase into liquid phase is not sufficient, which is an important factor restricting phosphorus recovery at present. The main form of phosphorus in the sludge products after AD and aerobic composting are NAIP. The results of bioavailability evaluation of phosphorus in sludge products showed that phosphorus in sludge biological treatment products could not be fully utilized in soil. In order to improve the nutritional value of sludge treatment products, it is suggested that the recyclability of phosphorus should be strengthened in the design and operation of sludge treatment project, and the research on the bioavailability evaluation of phosphorus in the products should be strengthened as well.

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Conflict of Interest

No potential conflict of interest was reported by the authors.

References


