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Transformation of phosphorus during drying and roasting of sewage sludge

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ABSTRACT

Sewage sludge (SS), a by-product of wastewater treatment, consists of highly concentrated organic and inorganic pollutants, including phosphorus (P). In this study, P with different chemical fractions in SS under different drying and roasting temperatures was investigated with the use of appropriate standards, measurements, and testing protocol. The drying and roasting treatment of SS was conducted in a laboratory-scale furnace. Two types of SS samples under different treatment temperatures were analyzed by ^{31}P NMR spectroscopy. These samples were dried by a vacuum freeze dryer at −50 °C and a thermoelectric thermostat drying box at 105 °C. Results show that the inorganic P (IP) content increased as the organic P content decreased, and the bio-availability of P increased because IP is a form of phosphorous that can be directly absorbed by plants. ^{31}P NMR analysis results indicate the change in P fractions at different temperatures. Non-apatite P was the dominant form of P under low-temperature drying and roasting, whereas apatite P was the major one under high-temperature drying and roasting. Results indicate that temperature affects the transformation of P.

1. Introduction

Phosphorus (P) is an important and irreplaceable nutrient for all living organisms. However, the extensive use of P may result in eutrophication in aquatic systems. Sewage sludge (SS), a byproduct of wastewater treatment, is rich in P. Sludge generation in different regions of China is uneven. East China produces 61% of the total SS output of China. The transportation and disposal of SS often account for 25–65% of the total operation costs of wastewater treatment plants. The average content of P in dried SS in China is 2.2% (Guo et al., 2009). In some European countries, the maximum P content of SS is as high as 15% (Hoffmann et al., 2010). The known world reserves of phosphate rock may be exhausted in 90–130 years (McNutt, 2010). Therefore, P recycling from SS can contribute to reducing pressure on P resource supply and controlling pollution.

Thermal treatment can result in a highly concentrated P content in SS (Franz, 2008; Cyr et al., 2007) and reduce the quantity of SS. Recently, studies have clearly shown that thermal treatment can enhance the anaerobic digestion of excess sludge. However, these studies focused on the thermal hydrolysis of SS and on organic solids that undergo dissolution and hydrolysis. Several studies have investigated the forms of P in SS at high temperatures (Franz, 2008; Cyr et al., 2007; Adam et al., 2009). Concentrated P has also been found in the studied heavy metals in SS during thermo-chemical treatment. Research in this field has therefore mainly focused on the removal of heavy metals in SS ash, the relationship of P and heavy metals, and the bio-availability of P when heavy metals are removed (Nowak et al., 2011; Tang et al., 2008; Kidd et al., 2007; Khan and Jones, 2009). García-Albacete et al. (2012) investigated the transformation of P, particularly non-apatite inorganic phosphorus (NAIP), into different forms by applying appropriate standards, measurements, and testing protocol. Meanwhile, the effect of temperature on the transformation of the P fraction has not been systematically studied. P with different chemical fractions in SS was investigated with the use of the standards, measurements, and testing (SMT) protocol (Pardo et al., 2003; Xie et al., 2011; García-Albacete et al.; 2012). This protocol, which was developed by the European Commission, classified P in SS into five forms, such as total phosphorus (TP), which includes IP and organic phosphorus (OP). IP was further classified into non-apatite IP and apatite P (AP). IP and non-apatite IP are the predominant fractions in SS (Pardo et al., 2003; Xie et al., 2011). The relationships of the five fractions of P are expressed by the equations TP = IP + OP and IP = NAIP + AP (Pardo et al., 2003). AP is bound to Ca and is obtained in P mining.

^{31}P NMR spectroscopy has been used in numerous studies to determine the distribution of OP and IP. The transformation of P forms in soil, sediments, and SS has been reported (Cade-Menun and Preston, 1996; Peng et al., 2009). ^{31}P NMR spectra were

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obtained for P fractions from SS at different treatment temperatures.

The results of this study can be beneficial to increasing the bioavailability of P in SS and the further recycling of P as apatite from SS. This research aims to investigate the relationship between temperature and P fractions. It also studies the transformation of OP as a source of plant-available P, non-apatite IP, and apatite IP.

2. Material and methods

2.1. Sample collection and pre-treatment

Two types of mechanical dehydration sludge were collected from Shenyang North Wastewater Treatment Plant and Dalian Wastewater Treatment Plant in China. Table 1 shows the properties of SS. The Shenyang SS samples were dried and roasted to constant weight at different temperatures for 48 h. The temperature of thermal treatment ranged from 60 °C to 240 °C. The drying and roasting treatment of SS was conducted in a laboratory-scale furnace in an open system. Some Dalian SS samples were dried with a vacuum freeze dryer for 72 h, and others were dried to constant weight in a furnace at a temperature that ranged from 60 °C to 105 °C. All treated samples were ground to less than 150 μm with a QM-QX ball grinding mill (Nanjing).

2.2. Instrumentation and reagent

Colorimetric determination of phosphate was conducted with molybdenum blue method (Kidd et al., 2007) at 882 nm with a WFJ2100 spectrophotometer (UNICO, Shanghai). A SHA-BA water bath oscillator (RONGHUA, China) was used in the extractions. A TG-18 M centrifuge (PINGFAN, China) was utilized to extract P phases and facilitate complete separation of the extract from the solid phases at 4000 × g for 10 min. A FD-1A-50 vacuum freeze dryer (BOYIKANG, Beijing) was used to dry the SS to obtain the freeze-dried samples. X-ray fluorescence (XRF) (ZSX100e, MINIFLEX, Japan) measurements were used to determine the major components of raw SS, such as C, H, S and N contents. An SSX-550 scanning electron microscope and an energy dispersive spectrometer (SEM-EDS) (SHIMADZU, Japan) were used to observe morphology and element content. An Advance-600 MHz nuclear magnetic resonance spectrometer (BRUKER, Switzerland) was utilized to observe changes in P fractions.

All reagents used in this study were of analytical reagent grade. In the SMT protocol and ^{31}P NMR experiment, hydrochloric acid (1 M and 3.5 M), sodium hydroxide (0.25 M and 1 M), and EDTA (0.05 M) were used as extracting reagents. Glassware and plasticware were soaked in 10% HNO_3 for 24 h and then rinsed with distilled water.

2.3. P fractions in SS

The SMT program was used in this study to determine P in all sludge samples. Each experiment was replicated three times. NMR measurements were used to observe changes in P fractions. The operating conditions of the SMT protocol and NMR experiment were described in a number of studies (Pardo et al., 2003; Xie et al., 2011; García-Albacete et al., 2012; Cade-Menun and Preston, 1996). Spectrophotometric determination of phosphate in all extracts was conducted with molybdenum blue method (Pardo et al., 2003). Phytic acid is a primary component in OP (De Groot et al., 1993). However, several studies indicate that adenosintriphosphate (ATP) is the primary constituent of OP (Jens and Sven, 2007). In this study, phytic acid was added to SS, which was dried at 80 °C and 90 °C to determine the transformation of OP and IP.

Table 1
Properties of sewage sludge tested in this study, wt%.

	Ash	Volatile matter	Fixed carbon	C	H	N	S
Shenyang SS	48.0	44.9	3.2	21.48	2.86	2.53	1.57
Dalian SS	21.6	66.7	11.7	42.49	6.79	6.63	1.22

2.4. ^{31}P NMR spectroscopy

Three grams of the freeze-dried sample and 3.0 g of the dried sample at 105 °C from Dalian were placed in 100 mL centrifuge tubes. Then, 1:20 (v/v) of EDTA (0.25 mol L^{-1} NaOH + 0.05 mol L^{-1} EDTA, 60 mL) was added to the centrifuge tubes, which were shaken for 24 h at a temperature of 25 °C. After centrifugation of the extracts at 10,000 gravities for 30 min, the supernatants were filtered through a 0.45 μm filter membrane and dried with a vacuum freeze dryer. The freeze-dried sample was re-dissolved in 1 mL of 0.25 mol L^{-1} NaOH and then centrifuged at 8000 gravities for 5 min at 4 °C. The supernatants (0.6 mL) were added in 0.5 mL of D_2O and then transferred to a 5 mm NMR tube. Solution ^{31}P NMR spectra were obtained with a 600 MHz spectrometer that operates at 242.739 MHz at 25 °C. A 7.0 μs observe pulse and a total acquisition time of 2.32 s (acquisition time: 0.32 s, pulse delay) were used. Spectra were collected with 30,000 scans. Chemical shifts were recorded relative to an external 85% H_3PO_4 standard (δ = 0 ppm).

3. Results and discussion

3.1. P fractions in SS

Table 2 summarizes the results of the SMT protocol for the Shenyang SS samples. The results are given as mean values

Table 2
Analytical results obtained in Shenyang SS (expressed in mg g^{-1}) using the SMT extraction protocol.

	60 °C	70 °C	80 °C	90 °C	105 °C
TP	10.2 ± 0.3	10.4 ± 0.4	10.4 ± 0.3	10.5 ± 0.2	10.6 ± 0.2
IP	7.6 ± 0.2	7.5 ± 0.1	7.5 ± 0.2	8.0 ± 0.1	8.2 ± 0.1
OP	1.6 ± 0.1	1.8 ± 0.2	1.9 ± 0.1	1.7 ± 0.1	1.4 ± 0.1
NAIP	3.4 ± 0.1	3.4 ± 0.2	3.5 ± 0.3	3.7 ± 0.3	4.0 ± 0.1
AP	3.9 ± 0.2	3.9 ± 0.2	4.0 ± 0.2	4.2 ± 0.2	4.2 ± 0.1

Concentrations are expressed as mean value ± standard deviation.

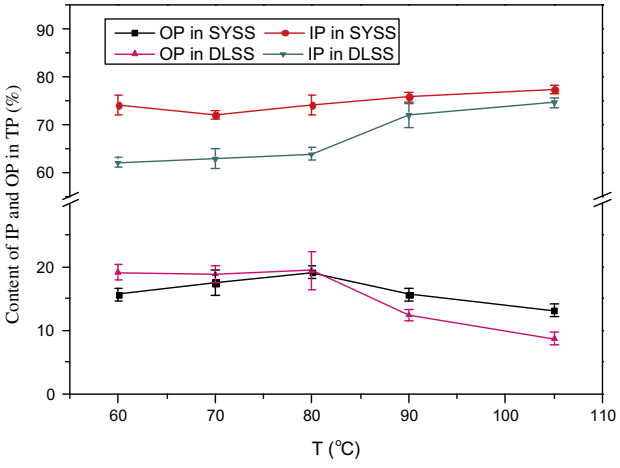

Fig. 1. Content of inorganic phosphorus and organic phosphorus in total phosphorus (%) from Shenyang sewage sludge (SYSS) and Dalian sewage sludge (DLSS).