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Effect of various types of thermochemical processing of sewage sludges on phosphorus speciation, solubility, and fertilization performance

Daniel Steckenmesser [a,*], Christian Vogel [b], Christian Adam [b], Diedrich Steffens [a]

[a] Institute of Plant Nutrition, Justus-Liebig University Giessen, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany
[b] Division 4.4 Thermochemical Residues Treatment and Resource Recovery, Bundesanstalt für Materialforschung und–prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

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ABSTRACT

Sewage sludge has one of the highest phosphorus (P) recovery potentials of all waste materials. Therefore, P-recycling from sewage sludge could contribute to closing the P-cycle. Recently, various thermal processes for P-recovery have been developed, but there is still a demand for information on the effect of different process parameters (e.g. additives and temperature) on P-speciation and especially on the fertilization performance. In the present study, two common methods (low-temperature conversion at 400–500 °C and thermochemical treatment at 950 °C) were investigated and combined to produce highly bioavailable P-fertilizers from two different types of sewage sludge based on chemical phosphorus precipitation (Chem-P) and enhanced biological phosphorus removal (Bio-P). The results of P-fractionation, X-ray diffraction analysis, and pot experiments with maize showed that Bio-P sludges attain high P-plant-availability after treatment at low temperatures (400 °C). In contrast, Chem-P sludges can adequately be treated at higher temperatures under reductive conditions with sodium additives to form highly bioavailable calcium-sodium-phosphate. Additionally, also highly heavy-metal contaminated sludges can be thermochemically treated at high temperatures to achieve the legal requirements for fertilizers.

1. Introduction

The world population increases annually by 1.2% (United Nations, 2015). Hence, to guarantee adequate world food supply, an effective agricultural land-use and increasing amounts of P-fertilizers are required. In accordance with the Food and Agriculture Organization of the United Nations (FAO) the consumption of P-fertilizers increases annually by 2.2% (FAO, 2015). Phosphorus is a finite resource and its natural mineral deposits are confined to only a few countries (China, USA, and Morocco) which implies that the bigger share of countries has to import phosphate rock as a P-source (Cordell et al., 2009; Dawson and Hilton, 2011). Thus, an efficient and sustainable recycling management is required in which alternate P-sources are used for fertilizer production in order to contribute to the P-cycle and to be autonomous regarding developments on the world market.

Phosphorus can be found in many mass flows in which waste water and especially sewage sludge has the highest potential for P-recycling. Additionally, sewage sludge is a waste that is produced in great quantities (approx. 2 Mt per year in Germany) (UBA, 2013). It has been used as fertilizer for decades for direct field application. Due to high loads of heavy metals and organic pollutants (Harrison et al., 2006; Marani et al., 2003), concerns about the direct field application of sewage sludge are on the rise. Hence, a decline of this method can be expected in future. If this will be proved true, other ways must be found to recycle P from these large amounts of sewage sludge.

One way to handle the emerging amount of sewage sludge is the centralized mono-incineration. The percentage of incineration increases steadily. In 2013, 58% of the accruing sewage sludge were incinerated in Germany, while only 42% were used in agriculture and landscaping (Destatis, 2016). Currently 37% of the arisen sewage sludge ash (SSA) is filled in mines, 29% is used for road building, further 29% are used for landfilling and only 5% are used as fertilizer (Destatis, 2016). However, for the use of the remaining SSA there are restrictions due to the heavy metal limits of the German waste and sewage sludge ordinance (BMJV, 2015). Therefore, 78% of the accruing SSAs are not useable for fertilizer production (Destatis, 2016; Krüger and Adam, 2015). Another aspect is the fertilizer efficiency of these SSAs. Krüger and Adam (2015) investigated SSAs from 23 mono-incineration facilities in Germany and valued most of them as not sufficient for use as fertilizer. Thus, a

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[*] Corresponding author.
E-mail address: daniel.steckenmesser@ernaehrung.uni-giessen.de (D. Steckenmesser).

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further treatment of these SSAs is necessary, in order to improve the fertilizer efficiency (Krüger and Adam, 2015).

Another way to handle the emerging sewage sludge is the decentralized use of small pyrolysis reactor units (Löhde, 2014). These units produce sewage sludge carbonizates (SSC) at 400–550 °C under reducing conditions. This process is comparable to low-temperature-conversion (LTC) (Bayer, 1995), whereby biogenic substances like sewage sludge can be converted into char, oil, reaction-water, and gas (Stadlbauer et al., 2003). The emerging oil and gas have high heating values and can be co-fired and used to heat the reactors (Inguanzo et al., 2002). The pyrolysis reactor units can be used directly after sewage sludge drying stages at waste water treatment plants (WWTP) to convert sewage sludge into a hygienic SSC that can be used as a P-fertilizer.

Dependent on the P-elimination method during waste water treatment, different P-forms can predominate in sewage sludge, SSC, and SSA. Iron phosphates like vivianite, strengite, or iron hydroxide adsorbed P resulted from chemical precipitation with iron salts (Frossard et al., 1997; Huang and Shenker, 2004). Iron phosphates decrease with increasing temperatures during an oxidative thermochemical treatment (Zhang et al., 2001). Reductive conditions also lead to decreasing amounts of P that is adsorbed on iron and/or aluminum compounds (Qian and Jiang, 2014). Aluminum phosphates like variscite resulted from chemical precipitation with aluminum salts (Huang and Shenker, 2004). Investigations of SSAs had been shown, that these phosphates are stabile to high temperatures (Adam et al., 2009a; Peplinski et al., 2009; Zhang et al., 2001). Several authors found, that the amount of calcium phosphates like chlorapatite ($Ca_5(PO_4)_3Cl$), stanfieldite ($Ca_4Mg_5(PO_4)_6$), and whitlockite ($Ca_{3-x}(Mg,Fe^{2+})_x(PO_4)_2$) increases with increasing temperature. This has been shown for thermochemical treatment at high temperatures (Nanzer et al., 2014; Zhang et al., 2001), as a function of additives (Peplinski et al., 2009) and for lower temperatures and different atmospheric conditions (Cao and Harris, 2010; Qian and Jiang, 2014). Weber (2010) showed for the LTC process that Na_2CO_3 can be used to enhance the P-plant-availability in the SSC. However, if the fertilizing effects are insufficient, a further treatment of these SSCs and SSAs are necessary.

To enhance the P-plant-availability of SSC and SSA, several thermochemical treatments (TCT) have already been investigated with promising outcome. Subjects of these investigations were the influence of different parameters of thermal processing (temperature, oxidative or reductive conditions, and additives) on the P-compounds and P-plant-availability of the product. Thus, $MgCl_2$ was used under oxidative conditions at different temperatures (450–1000 °C) to eliminate heavy metals on the one hand and to increase the P-plant-availability on the other hand due to the formation of farringtonite ($Mg_3(PO_4)_2$) and stanfieldite ($Ca_4Mg_5(PO_4)_6$) (Adam et al., 2009a; Peplinski et al., 2009; Vogel et al., 2010). Furthermore, the use of Na_2CO_3 or Na_2SO_4 under reductive conditions reduce heavy metals and increase the P-plant-availability of the product (Herzel et al., 2016; Stemann et al., 2015; Vogel et al., 2016). This increase is based on the formation of calcium-sodium-phosphate ($CaNaPO_4$; also called buchwaldite), which has a much higher P-plant-availability than chlorapatite or whitlockite.

The aim of this study is to combine LTC and TCT to obtain highly plant-available P-fertilizers from sewage sludge with low heavy metal contents for agricultural use. Therefore, a screening of LTC (first step; under different temperatures and Na_2CO_3 addition) and TCT (second step; with different additives) was carried out to produce P-fertilizers from two different types of sewage sludge (firstly chemical precipitation with iron chlorides and secondly enhanced biological P removal). The characterization of the recycling P-fertilizers was first done by the P-solubility extraction tests, P-fractionation and P-speciation by XRD. Afterwards, the P-plant-availability was measured in pot experiments with maize.

2. Material and methods

2.1. Sewage sludge

Two types of sewage sludge from Germany were selected and they differ in the removal of P (chemical P-precipitation and enhanced biological P-removal) and in the post treatment of sewage sludge (aerobic and anaerobic stabilization). The first one was simultaneously precipitated with $FeCl_2$ and afterwards directly fermented which resulted in an anaerobically stabilized sludge (labelled as Chem-P). The second one was in a first step biologically precipitated, aerobically stabilized, and in a second step precipitated by $Al_2(SO_4)_3$ (labelled as Bio-P). The Chem-P sludge was dried by a low-temperature drier, whereas the Bio-P sludge was dried by a solar drier. The water contents of the resulting sewage sludge were lower than 12% (see Table 1). Chem-P has a higher P-content compared to Bio-P, which can be explained by the differences between the catchment areas of the sewage treatment plants. The sewage treatment plant of Chem-P has a more industrial catchment area and gets wastewater from an industrial scale abattoir, while the sewage treatment plant of Bio-P is in a more rural area.

2.2. Sample preparation

The sewage sludge was thermochemically treated without any pre-treatment (grinding or further drying). Before use, water content (DIN 51718), loss on ignition (LOI), and ash content (DIN 51719) were determined in a muffle oven (see Table 1). For elemental analysis sewage sludge and SSC were dried at 105 °C, grinded, and passed through a 0.63 mm sieve.

2.3. Low-temperature-conversion (LTC)

The LTC was done in a tube furnace (Hereaus, Haunau, Germany) under N_2 gas atmosphere (anaerobic). Within the furnace a high-quality steel tube was filled with 600 g of sewage sludge. Glass wool was used to keep the substrate in position without disturbing the gas flow and to ensure that the substrate was in the heat area with constant temperature.

Two pyrolysis temperatures (400 and 500 °C) as well as the effect of soda (Na_2CO_3) as a catalytic additive (8% from net weight) were investigated to determine their influence on P-solubility and -plant-availability. The heating rate was 10 K min^{-1} and the N_2-gas

Table 1
Water content (H_2O), loss on ignition (LOI), ash content, and elemental composition of both sewage sludges (Chem-P and Bio-P).

	Chem-P (% DM)	Bio-P (% DM)
Water content (H_20)	6.61 ± 0.11	11.44 ± 0.14
LOI	63.13 ± 0.30	62.40 ± 0.17
Ash content	34.95 ± 0.07	37.51 ± 0.31
C	30.37 ± 0.25	28.50 ± 0.23
H	4.43 ± 0.07	4.56 ± 0.19
N	4.41 ± 0.03	4.40 ± 0.05
S	1.76 ± 0.11	1.30 ± 0.06
P	4.69	2.99
Fe	6.30	1.94
Al	0.83	3.79
Ca	4.69	1.94
Mg	0.69	0.76
K	0.69	0.49
Na	1.05	0.09
Si	2.78	9.82

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