



Vivianite as an important iron phosphate precipitate in sewage treatment plants



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ABSTRACT

Iron is an important element for modern sewage treatment, inter alia to remove phosphorus from sewage. However, phosphorus recovery from iron phosphorus containing sewage sludge, without incineration, is not yet economical. We believe, increasing the knowledge about iron-phosphorus speciation in sewage sludge can help to identify new routes for phosphorus recovery. Surplus and digested sludge of two sewage treatment plants was investigated. The plants relied either solely on iron based phosphorus removal or on biological phosphorus removal supported by iron dosing. Mössbauer spectroscopy showed that vivianite and pyrite were the dominating iron compounds in the surplus and anaerobically digested sludge solids in both plants. Mössbauer spectroscopy and XRD suggested that vivianite bound phosphorus made up between 10 and 30% (in the plant relying mainly on biological removal) and between 40 and 50% of total phosphorus (in the plant that relies on iron based phosphorus removal). Furthermore, Mössbauer spectroscopy indicated that none of the samples contained a significant amount of Fe(III), even though aerated treatment stages existed and although besides Fe(II) also Fe(III) was dosed. We hypothesize that chemical/microbial Fe(III) reduction in the treatment lines is relatively quick and triggers vivianite formation. Once formed, vivianite may endure oxygenated treatment zones due to slow oxidation kinetics and due to oxygen diffusion limitations into sludge flocs. These results indicate that vivianite is the major iron phosphorus compound in sewage treatment plants with moderate iron dosing. We hypothesize that vivianite is dominating in most plants where iron is dosed for phosphorus removal which could offer new routes for phosphorus recovery.

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1. Introduction

Phosphorus (P) is an essential element for all life. It is often a limiting nutrient for crops and thus a crucial part of fertilizers. Currently, the use of P is not sustainable and its supply is not guaranteed in the future: (I) Phosphate rock reservoirs, the main source of P for fertilizers, are depleting (Scholz and Wellmer, 2016;

Walan et al., 2014), (II) these reservoirs are located in a few countries (De Ridder et al., 2012), (III) for current P applications and depletions regional imbalances exist (Macdonald et al., 2011; van Dijk et al., 2016) and (IV) P surpluses cause eutrophication in surface waters (Carpenter, 2008). The recovery of P from secondary resources would help to make its use in our society circular and more sustainable (Carpenter and Bennett, 2011; Childers et al., 2011).

Sewage is an important secondary source for P (van Dijk et al., 2016). In sewage treatment plants (STPs), P is typically removed to diminish eutrophication in surface waters by chemical P removal (CPR) or enhanced biological P removal (EPBR). In both cases, P is concentrated in the sewage sludge. Iron (Fe) dosing for CPR is efficient, simple and cheap (Geraarts et al., 2007; Paul et al., 2001; WEF, 2011). Future energy producing STPs rely on chemical P and

Abbreviations: CPR, Chemical Phosphorus Removal; COD, Chemical Oxygen Demand; DO, Dissolved Oxygen; DOC, Dissolved Organic Carbon; EBPR, Enhanced Biological Phosphorus Removal; Fe₂O₃, Hematite; FeP, Iron Phosphorus Compounds; FeS_x, Iron Sulphide Compounds; IRB, Iron Reducing Bacteria; o-P, Orthophosphate; SRT, Solid Retention Time; STP, Sewage Treatment Plant; TS, Total Solids.

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chemical oxygen demand (COD) removal (Böhnke, 1977; Wilfert et al., 2015). Additionally, Fe is commonly applied in modern sewage treatment also for other reasons than CPR. Ferric, Fe(III) and ferrous, Fe(II) iron salts are dosed as flocculants to remove COD (Li, 2005), to prevent the emission of hydrogen sulphide (H_2S) in sewer systems and digesters (Hvitved-Jacobsen et al., 2013; Nielsen et al., 2005) and to improve sludge dewatering (Higgins and Murthy, 2006). Additionally, Fe may originate from groundwater intrusion into the sewer systems (Hvitved-Jacobsen et al., 2013; Kracht et al., 2007). Thus, in most STPs, part of the P will be bound to Fe. An economic feasible recovery of P from sewage sludge containing iron phosphorus compounds (FeP), without sludge incineration, is a technological challenge that remains unsolved, also due to scarce information on FeP mineralogy in STPs (Wilfert et al., 2015).

The initial reactions, after Fe(III) or Fe(II) addition to sewage and the subsequent removal of P are complex (El Samrani et al., 2004; Luedecke et al., 1989; Smith et al., 2008; Takács et al., 2006). These reactions are important as they drive primary P removal from sewage by bringing P from the liquid to the solid phase. In STPs, the solid retention time (SRT) can be a few hours, as in the A-stage of AB-processes (Böhnke, 1977; Böhnke et al., 1997), but it is usually on the time scale of 5–20 days when the conventional activated sludge process is applied (Tchobanoglous et al., 2013). In those processes, alternating redox conditions are applied to achieve COD and nitrogen removal. Hence, once formed the initial FeP may change due to oxidation of Fe(II) or reduction of Fe(III) respectively (Nielsen, 1996; Nielsen et al., 2005; Nielsen and Nielsen, 1998; Rasmussen and Nielsen, 1996) or due to aging effects (Recht and Ghassemi, 1970; Szabó et al., 2008). Most likely, the FeP, that end up in the surplus sludge and that determine the P removal efficiency of STPs, differ from the initial precipitates.

Several researchers reported the ferrous iron phosphate mineral vivianite ($\text{Fe}(\text{II})_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$) in surplus sludge and anaerobically digested sludge (Frossard et al., 1997; Ghassemi and Recht, 1971; Seitz et al., 1973; Singer, 1972). Frossard et al., 1997 were able to quantify vivianite in sewage sludge using Mössbauer spectroscopy even though the sludge samples in this study were exposed to air. This could have resulted in full/partial oxidation of Fe(II) compounds and partial transformation of vivianite to amorphous FeP (Roldan et al., 2002) or to other changes of the P fractions (Kraal et al., 2009). Additionally, all Mössbauer measurements were done at room temperature (300 K). Complex samples should ideally be measured at lower temperatures (e.g. 4.2 K) as well, to reveal unambiguously the spectral contributions and magnetic properties of the Fe phases. (Murad and Cashion, 2004).

We have investigated two STPs, with different treatment strategies to determine the fate of Fe and FeP during treatment. The STP Leeuwarden applies EBPR, additionally respectively Fe(II) or Fe(III) are dosed in two different treatment lines. The STP Nieuwveer uses the AB technology (Böhnke et al., 1997; de Graaff et al., 2016), here Fe(II) is dosed. AB-plants in combination with cold anammox have the potential to be energy factories (Jetten et al., 1997; Siegrist et al., 2008).

The fate of Fe and FeP was evaluated by various measurements on the liquid and solid fractions of the sewage (sludge) at different locations in the treatment line. Mössbauer spectroscopy (qualitative and quantitative analyses of Fe compounds), XRD (semi-quantitative analyses of all crystalline material) and SEM-EDX (particle morphology and elemental composition) were used to characterize the solid fractions. Mass balances for P and Fe helped to identify the significance of different sources (influent, external sludge, Fe dosing) and sinks (effluent, sludge disposal) for these elements. Mössbauer spectroscopy and XRD were used to estimate P bound in vivianite and sulphide extraction was used to quantify P bound to Fe. Thereby, the P recovery potential of a technology that

targets specifically on FeP was determined.

Identifying the forms of FeP in activated sludge would help to obtain thermodynamic (e.g. equilibrium concentrations) and stoichiometric (molar Fe:P ratios) information that is necessary to develop technologies to recover P from FeP. Although, in literature, some indications for vivianite formation as major P compound during sewage treatment can be found, the role of vivianite and its importance has been neglected, the reason why this study was carried out.

2. Methods & material

2.1. STPs and sampling

In the AB plant Nieuwveer (influent: $75,706 \text{ m}^3 \text{ d}^{-1}$ in 2014), Fe(II) is added in the aerated ($\approx 0.3 \text{ mg dissolved oxygen (DO) L}^{-1}$) A-stage for P and COD removal. SRTs are 15 h in the A-stage, 16 days in the B-stage (DO in aerated sections $\approx 1.8 \text{ mg DO L}^{-1}$) and 25 days during anaerobic digestion. In the EBPR plant Leeuwarden ($38,000 \text{ m}^3 \text{ d}^{-1}$ in 2014), the influent is split in two treatment lines (60% of the sewage goes to Line 1). Besides CPR, Fe is dosed to prevent H_2S emissions into the biogas during anaerobic digestion. In Line 1, Fe(III) is dosed and in Line 2 Fe(II) is dosed in the nitrification zone ($\approx 1.5 \text{ mg DO L}^{-1}$). SRTs before digestion are around 15 days (50% in the aerated zone) and during anaerobic digestion around 42 days. The digesters of both STPs, receive external sludge which accounts for about 30% (Nieuwveer) and about 25% (Leeuwarden) of the total digested sludge. At both locations, samples were taken to analyse the composition of the of the sewage (sludge). From these measurements (Table A. 1 and Table A. 2) Fe and P mass balances were calculated. To calculate Fe and P loads, average daily flow rates of the sampling days were used. Samples were taken between December 2014 and March 2015, after a period of 48 h without precipitation. The STP Leeuwarden was sampled three times. Results reported in Table A. 1 and for the mass balances are average values of the triplicate measurements and of the daily loads of these samplings. The STP Nieuwveer was sampled once in March 2015.

Samples were stored and transported in cooling boxes on ice to reduce microbial activity. Sample processing started 1 h (Leeuwarden) and 3 h (Nieuwveer) after sampling. Sample drying started latest 8 h after sampling and was completed within 24 h. Sampling and sample processing were done under anaerobic conditions to prevent oxidation and degassing of samples. Sewage was collected; using syringes with attached tubing that were washed several times with sewage. Sewage sludge was taken from valves using a funnel with attached tubing. Samples were then filled in serum bottles. To rinse bottles, about three times their volume was flowed through the bottle by inserting the end of the tubing to the bottom of the bottle. Then the bottles were sealed with butyl rubber stoppers (referred to as anaerobic samples hereafter). With these samples the composition of the liquid phase was determined and material for solid analyses was obtained. For total solids (TS), volatile solids (VS) and to determine the total elemental composition of the sewage (sludge), separate samples, without special precautions to prevent sample oxidation, were taken (hereafter, referred to as mass balance (MB) samples). Separate sampling was considered to be necessary as the TS content of the anaerobic samples could change due to rinsing of serum bottles.

In Nieuwveer, the influent sample was a mixture of raw influent and recirculated effluent (40% of the effluent is recirculated). For the mass balances, the Fe and P concentrations of the raw effluent were calculated. The external sludge sample was taken from a pre-storage tank, and contained an unknown mixture of external sludge. In Leeuwarden, P loads from external sludge were below

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