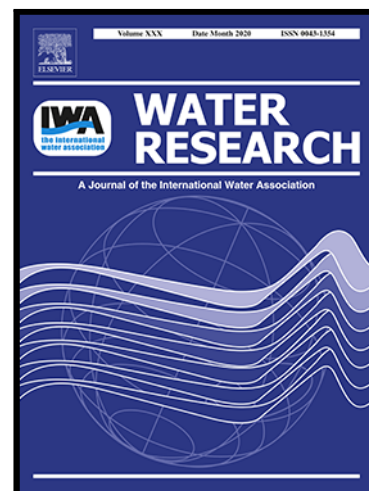


Effects of aging of ferric-based drinking water sludge on its reactivity for sulfide and phosphate removal

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PII: S0043-1354(20)30716-8
DOI: <https://doi.org/10.1016/j.watres.2020.116179>
Reference: WR 116179



To appear in: *Water Research*

Received date: 24 February 2020
Revised date: 30 June 2020
Accepted date: 13 July 2020

Please cite this article as: Sirajus Salehin , Jagadeesh kumar Kulandaivelu , Mario Rebosura Jr. , Olaf van der Kolk , Jürg Keller , Katrin Doederer , Wolfgang Gernjak , Bogdan C. Donose , Zhiguo Yuan , Ilje Pikaar , Effects of aging of ferric-based drinking water sludge on its reactivity for sulfide and phosphate removal, *Water Research* (2020), doi: <https://doi.org/10.1016/j.watres.2020.116179>

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Highlights

- Akaganeite is the main iron oxide species in ferric DWS
- Akaganeite transforms from amorphous to more crystalline form during DWS aging
- Sulfide removal capacity of ferric DWS decreases with increased sludge age
- Aeration during activated sludge treatment breaks the crystalline form of akaganeite
- Enhanced P removal in WWTPs can be achieved by using ferric DWS

Effects of aging of ferric-based drinking water sludge on its reactivity for sulfide and phosphate removal

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Keywords: drinking water sludge, resource recovery, sulfide control, phosphate removal, coagulant reuse, circular economy.

Abstract

Recent studies demonstrated the practical potential of multiple beneficial reuse of ferric-rich drinking water sludge (ferric DWS) for sulfide and phosphate removal in wastewater applications. In practice, ferric DWS is often stored on-site for periods ranging from days to several weeks (or even months), which may affect its reuse potential through changes in iron speciation and morphology. In this study, we investigated for the first time the impact of ferric DWS ‘aging’ time on the iron speciation and morphology and its subsequent impact on its reactivity and overall sulfide and phosphate removal capacity. A series of coagulation tests were conducted to generate ferric DWS of a practically relevant composition by using raw influent water from a full-scale drinking water treatment plant (DWTP). A comparison with ferric DWS from 8 full-scale DWTPs confirmed the similitude. The presence of akaganeite (β -FeOOH) was detected in ferric DWS (through XRD analyses), independent of the DWS storage time. However, the morphology of akaganeite changed over time from a predominant poorly-crystalline phase in ‘fresh’ DWS ($8 \pm 0.1\%$ of total Fe) to a highly crystalline phase ($76 \pm 3\%$ of total Fe) at a sludge aging time of 30 days which was confirmed by means of Rietveld refinement in XRD analyses ($n=3$). Subsequent batch tests showed that its sulfide removal capacity decreased significantly from 1.30 ± 0.02 mmol S/mmol Fe (day 1) to 0.60 ± 0.01 (day 30), a decrease of 54 % ($p < 0.05$). The level of crystallinity however had no impact on sulfide removal kinetics, most sulfide being removed within 10 minutes. Upon aeration of sulfide-loaded ferric DWS in activate sludge, amorphous iron oxides species were formed independent of the initial DWS crystallinity which resulted in efficient P removal at capacities similar to that of conventional FeCl_3 dosing.

Introduction

The majority of drinking water treatment plants (DWTPs) rely on coagulation and flocculation for the removal of turbidity, colour, natural organic matter (NOM) and pathogens from raw water (Bratby, 2016; Matilainen et al., 2010; Okour et al., 2009). Amongst the various coagulants used at DWTPs, the most commonly used are aluminium sulfate (often referred to as alum) and ferric salts (i.e. either in the form of ferric sulfate or ferric chloride) (Pikaar et al., 2014). An unavoidable by-product of coagulation-flocculation is the generation of large amounts of drinking water sludge (DWS) rich in aluminium or iron, depending on the type of coagulant used (Babatunde et al., 2007). As examples showing the enormous amounts produced, DWS generated in the United Kingdom and The Netherlands exceeds 130,000 and 29,700 wet tonnes, respectively per year (Aquaminerals, 2018; Binnie et al., 2018).

Management of DWS incurs large costs and often comprises a substantial fraction of the operational expenditure of DWTPs, with landfilling often used as ultimate disposal route (Frias et al., 2013; Keeley et al., 2016). Therefore, significant research efforts have been made focussing on coagulant recovery, purification and direct reuse within the drinking water treatment process. The benefits of such an approach are twofold as it results in a reduced chemical demand in terms of 'fresh' coagulant as well as in a reduced DWS production (Keeley et al., 2014; Keeley et al., 2016). While the practical feasibility of various approaches including Donnan dialysis (Prakash et al., 2003), liquid ion exchange (Sthapak et al., 2008) and ion exchange with cation resin (Petruzzelli et al., 2000) has been successfully demonstrated, the relatively low coagulant prices make selective recovery and purification approaches economically challenging (Keeley et al., 2012). Moreover, direct reuse within the drinking water treatment process comes with certain technical challenges as the purification

process needs to adhere to stringent regulatory requirements in terms of product quality in order to safeguard human health (Keeley et al., 2016).

Considering the above described limitations of direct reuse within the drinking water treatment process, there is a general interest in low-cost and low risk coagulant reuse approaches. In this context, the reuse of ferric based DWS in a sewer context is of special interest. Iron salts are the most commonly used chemicals to combat hydrogen sulfide induced sewer corrosion, a notorious and costly problem for utilities globally (Pikaar et al., 2014). Considering the high iron content of ferric based DWS, it has the potential to be reused in sewers for sulfide control. Indeed, the effective reuse of ferric based DWS for efficient sulfide control in laboratory scale rising main sewer reactors was demonstrated previously (Sun et al., 2015). Importantly, in a very recent study, the feasibility of the multiple reuse of iron-rich DWS for sulfide control in sewers, followed by phosphate removal in wastewater treatment and sulfide control during anaerobic digestion at the downstream wastewater treatment plant (WWTP) was demonstrated through long-term continuous experiments using a laboratory scale reactor system mimicking the urban wastewater system (Rebosura et al., 2020). It was found that DWS achieved similar treatment performance compared with FeCl_3 dosing in sewers in terms of sulfide control and phosphate removal (Rebosura et al., 2020; Rebosura et al., 2018).

While the above described studies clearly highlight the potential of beneficial reuse of ferric DWS in sewers and downstream WWTPs, the detailed characterization and potential transformation of iron species prior to reuse was not investigated in detail. Such information is essential as iron chemistry is complex with potential transformations in iron speciation and morphology that may occur over time from more amorphous and reactive species that are thermodynamically unstable (e.g. ferrihydrite and akaganeite) to more crystalline and less reactive species such as goethite and hematite (Atkinson et al., 1977; Baltpurvins et al., 1996;

Cornell et al., 1989). The ultimate iron speciation and rate of transformation is complex and depends on several factors including solution pH, the anions present in solution, presence of oxygen and the storage temperature. To our best knowledge, no studies have been conducted investigating the aging of Fe-DWS under the prevalent anaerobic conditions occurring in real-life application. As in a practical situation DWS is often stored on-site from days up to several weeks, such transformation may thus occur, with a potentially negative impact on the reuse ability of DWS. Therefore, this study aimed to determine the impact of the storage time on the physicochemical changes of ferric DWS, and subsequently its reactivity and capacity in sulfide removal in sewers and in phosphorus removal in the downstream wastewater treatment plant. For this purpose, a series of laboratory-scale jar tests (i.e. coagulation experiments) were conducted to generate Fe-DWS using real influent from a local water treatment plant (in South-East Queensland) and subsequently stored under anaerobic conditions to mimic the storage conditions of Fe-DWS encountered in real-life applications. Importantly, to confirm that the produced ferric DWS was of a similar composition with that obtained in real-life applications, we conducted an industry survey of ferric DWS originating from 8 full-scale DWTPs (with ferric chloride as coagulant in their treatment process).

The produced Fe-DWS was characterized with XRD (combined semi-quantitative) and SEM-EDS analyses in order to investigate and quantify any changes in iron speciation and morphology in the DWS at increasing sludge aging times over a period of 30 days. The impact on sulfide removal in sewers and phosphate removal in activated sludge tanks was assessed through comprehensive batch sulfide and phosphate removal experiments using the produced ferric DWS at different sludge aging times.

2. Materials and methods

2.1 Coagulation experiments for the production of ferric DWS

Coagulation experiments were conducted to produce ‘fresh’ ferric DWS. In order to produce Fe-DWS with a composition similar to that obtained in a practical situation, surface water originating from a dam used as raw influent for a main water treatment plant in South-East Queensland, Australia was used in all coagulation experiments. Moreover, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was added at a typical dosing rate commonly applied for coagulation of surface water. Finally, an industry survey was conducted to confirm that the Fe-DWS produced in this study is similar to that of Fe-DWS from full-scale plants (see Table 1).

All coagulation experiments were conducted by means of jar tests using a flocculator (Velp Scientific, USA). The jar tests were conducted at ambient temperatures ($22.2 \pm 1^\circ\text{C}$) following a standard coagulation protocol. The pH of the raw influent used was 6.45 ± 0.12 , however due to the acidity of FeCl_3 , the pH dropped to 4.1 ± 0.3 after coagulant addition. Therefore, prior to the jar tests, simple titration experiments were performed to evaluate the volume of NaOH (as 1% solution) needed to adjust the pH to the desired values of 5.5 ± 0.1 at the dosing rates applied (data not shown). Subsequent jar tests were conducted using 6 beakers filled with 1.5 L untreated surface water to which the amount of NaOH determined by the titration experiments was added, while the solution was mixed at a speed of 120rpm using overhead stirrers attached to the flocculator. Immediately afterwards, the coagulant was added with rapid mixing continued for 60 seconds. The initial rapid mixing to promote coagulation was followed by a period of slow mixing at 20 rpm for a duration of 20 minutes. Finally, the solutions were allowed to settle for 30 minutes.

The first set of experiments was the coagulation tests using ferric chloride ($n=3$). Ferric chloride was dosed at a rate of $17.87 \text{ mg Fe}^{3+}/\text{L}$ (equivalent to 86 mg/L as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). Samples were taken for analyses of dissolved organic carbon (DOC), UV_{254} ,

specific UV absorbance (SUVA), natural organic matter (NOM), total and soluble Fe and P concentrations before and after jar testing in order to assess the treatment performance of the coagulation process. The obtained water quality parameters are presented in Table S1.

The second set of experiments was conducted to generate sufficient Fe-DWS for the detailed characterization and aging studies followed by sulfide and phosphate removal experiments. At the end of each coagulation experiment, the produced ferric DWS was collected in 50 mL centrifuge tubes and immediately centrifuged at $3750 \times g$ for 20 minutes to produce thickened sludge with a dry solids content of 65 ± 2.7 g/L. Subsequently, the headspace of the tubes containing the thickened ferric DWS was sparged with N_2 and immediately closed with a lid to ensure anaerobic conditions and stored at ambient temperatures (i.e. 22 ± 1 °C) over a period of 30 days.

Table 1. Comparison of produced ferric DWS characteristics with real-life ferric DWS from full-scale WTP (n=8, obtained from industry survey). Data presented are mean \pm standard deviation.

Parameter	Ferric DWS composition obtained in this study (n=3)	Ferric DWS composition from full-scale drinking water treatment plants (n=8)
Fe (mg/g TS)	392 ± 4	311 ± 38
Total COD (mg/g TS)	139 ± 5	140 ± 25
Al (mg/g TS)	2 ± 0.02	2 ± 0.6
P (mg/g TS)	0.6 ± 0.01	1.5 ± 0.2
S (mg/g TS)	3 ± 0.04	No data
Mn (mg/g TS)	1 ± 0.2	1.5 ± 0.4
Pb (mg/g TS)	0.2 ± 0.01	0.2 ± 0.1
Cu (mg/g TS)	0.4 ± 0.01	0.3 ± 0.1

Zn (mg/g TS)	0.06 ± 0.00	0.1 ± 0.06
Ni (mg/g TS)	0.07 ± 0.00	0.03 ± 0.02

2.2 Sludge characterization

Samples were taken at different sludge aging times from the Fe-DWS storage container and stored at $-18\text{ }^{\circ}\text{C}$ followed by subsequent freeze-drying ($-50\text{ }^{\circ}\text{C}$, 0.1 millibar). The freeze-dried samples were ground to thin powder under anaerobic conditions and subsequently characterized through X-ray Diffraction (XRD) (qualitative and semi-quantitative) and Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM-EDS) analyses.

XRD analyses was conducted using a D8 Bruker diffractometer equipped with a (θ , 2θ) goniometer and a position sensitive detector (Cu $K\alpha 1$ radiation at $\lambda=1.55\text{ \AA}$). Reflections were collected within the $[5-80^{\circ}]$ 2θ range, with a step width of 0.02 and 1.2 seconds/step of collecting time. The resultant 2θ peaks were analysed with the XRD software Diffrac.Eva (version 4) and matched with the ICDD PDF-4+ 2019 database.

Semi-quantitative XRD analyses (i.e. Rietveld refinements) were conducted to evaluate the degree of crystallinity of the Fe-DWS as a function of the sludge aging time as well as to determine the amount of different types of iron oxide in the Fe-DWS using TOPAS V-4.2 software. For this purpose, corundum ($\alpha\text{-Al}_2\text{O}_3$) was used as an internal standard for all semi-quantitative measurements following a procedure described previously (Salehin et al., 2019; Salehin et al., 2020).

The morphology and elemental composition of Fe-DWS were characterized by means of SEM-EDS analysis. A high-resolution Scanning Electron Microscope (JEOL JSM-6610) was used to obtain secondary electron micrographs at an applied accelerating voltage of 15

kV. The SEM was equipped with an X-ray detector for elemental analysis (Oxford Instruments/50 mm² X-MAX SDD X-ray detector). Samples were placed on stubs attached with high-purity conductive double-sided adhesive carbon tapes. The samples were subsequently carbon coated using a Quorum Q150T Turbo-Pumped Sputter Coater as a means to avoid charge build-up and to improve secondary electrons signal.

2.3 Sulfide and phosphate removal experiments

The sulfide and phosphate removal experiments were conducted using untreated sewage from a local pumping station wet well that only receives household wastewater in a residential zone (Brisbane, Queensland). The sewage was collected on a weekly basis and immediately stored at 4 °C. The sulfide removal experiments were conducted under anaerobic conditions in gas-tight PerspexTM cylindrical reactors with a working volume of 0.5 L, whereas the phosphate removal experiments were conducted in a beaker with a working volume of 150mL.

Prior to use, the sewage was filtered to remove any solids, sparged with N₂ for 30 minutes to ensure anaerobic conditions and heated up to ambient temperature at 22.1 ± 1 °C. The sewage contained sulfate at concentrations of 8.5 ± 0.8 mg S/L, sulfide at 2.9 ± 0.4 mg S/L, phosphate at 6.1 ± 0.6 mg PO₄-P/L, ammonium at 41.6 ± 5.9 mg NH₄-N/L, and a total and soluble COD at 397.2 ± 28.3 and 245.7 ± 10.8 mg COD/L, respectively. Prior to each experiment, sulfide and phosphate were spiked to the sewage to reach an initial concentration of 20 mg/L for both sulfide-S and PO₄-P using standard reagent grade salts (Na₂S·9H₂O and KH₂PO₄, from Sigma-Aldrich). The produced Fe-DWS was mixed with deoxygenated demineralized water to make a slurry with a Fe concentration of 2.7 g Fe/L. The slurry was added to the reactor to reach Fe concentrations ranging between 17.5 mg to 70 mg Fe/L,

depending on the experiment conducted. The latter concentration equalled to Fe:S molar ratios of 0.5:1 and 2:1, respectively. The pH levels were monitored online using a pH sensor probe (pH-110 Digital Industrial pH/ORP Sensor Electrode. All experiments were conducted in triplicate and at a constant pH of 7.1 ± 0.1 , unless specified otherwise.

The sulfide removal experiments were divided into 3 different sets. The first set of experiments was conducted to determine the impact of sludge aging time on sulfide removal efficiency. For this purpose, Fe-DWS subjected to different aging times (i.e. 1, 3, 7, 10, 15 and 30 days) were dosed to sewage at an Fe:S molar ratio of 0.5:1. This Fe:S dosing ratio was chosen to ensure sulfide is in excess so that the sulfide removal capacity of the ferric DWS can be determined. The second set of experiments was conducted to investigate the impact of different pH levels towards sulfide control in sewage, within a range typically observed in sewage (i.e. pH 6.5, 7.0 and 7.5). For this purpose, 'fresh' Fe-DWS (day 1) was dosed to sewage at Fe:S molar ratio of 0.5:1. The third set of experiments was conducted to confirm that complete sulfide removal can be achieved by dosing Fe-DWS (day 1) at a Fe:S molar ratio of 2:1. Each of the batch tests described above was conducted over a 1 hour period to ensure that stable dissolved sulfide concentrations were reached.

The fourth set of experiments was conducted to investigate the feasibility of regenerating in-sewer dosed Fe-DWS aiming to achieve efficient P removal in aerated activated sludge tanks of down-stream WWTPs. For this purpose, Fe-DWS mixed sewage was fed to aerated activated sludge at a ratio of 1:1 (v/v), a similar ratio used by Gutierrez et al., (2010) in which the regeneration of in-sewer dosed FeCl_3 for P removal in downstream WWTPs was investigated (Gutierrez et al., 2010). The Fe-DWS mixed sewage was generated using Fe-DWS with three different sludge ages (i.e. 1, 15 and 30 days) with sulfide and phosphate spiked sewage to reach initial concentrations of 20 mg/L. Fe-DWS was added (in slurry form) to sewage at concentrations of 17.5, 24.5, and 35 mg Fe-DWS/L, equalling to

Fe:S molar ratios of 0.5:1, 0.7:1 and 1:1 for sludge ages of 1, 15 and 30 days, respectively. The activated sludge was collected from a laboratory-scale Sequence Batch Reactor (SBR) fed with domestic sewage (Rebosura et al., 2020). The domestic sewage contained phosphate and sulfate concentrations of 7.34 ± 1.09 mg PO₄-P/L and 17.90 ± 5.07 mg SO₄-S/L, respectively. After mixing the Fe-DWS mixed sewage (after sulfide removal) with the activated sludge, the initial molar Fe:P ratios during the Fe-DWS regeneration experiments were 0.8:1, 1:1 and 1.4:1 for sludge ages of 1, 15 and 30 days, respectively. Immediately after mixing the activated sludge with the Fe-DWS mixed sewage, liquid samples were taken for analysis of total-Fe, PO₄-P and dissolved inorganic sulfur species (i.e. sulfide, sulfite, thiosulfate and sulfate). Subsequently, air was supplied by means of a gas frit over a 2 hour period to ensure that stable phosphate concentrations were reached. Liquid samples were taken at $t = 5, 15, 30, 60$ and 120 minutes and analysed for PO₄-P and dissolved inorganic sulfur species. The experiments were conducted in triplicate.

2.4 Chemical analyses

pH and temperature were measured using a handheld meter (SPER Scientific). Turbidity was measured using a portable turbidity meter (TN400, Watertest Systems, Australia). UV absorbance was measured by a Cary 50 UV spectrometer in a 1 cm quartz cuvette. Prior to analysis, samples were pre-filtered with $0.22 \mu\text{m}$ membrane filters (Millipore, Millex GP). SUVA (specific ultraviolet absorbance) was calculated according to (Edzwald, 1993). Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-L CSH Total Organic Carbon Analyser with a TNM-L TN unit. Dissolved sulfur species (i.e. sulfide, sulfate, sulfite and thiosulfate) were measured using an Ion Chromatograph (IC) coupled with a UV and conductivity detector (Dionex ICS-2000). Samples were immediately filtered after

collection (0.22 μm , Millipore, Millex GP) and preserved with a sulfide anti-oxidant buffer (SAOB) solution, according to (Keller-Lehmann et al., 2006). Total and soluble Al, Fe, P, and S concentrations were analysed by means of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Perkin Elmer Optima 7300 DV, Waltham, MA, USA). Phosphate ($\text{PO}_4\text{-P}$) concentrations were analysed using a Lachat Quickchem 8000 (Lachat Instrument, Milwaukee, Wisconsin) flow injection analyser (FIA). Total and soluble COD concentrations were measured by means of COD cuvette tests (Merck, range 25-1500 and 500-10000 mg/L). Total solids (TS) and volatile solids (VS) were analysed according to standard methods (APHA, 1995).

3. Results and discussion

3.1 The impact of aging on the iron speciation and morphology of ferric DWS

Figure 1A shows the X-ray diffraction patterns of the ferric DWS at various aging times. It can be seen that akaganeite (β -FeOOH), a chloride containing ferric oxyhydroxide mineral, was the main iron oxide species present in the sludge. The presence of chloride in akaganeite was confirmed through SEM-EDS analyses (Fig. S2). In addition to akaganeite, the DWS also contained between 4-10% of silica (SiO_2) in the inorganic fraction, a concentration within the range typically observed in drinking water sludge (Shahin et al., 2019).

While akaganeite was the predominant iron species present independent of the DWS aging time, Fig. 1A clearly shows the change in the morphology of akaganeite from a more amorphous (day 1) to a more crystalline phase (day 30). Subsequent semi-quantitative XRD revealed that crystalline akaganeite comprised $8 \pm 0.1\%$, $24 \pm 0.4\%$ and $76 \pm 3\%$ of the total Fe content of the DWS at a sludge age of 1, 14 and 30 days, respectively (Fig. 1B).

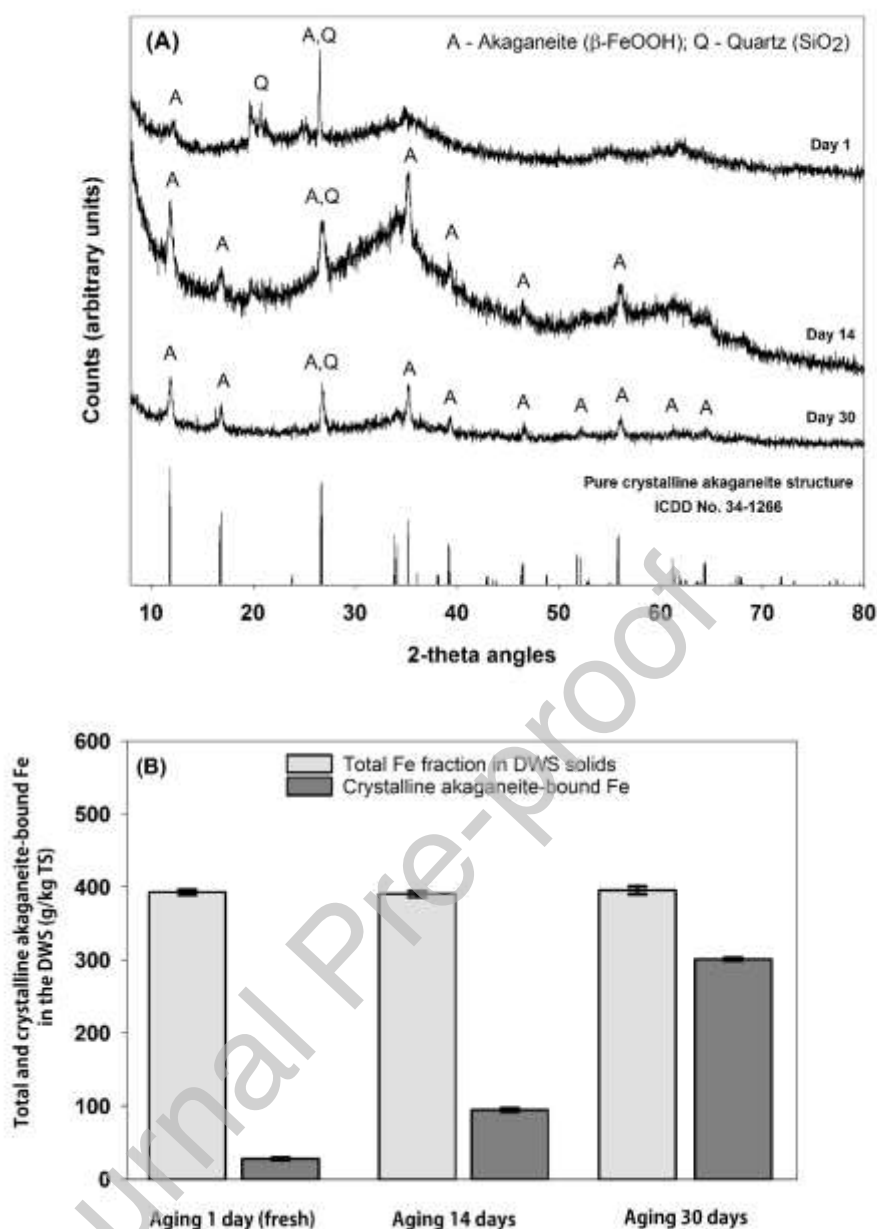


Figure 1. (A) X-ray diffraction patterns of ferric DWS showing the gradual increase in akaganeite (β -FeOOH) crystallinity with increasing aging times and (B) calculated fraction of crystalline akaganeite-bound Fe within the DWS at different sludge age.

Our results show that natural organic matter (NOM) (i.e. humic and fulvic acid-like substances) was removed from raw water during the coagulation process and was captured within the Fe-DWS matrix (see supplementary information Fig. S1). It has been reported that NOM is usually removed via adsorption at the anoxic-oxic interfaces of iron oxyhydroxides

(Chen et al., 2014; Kaiser et al., 2000; Liao et al., 2017; Riedel et al., 2013). Interestingly, it has been reported that NOM plays an important role in inducing akaganeite crystallization (Nesterova et al., 2003). This suggests that the trapped NOM within Fe-DWS matrix may have promoted the gradual akaganeite crystallization via interstitial pores of the DWS matrix. Further research is warranted to fundamentally understand the potential impact of NOM on the aging of Fe-DWS.

3.2 Impact of sludge aging on sulfide removal from sewage

Figure 2A shows the impact of sludge aging time (and thus the level of crystallinity of the Fe-DWS) on the sulfide removal efficiency at a constant dosing ratio of 0.5 Fe-DWS:sulfide-S. The figure shows that the sludge aging time had a significant impact on the sulfide removal efficiency with a decrease in dissolved sulfide removed from 13.66 ± 0.41 to 6.34 ± 0.51 mg S/L at sludge ages of 1 and 30 days, respectively ($p < 0.05$). The latter equalled to sulfide removal capacities of 1.30 ± 0.02 mmol sulfide-S/mmol Fe (day 1) and 0.60 ± 0.01 mmol sulfide-S/mmol Fe (day 30) (see Fig. 2B), a decrease of $53.7 \pm 1.5\%$. Interestingly, in a recent study in which aged Fe-DWS from a full-scale drinking water treatment was added to a lab-scale sewer reactor very similar sulfide removal capacities were observed (i.e. 0.61 mmol sulfide-S/mmol Fe or 1.64 mmol sulfide-S/mmol Fe) (Rebosura et al., 2020). Equally important, the sulfide removal capacity obtained using ‘fresh’ Fe-DWS (i.e. day 1) was only slightly less than the theoretical sulfide removal capacity for conventional FeCl_3 dosing (see Fig. 2B). Previous studies reported on the increase in crystallinity of iron oxyhydroxide particles at higher floc ages (Dzombak et al., 1990; Smith et al., 2008). Furthermore, it was found that the increase in crystallinity was accompanied with a decrease in the surface area and active sites. The latter may explain the observed decrease in sulfide removal in our experiments. For further fundamental understanding as well as quantitative assessment of the

particle size and any changes in surface area of the Fe-DWS as a function of the sludge aging time, BET surface area and particle size analysis as well as sequential extractions are warranted.

Overall, the results highlight a strong relation between the degree of akaganeite crystallinity and overall sulfide removal capacity, albeit not affecting the fast reaction kinetics. Sulfide removal was found to be fast with most of the sulfide being removed within 10 minutes, independent of the sludge aging time (Fig. 2A). It has been postulated that the reaction of sulfide with ferric oxide species is a surface controlled process (Canfield, 1989; Cornell et al., 1989). Since it is commonly accepted that amorphous iron oxides have higher surface areas than crystalline iron oxides (Chitrakar et al., 2006; Kumar et al., 2019; Wilfert et al., 2015), this supports our finding that the sulfide removal capacity decreased at increasing sludge aging times. Furthermore, the reaction of sulfide with ferric oxide species involves multiple steps. In the first step, chemical adsorption of hydrogen sulfide onto the ferric oxide surface takes place. The chemi-sorbed sulfide subsequently reacts with the ferric oxide, thereby reducing it to soluble ferrous ions while the sulfide is oxidized to elemental sulfur (Afonso et al., 1992; Peiffer et al., 1992; Poulton, 2003; Poulton et al., 2004; Sun et al., 2014). The kinetics of this so-called sulfide induced reductive dissolution of iron process highly depends on the type of ferric oxides, and is reported to be in the order of minutes for more reactive species such as amorphous akaganeite (Poulton, 2003; Poulton et al., 2004). Subsequently the formed Fe^{2+} rapidly reacts with any dissolved sulfide present in solution to form insoluble FeS. Indeed, analysis of the iron concentrations confirmed that the soluble iron concentrations were negligible throughout the duration of the experiments (data not shown). In addition, SEM-EDS analyses were conducted after reaction with sulfide in order to illustrate any change in morphology as well as to determine the elemental composition (see supplementary information). Figure S4 shows that after the reaction with sulfide, the surface

of ferric DWS significantly changed from a prevalent smooth to a very rough surface. The EDS elemental analyses conducted on the ferric DWS particles after reaction with sulfide revealed that the iron to sulfur molar ratio (Fe:S) equalled to about 1:1, which implies that mackinawite was formed (Lan et al., 2014).

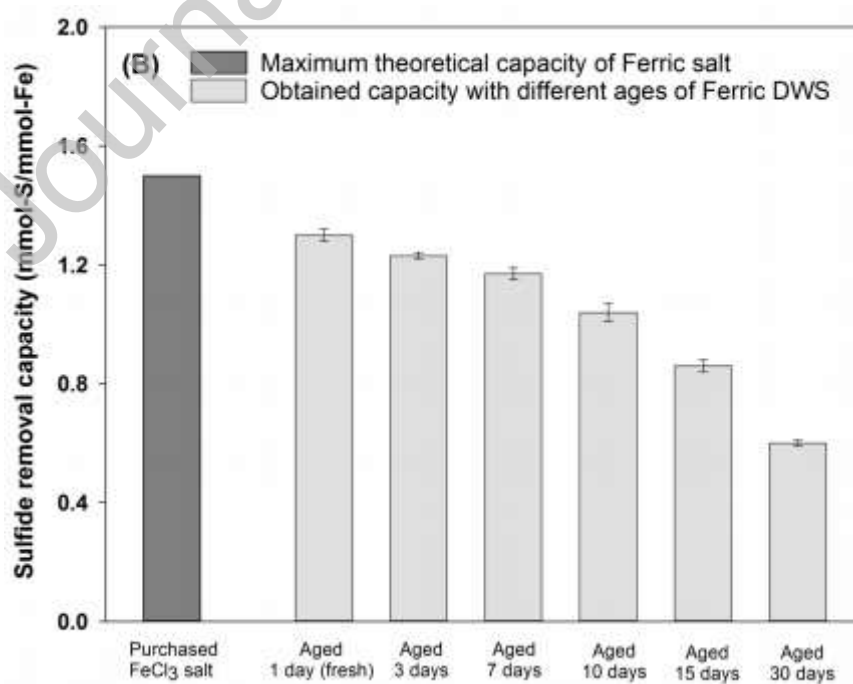
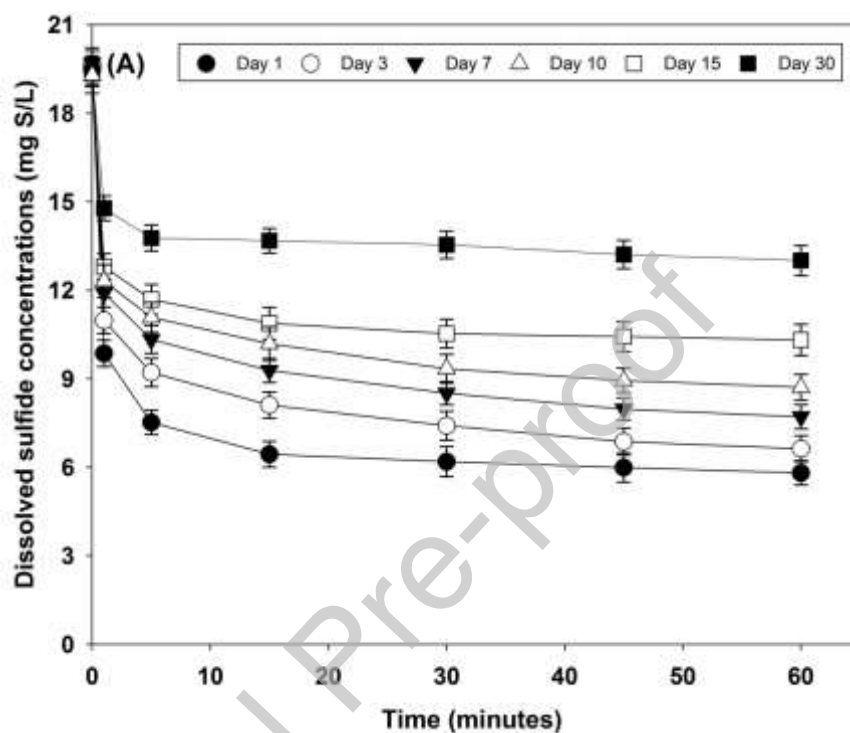


Figure 2. (A) Impact of aging of ferric DWS on dissolved sulfide removal with molar DWS-Fe:sulfide-S dosing of 0.5:1 and (B) sulfide removal capacity of ferric DWS at various aging times. Data presented are mean \pm standard deviation (n=3).

During conventional FeCl_3 dosing, the sewage pH has a significant impact on the iron dosing requirements to achieve the desired level of sulfide control, especially around the circumneutral pH values often observed in sewers. Therefore, we conducted an additional set of experiments in which we assessed the impact of the pH on the sulfide removal efficiency using ‘fresh’ DWS (day 1) at a Fe-DWS:sulfide-S dosing ratio of $\sim 0.5:1$. Figure 3 shows that the amount of sulfide removed decreased from 14.45 ± 0.4 at pH 7.5 to 12.21 ± 0.3 mg S/L at pH 6.5. The latter equalled to theoretical sulfide removal capacities of 1.32 ± 0.01 and 1.11 ± 0.02 mmol sulfide-S/mmol Fe for pH 7.5 and 6.5, respectively, a significant ($p < 0.05$) reduction of $15.2 \pm 0.6\%$. Previous studies investigating the impact of the pH on sulfide precipitation in sewage using conventional iron salt dosing showed a more profound impact of the pH (Firer et al., 2008; Nielsen et al., 2008). For example, Nielsen *et al.*, (2008) found that at pH levels below 7, less than 40% of the iron salts dosed was used for sulfide removal. While both the pH and sludge age affect sulfide removal efficiency, our results show that the increase in crystallinity of akaganeite due to aging of the DWS had a more profound impact. Finally, an additional experiment at a DWS-Fe:sulfide-S dosing ratio of 2:1 confirmed that complete sulfide removal can be achieved (see supplementary Fig. S3).

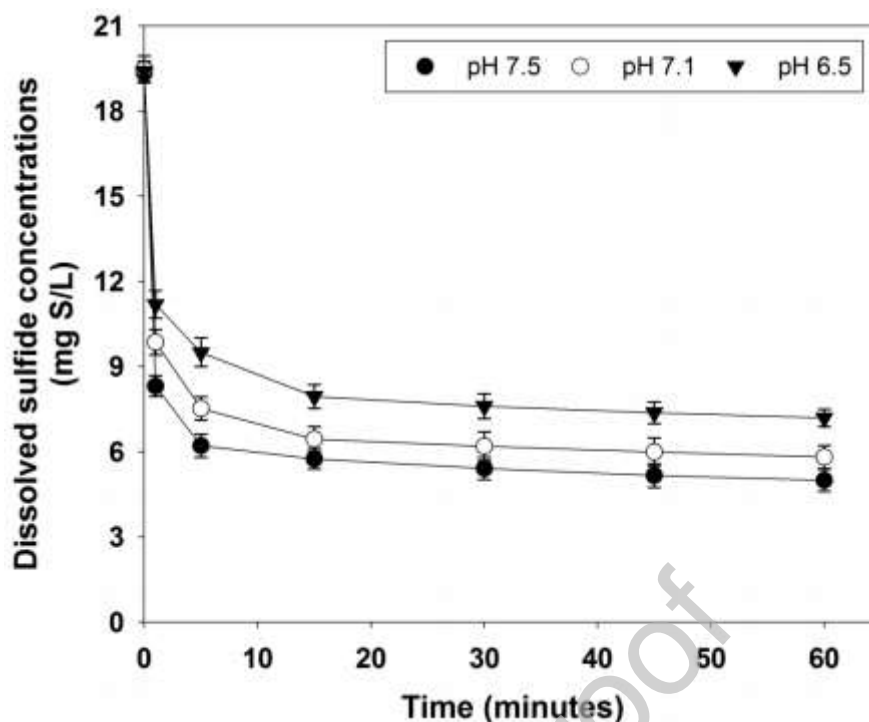


Figure 3. Impact of pH on sulfide removal from sewage by ‘fresh’ DWS (day 1). Data presented are mean \pm standard deviation ($n=3$).

3.3 The impact of aging of DWS on down-stream phosphate removal in activated sludge tanks

Figure 4A shows the P removal efficiency at different Fe-DWS dosing ratios and aging times in aerated activated sludge. P removal kinetics were lower for the ‘fresh’ Fe-DWS sludge. The latter was most likely due to the lower Fe:P molar ratios and lower initial P concentration. A similar observation was made in a study of Gutierrez *et al.*, (2010), in which FeCl_3 dosed in sewers was fed to aerated activated sludge like in this study (Gutierrez *et al.*, 2010). Importantly, independent of the Fe-DWS dosing ratios and aging time, the overall phosphate removal capacity in aerated activated sludge remained constant ($p < 0.05$) (see Fig.4B). Lastly, the calculated initial dissolved sulfide concentration was around 6 mg S/L. However, dissolved sulfide was no longer detected for the remainder of the experiments due

to rapid stripping and oxidation of the dissolved sulfide induced by the aeration process. As such, the initial presence of dissolved sulfide did not affect the P removal results under the prevalent aerobic conditions.

Figure 4C shows the X-ray diffraction patterns of Fe-DWS at an aging time of 30 days before and after being subjected to aeration in the presence of active sludge. A distinct change in morphology of the Fe-DWS changed from a more crystalline phase to a completely amorphous phase can be observed. As discussed in more detail in section 3.1, the reaction of sulfide with ferric oxides species is a surface-controlled process that over time results in the formation of elemental sulfur and FeS. FeS, often referred as mackinawite is a poorly-crystalline iron sulfide species. Moreover, previous studies showed that oxidation of Fe(II) results in the formation of amorphous Fe(III) oxyhydroxides (Cornell et al., 2003; Poulton et al., 2004; Yuan et al., 2019). Thus, upon aeration of sulfide-loaded Fe-DWS in the activated sludge, amorphous ferric oxyhydroxide species would be formed and subsequently react with phosphate. The latter strongly supports our finding that the P removal capacities was constant independent of the initial DWS sludge age. Finally, upon aeration P uptake would be accompanied with release and oxidation of sulfide to sulfate (Gutierrez et al., 2010). The molar ratio between the amount of iron added and the phosphorus removed (Fe:P) was calculated to be 1.60 ± 0.05 , indicating that precipitation was the predominant removal mechanism. Interestingly, this Fe:P molar ratio was very similar to our previous study in which virgin FeCl_3 was dosed to the same system (i.e. FeCl_3 versus ferric DWS) (Rebosura et al., 2018). It was beyond the scope of this study to fundamentally understand the mechanisms behind the transformation of crystalline akaganeite to an amorphous or poorly crystalline structure induced by aeration. Interestingly, Sun *et al.*, (2014) reported on the regeneration of purchased ferric hydroxide (a commercial product of akaganeite) through aeration (Sun et al., 2014). In that study it was found that regeneration of spent ferric hydroxide through aeration

resulted in the formation of amorphous ferric oxide particle, albeit the underlying mechanisms behind this change in structure could not be elucidated.

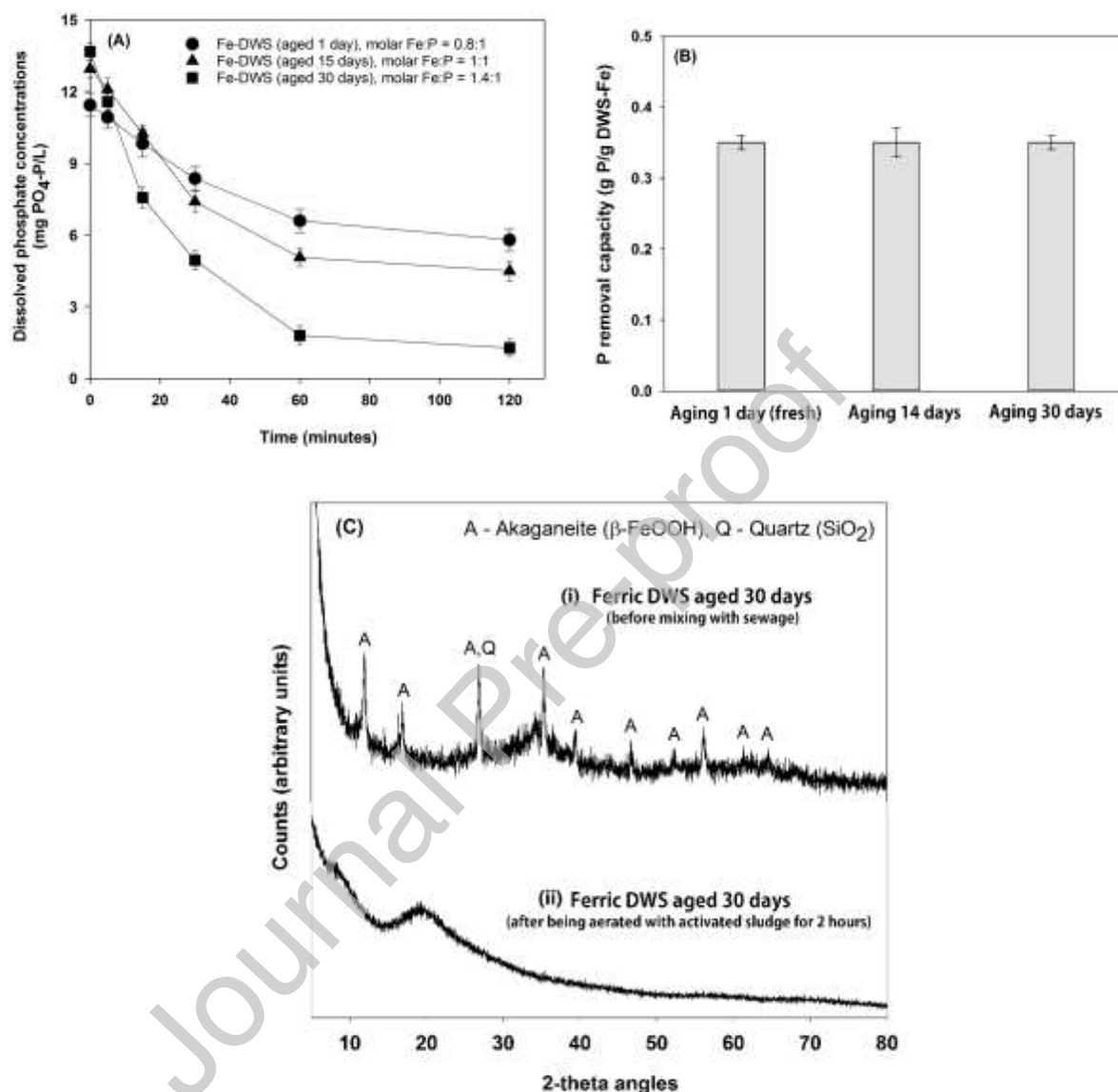


Figure 4. (A) Batch experiments for P removal in activated sludge through aeration of sulfide loaded Fe-DWS, (B) P removal capacities (g P / g Fe-DWS) of sulfide loaded Fe-DWS subjected to aeration in activated sludge at different aging times and (C) X-ray diffraction patterns of (i) Fe-DWS at an aging time of 30 days prior to use and (ii) Fe-DWS at an aging time of 30 days used for sulfide removal (i.e. sulfide-loaded Fe-DWS) and subsequently being subjected to aeration with activated sludge for 2 hours.

3.4. Implications for practice

In this study, we investigated the impact of aging on the capacity of ferric DWS as a sulfide control method in sewers. To do so, a series of coagulation tests were conducted to generate ferric DWS using raw influent water from a full-scale drinking water treatment plant. The composition of the produced ferric DWS was compared with analysis from 8 full-scale WTPs through an industry survey. That latter confirmed that the ferric DWS produced in this study was similar to that of ferric DWS produced in full-scale situations, strongly supporting the practical relevance of our findings.

It was found that the iron oxide speciation remained constant with akaganeite (β -FeOOH) being the predominant iron oxide species present in the ferric DWS, independent of sludge aging time. On the other hand, the sludge aging time had a significant impact on the iron oxide morphology. A clear change from a highly amorphous structure for freshly produced ferric DWS (day 1) to a more crystalline form after 30 days of storage time was observed. Importantly, this change was accompanied with a significant decrease in sulfide removal capacity ($p < 0.05$), most likely due to a decrease in available surface sites for adsorption at increasing crystallinity (Kumar et al., 2019; Wilfert et al., 2015). This finding is important with respect to real-life implementation of ferric DWS addition to sewers as a sulfide control method. Ideally, 'fresh' ferric DWS produced at the drinking water treatment plant is directly fed into the surrounding sewer via a dedicated pipeline to ensure the highest sulfide removal capacity of the sludge, thereby minimizing overall ferric DWS requirements. Alternatively, ferric DWS can be stored on site and transported to nearby 'hotspot' of sewer corrosion and odour complaints, albeit with a decrease in sulfide removal capacity on a per unit Fe basis at increasing storage times.

The reaction kinetics were not affected, with most sulfide being removed within 10 minutes, independent of the Fe-DWS storage time. Considering typical HRTs in sewers are in the order of several hours (i.e. 2-6 hours), the addition of Fe-DWS is thus very suitable in a sewer context. The practical relevance is further supported by the fact that discharge of drinking water sludge is adopted in various parts of the world. For example, about 9% and 25% of the total drinking water sludge produced in the USA and United Kingdom is discharged into sewers (Keeley et al., 2014; Walsh, 2009). However, it is important to note that this often involves the discharge of aluminium DWS and is done simply because it is the cheapest DWS disposal route in these situations (Miyanoshita et al., 2009). It has been found that aluminium DWS removes phosphate when dosed to sewers (Makris et al., 2004).

Another important observation is that aeration of less reactive crystalline ferric DWS in the activated sludge tank of the downstream WWTPs significantly changes the morphology from crystalline akaganeite to highly amorphous iron oxide species, independent of the sludge aging time. Importantly, the obtained P removal capacities were very similar to that obtained with FeCl_3 dosing (i.e. 0.35 ± 0.02 g P / g Fe in this study versus 0.36 ± 0.01 g P / g Fe for FeCl_3 dosing, respectively (Rebosura et al., 2018).

Alum and ferric chloride are the most commonly used coagulants for the production of drinking water. The process economics, determined by the local coagulant price, is the key factor determining the choice for water utilities between ferric chloride and alum rather than treatment performance, with both coagulants meeting desired treatment performances in terms of removal of NOM, turbidity and colour (Volk et al., 2000). The fact that Fe-DWS can be beneficially reused in sewers for sulfide control may bring economic benefits for water utilities by reducing the costs for DWS management and disposal costs. It also reduces the chemical demand for wastewater treatment for chemical P removal in activated sludge tanks and sulfide control in digesters. However, there could also be increased costs in wastewater

treatment such as to increased sludge handling and disposal costs and aeration costs in wastewater treatment plants due the increased solids and COD load due to DWS dosing (Rebosura et al., 2020; Sun et al., 2015). All of the above requires careful consideration and should be evaluated through long-term field trials. Finally, cross-sectional collaboration between the water and wastewater utilities will be essential in order for creating awareness of the benefits that an integrated catchment-wide coagulant dosing strategy can bring for both drinking water and wastewater systems.

5. Conclusions

In this study, we investigated the impact of aging of ferric-rich drinking water sludge (DWS) on its reactivity and capacity for sulfide removal in sewers and phosphate removal in downstream wastewater treatment plants. The key findings of the work are:

- Akaganeite (β -FeOOH) was found to be the main iron oxide species in the DWS, independent of the sludge aging time.
- The sludge aging time had a clear impact on the akaganeite morphology from a predominant poorly-crystalline phase for 'fresh' DWS ($8 \pm 0.1\%$ crystallinity) to a more crystalline phase ($76 \pm 3\%$ crystallinity) at a sludge aging time of 30 days.
- The increase of the fraction of crystalline akaganeite was associated with a significant decrease in the total sulfide removal capacity, but did not affect the reaction kinetics with most sulfide being removed within the first 10 minutes.
- Sulfide driven reductive dissolution of crystalline akaganeite followed by aeration in downstream activated sludge tanks changed the akaganeite from a crystalline to a highly amorphous iron oxide species, thereby achieving efficient phosphate removal.

Declaration of interests

None

Acknowledgements

This research was funded by ARC Linkage Project LP140100386: An integrated approach to iron salt use in urban water systems. Sirajus Salehin acknowledges scholarship support from the University of Queensland. The authors acknowledge Mr. Nathan Clayton and Mr. Nigel Dawson for their helpful assistance with the chemical analyses. The authors also acknowledge the support of the AMMRF at the Centre for Microscopy and Microanalysis at the University of Queensland. Wolfgang Gernjak is a member of the Consolidated Research Group ICRA TECH - 2017 SGR 1318 funded by the Economy and Knowledge Department of the Catalan Government.

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