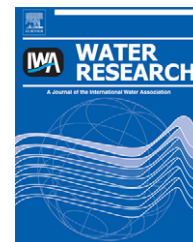


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Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment

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ABSTRACT

Chemical phosphorus (P) removal during aerobic wastewater treatment induced by iron salt addition in sewer systems for sulfide control is investigated. Aerobic batch tests with activated sludge fed with wastewater containing iron sulfide precipitates showed that iron sulfide was rapidly reoxidised in aerobic conditions, resulting in phosphate precipitation. The amount of P removed was proportional to the amount of iron salts added, and for the sludge used, ratios of 0.44 and 0.37 mgP/mgFe were obtained for ferric and ferrous dosages, respectively. The hydraulic retention time (HRT) of iron sulfide in sewers was found to have a crucial impact on the settling of iron sulfide precipitates during primary settling, with a shorter HRT resulting in a higher concentration of iron sulfide in the primary effluent and thus enabling higher P removal. A mathematical model was developed to describe iron sulfide oxidation in aerated activated sludge and the subsequent iron phosphate precipitation. The model was used to optimise FeCl_3 dosing in a real wastewater collection and treatment system. Simulation studies revealed that, by moving FeCl_3 dosing from the WWTP, which is the current practice, to a sewer location upstream of the plant, both sulfide control and phosphate removal could be achieved with the current ferric salt consumption. This work highlights the importance of integrated management of sewer networks and wastewater treatment plants.

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1. Introduction

Sulfide production in sewers is a serious concern for water utilities as it causes detrimental problems such as malodours, health hazards and corrosion (Thistlethwayte, 1972; USEPA, 1974; Boon, 1995; Hvitved-Jacobsen, 2002; Zhang et al., 2008). Iron salts, either in ferric or ferrous forms, are often added to sewers as the salts of chloride (Jameel, 1989; Nielsen et al., 2005), sulfate (USEPA, 1974) or nitrate (Padival et al., 1995) for reducing hydrogen sulfide release to sewer air (Nielsen et al., 2005). Fe^{2+} removes sulfide by precipitating it as ferrous sulfide (FeS), while Fe^{3+} oxidizes sulfide chemically to elemental sulfur, with itself

being reduced to Fe^{2+} , which subsequently precipitates sulfide forming FeS (Nielsen et al., 2005).

Phosphorus is one of the nutrients responsible for eutrophication and hence its discharge to receiving waters is strictly regulated in many parts of the world. In order to achieve stipulated standards of nutrient discharge, iron salts are often added to wastewater treatment plants (WWTP) to precipitate phosphate as insoluble ferric hydroxyl-phosphate complexes. Ferric chloride is most commonly used for P precipitation in activated sludge plants (Rasmussen and Nielsen, 1996; Nielsen et al., 2005) but ferrous salts may also be used (Singer, 1972; Jameel, 1989). Simultaneous dosing of ferrous and ferric salts

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has been shown as a more effective method for P removal than the dosing of a single iron form (Tomar and Abdullah, 1994; De Haas et al., 2000a). Various empirical expressions describing the resulting products of P precipitation have been proposed in literature. These expressions indicate varying stoichiometric ratios between phosphorus and iron. De Haas et al. (2000b) proposed a formula for ferric hydroxyl–phosphate complex under P-limiting conditions ranging from $\text{Fe}_3(\text{X}^{2+})\text{PO}_4(\text{OH})_8$ to $\text{Fe}_{2.33}(\text{X}^{2+})_{2.5}\text{PO}_4(\text{OH})_9$, with X^{2+} being a divalent cation (e.g. Mg^{2+} or Ca^{2+}).

Problems in sewer networks and wastewater treatment plants are often managed separately without considering the impact of operation in one system on the other. Dosing of chemicals to sewer networks changes wastewater composition, and is therefore expected to have various impacts on WWTP performance (Hvitved-Jacobsen, 2002). In the case of ferrous or ferric salt dosage to sewers, FeS produced ultimately enters the WWTP, with environmental conditions changed from reductive to oxidative. Part of the FeS particles generated in sewers could be oxidised in the aerobic tanks, releasing a portion of the iron as regenerated ferric ions, which would subsequently precipitate phosphate. This effect, if occurring to a large extent, would lead to significant P removal at the WWTP, resulting in reduced chemical consumption for P removal or reduced load to biological phosphorus removal processes.

This paper aims to assess the impact of iron salt dosage to sewers for sulfide control on P removal during aerobic wastewater treatment. The work was conducted by integrating lab-scale experiments with mathematical modelling. Batch tests were carried out with activated sludge from a full scale WWTP and real domestic wastewater. Based on the experimental results, a mathematical model was formulated to describe the aerobic regeneration of ferric ions and their subsequent precipitation with phosphate. Integrated sewer and WWTP modelling was conducted to optimise ferric salt dosage in a real sewage collection and treatment system to achieve simultaneous sulfide control and phosphorus removal.

2. Material and methods

2.1. FeS reoxidation tests

Aerobic iron sulfide oxidation was studied through batch tests carried out with sludge from a full scale WWTP and real domestic sewage. Activated sludge mixed liquor was collected on test days from the Luggage Point WWTP (Brisbane) designed for biological carbon and nitrogen removal, but not for enhanced biological phosphorus removal (EBPR). Domestic sewage was collected from a local wet well prior to each test. Sewage composition in terms of inorganic sulfur compounds, phosphate, nitrogen compounds, Fe^{2+} and Fe^{3+} , and volatile fatty acids (VFA) is shown in Table 1.

Three cylindrical reactors, named as R1, R2 and R3, each with a volume of 3.5 L, were filled up with 3 L mixed liquor. The reactor contents were then sparged with nitrogen gas for 0.5 h to remove any oxygen present. Anaerobic condition in the reactors was confirmed by continuous DO reading of below 0.05 mgO_2/L . The anaerobic mixed liquor was then left under

quiescent conditions for 30 min for sludge settling. After this, 1.5 L supernatant was withdrawn from each reactor.

A batch of domestic sewage was sparged with N_2 gas for 0.5 h to strip off oxygen. At the end of this operation, DO level in the sewage was below 0.05 mgO_2/L . Each of the 3 containers: F1, F2 and F3, were first filled with 1.5 L of the oxygen-devoid sewage. A pre-determined volume of sulfide stock solution (6 g/L $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) was added to each container in order to obtain the intended sulfide concentration (Table 2). Pre-calculated volumes of stock solutions of Fe^{2+} and Fe^{3+} (3 g/L $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, 3 g/L $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) were then injected into containers F2 and F3, respectively, creating iron sulfide precipitates. The amounts of stock solutions added to F2 and F3 were lower than the stoichiometric demands of Fe^{2+} or Fe^{3+} ions for the complete precipitation of the sulfide added, to avoid the presence of free iron in the bulk. Since no iron salts were dosed to F1, iron concentration in F1 was negligible (Table 1). After the addition of chemicals, the contents of containers F2 and F3 were gently mixed until blackening of the wastewater was observed (for about 2 min) indicating the formation of sulfide precipitates. Measurement of liquid phase samples at the end of the mixing period confirmed that there was no residual iron present in the bulk (methods to be described in Section 2.3).

Contents of F1, F2 and F3 were then gently added into reactors R1, R2 and R3, respectively, each containing 1.5 L of settled sludge. All reactors were then mixed for 20 min using a magnetic stirrer at 300 rpm. The mixed liquor in all reactors was then aerated by supplying air through stone diffusers connected to compressed air. The DO concentration was manually maintained between 1.5 and 2.0 mgO_2/L , typical for aerobic activated sludge systems (Metcalf and Eddy, 2003). The aeration was continued for various durations as detailed in Table 2.

During aeration, liquid samples were withdrawn from each reactor every 20 min in the first 80 min (1.3 h). For the tests lasting for 6 h, samples were taken every 60 min afterwards. The durations of the tests were selected to reproduce typical hydraulic retention times (HRT) for activated sludge processes, which is 0.5–8.0 h (Metcalf and Eddy, 2003). The samples were analysed for phosphate, ammonium, nitrite, nitrate, Fe^{2+} , Fe^{3+} and dissolved inorganic sulfur species. In addition, pH was also monitored. All the tests were performed at $22 \pm 1^\circ\text{C}$. More information on the FeS reoxidation procedure can be obtained from Fig. i (Supplementary material).

2.2. Iron sulfide settling tests

In many wastewater treatment plants, sewage is first allowed to settle in a primary clarifier before it reaches biological reactors. The iron sulfide precipitate formed due to iron dosing in a sewer may (partially) settle in a primary clarifier thereby affecting the amount of iron transported to the bioreactors. Iron sulfide settling tests were carried out to examine the dependency of iron sulfide settling on settling time and the time between iron salt addition and the start of settling. Five different cylindrical beakers named M1 to M5 (3.5 L volume and 17 cm of inner diameter) were filled with 3 L of domestic sewage each. Each of these containers was added with 10 mL of sulfide stock solution (6 g/L $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) and 10 mL of ferrous stock solution (3 g/L $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$) creating iron

Table 1 – Composition of domestic sewage used as feed in reoxidation tests ($n = 8$).

Constituent	Unit	Concentration mg/L	Constituent	Unit	Concentration mg/L
Dissolved sulfide	mgS/L	0.12 ± 0.03	Fe ²⁺	mg/L	0.22 ± 0.05
SO ₃ ²⁻	mgS/L	0.09 ± 0.02	Fe ³⁺	mg/L	0.03 ± 0.01
SO ₄ ²⁻	mgS/L	16.75 ± 1.04	NH ₄ ⁺	mgN/L	54.13 ± 1.60
S ₂ O ₃ ²⁻	mgS/L	1.69 ± 0.36	NO ₂ ⁻	mgN/L	0.03 ± 0.01
Total S	mgS/L	18.65 ± 1.19	NO ₃ ⁻	mgN/L	0.22 ± 0.06
PO ₄ ³⁻	mgP/L	9.60 ± 0.36	VFA	mgCOD/L	50–100

sulfide (FeS) at an expected initial concentration of about 20 mgFe/L. Measurement of liquid phase samples confirmed that there was no residual iron present in the bulk. The contents of the beakers were then stirred using magnetic stirrers at 240 rpm for 0.5, 1, 2, 6 and 24 h, respectively. The mixing time was varied to simulate a range of possible transport time of the iron-receiving sewage from the location of iron addition to the primary settling tank. For example, a short mixing duration (e.g. 1 h) simulates iron dosing towards the end of the sewer pipe, while a long mixing duration (e.g. 24 h) corresponds to iron dosing at an upstream section of a long pipe. After the designated settling periods, the stirrers were stopped and the suspended solids in each of the test beakers were allowed to settle. Samples were taken from a location 5 cm below the water surface at the intervals between 15 and 120 min. The whole sampling procedure lasted for 4 h. The collected samples were digested and the iron contents measured using methods to be described in Section 2.3. The iron concentration detected in the sample was assumed to originate from iron sulfide (residual soluble iron was negligible). All the tests were performed in a temperature controlled room at $22 \pm 1^\circ\text{C}$. More information on the iron sulfide settling experimental procedure can be obtained from Fig. ii (Supplementary material).

2.3. Analytical methods

Liquid samples were filtered through a 0.22 μm pore diameter unit (Millipore, Millex GP). Phosphate (P-PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) were analysed using

a Flow Injection Analyser (Lachat QuikChem8000, Lachat Instrument, Milwaukee). Samples for sulfate (SO_4^{2-}), sulfide (HS^-), thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and sulfite (SO_3^{2-}) analysis were stored in 2 mL sample vials containing 0.5 mL of sulfide anti-oxidant buffer (SAOB) solution and with PTFE/silicon septa. SAOB solution was prepared as described in Keller-Lehmann et al. (2006). The dissolved sulfur species were measured using a compact Dionex ICS-2000 ion chromatograph (IC) with an AD25 absorbance (230 nm) and a DS6 heated conductivity detector (35°C) in series. Preceding the conductivity detectors, a Dionex ASRS-ULTRA II 4-mm suppressor (131 mA) was attached. Samples were injected into the IC with a Dionex AS50 auto-sampler. Extreme care was taken to avoid contact with air during sampling. All the samples were immediately placed in the instrument for analysis. The time between sampling and chemical analysis varied between 0.5 and 6 h. Iron samples digestion was carried out with the addition of Spectroquant Crack set 10, a reactive based on the sulfuric + peroxodisulfate digestion method 3030D (APHA, 2006). Concentrations of iron (Fe^{2+} and Fe^{3+}) were analysed using a Merck Iron test kit (Spectroquant®) together with a Varian Cary 50 concentration UV-VIS-NIR spectrophotometer. pH was measured with a TPS minichem-pH controller (Version 2.1.1). Dissolved oxygen was measured using a DO probes YSI InPro 6050, connected to a 4100 Mettler Toledo O₂ transmitter.

2.4. Model implementation and parameter estimation

A model was proposed to describe the results of the FeS reoxidation batch tests. Model parameters were estimated

Table 2 – Experimental conditions applied in the FeS reoxidation tests.

Experimental set	Reactor	Initial Concentration (mg/L)			Duration of test (h)	Num. of repeats
		S ²⁻	Fe ²⁺	Fe ³⁺		
Set 1	R1	20	–	–	6.0	3
	R2	20	20	–		
	R3	30	–	20		
Set 2	R1	20	–	–	1.3	3
	R2	20	20	–		
	R3	30	–	20		
Set 3	R1	10	–	–	1.3	1
	R2	10	10	–		
	R3	15	–	15		
Set 4	R1	5	–	–	1.3	1
	R2	5	5	–		
	R3	7.5	–	5		

from the experimental data using the Nelder-Mead Simplex minimization algorithm. The confidence intervals of parameter estimates were determined using the Fisher Information Matrix (FIM) as described in Dochain and Vanrolleghem (2001).

2.5. Model application

2.5.1. Background

A wastewater collection and treatment system in South East Queensland, Australia, was used as a case study to assess the implications of the experimental findings in this work through modelling and simulation. The sewer system collects domestic sewage from 13 pump stations with an average total daily flow of 26 ML. The WWTP was designed for biological carbon and nitrogen removal and chemical phosphorus removal. The sewage is settled in a primary settling tank with 6.0–7.0 h HRT before it enters the secondary treatment unit. The average phosphate concentration in the influent to the treatment plant is 6.4 mgP/L. Ferric chloride is currently dosed to the inlet of the secondary settling tank at 10 mgFe³⁺/L of influent flow to achieve phosphate removal through precipitation. The effluent phosphate concentration is currently maintained at an average level of 2.5 mgP/L.

There have been odour problems at the WWTP inlet due to high sulfide levels (2.2–14.9 mgS/L). For the mitigation of this problem, oxygen injection at 6 locations across the sewer network was used with limited effectiveness. The injection was stopped recently and alternative strategies were being sought.

2.5.2. Simulation study

One option to the problem described in Section 2.5.1, according to the experimental findings of this work, was to move ferric salt dosing from the treatment plant to the sewer network. This option was assessed through integrated sewer network and WWTP modelling. A dynamic rising main sewer model previously calibrated for this sewer network (Sharma et al., 2008b) was employed to predict the in-sewer carbon

and sulfur transformations including chemical sulfide precipitation with iron (see Sharma et al., 2008a for details of the model). The performance of the WWTP was modelled using the IWA Activated Sludge Model (ASM) No. 2d (Henze et al., 2000), enhanced with the additional components developed in this study characterising the reoxidation of FeS and the subsequent phosphate precipitation. The default model parameter values recommended in Henze et al. (2000), corrected for 25 °C using the Arrhenius relationship ($k_{25^{\circ}\text{C}} = k_{20^{\circ}\text{C}} \times 1.07^{25^{\circ}\text{C}-20^{\circ}\text{C}}$), along with the parameter values determined in this study were used.

Sulfide production in the sewer and the WWTP performance under the current operational conditions were simulated first. The FeCl₃ injection point was then moved to a location 0.5 km upstream of the WWTP inlet (with HRT between the dosing point and the WWTP inlet ranging between 3 and 54 min, varying with the wastewater flow rate). The impact of this strategy on sulfide control and P removal was then assessed and compared with the current situation.

3. Results

3.1. Iron sulfide reoxidation tests

Typical concentration profiles of phosphate, sulfate, and sulfide during a 6 h batch test are shown in Fig. 1. Residual sulfide and thiosulfate was detected at the beginning of the test, with the highest level measured in R1 as no iron salt was added in this case. The start of aeration in R1 resulted in quick removal of sulfide and thiosulfate with immediate increase of sulfate. Sulfite was not detected. By the end of the test, majority (72%) of the sulfide initially present in R1 was converted to sulfate, with the remaining 28% likely stripped. Similarly, the sulfide and thiosulfate initially present in R2 and R3 (after FeS formation) disappeared within minutes once aeration was started. There was an immediate increase in

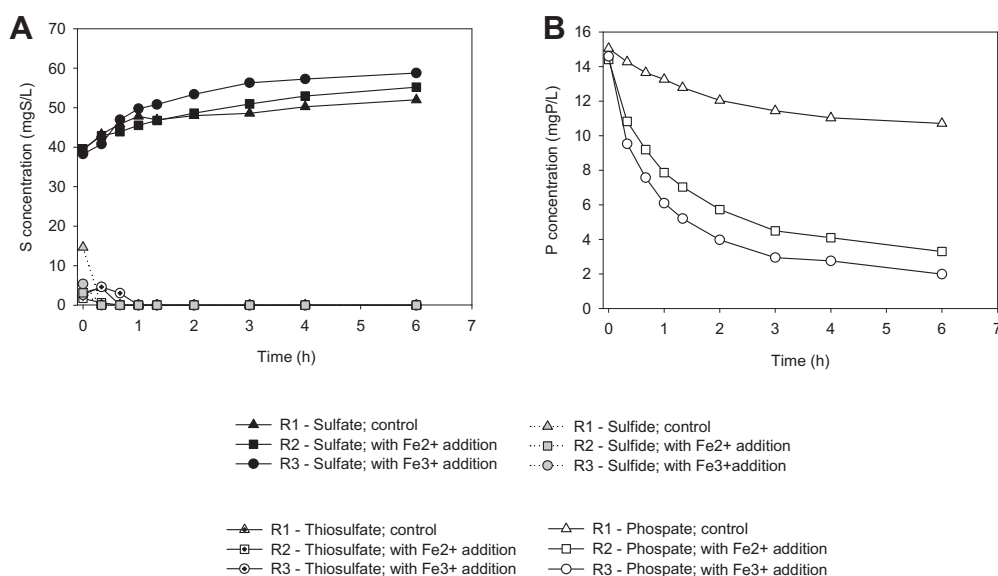


Fig. 1 – Results of a typical 6 h reoxidation batch test corresponding to experimental set 1. (A) Sulfate, sulfide and thiosulfate profiles (B) Phosphorus profiles. Sulfite and free iron concentrations were negligible at all times (data not presented).

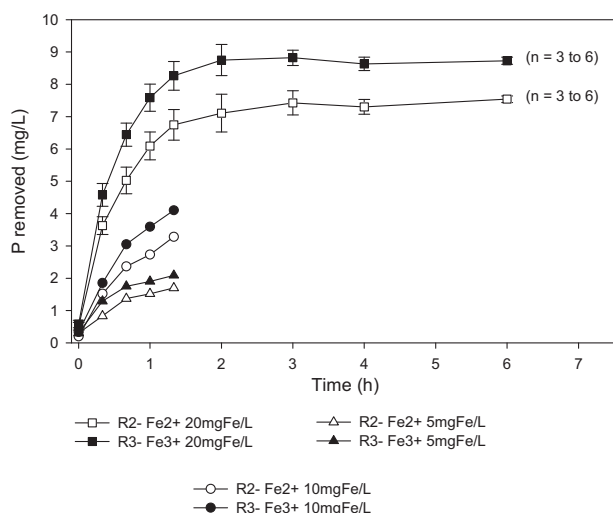


Fig. 2 – Phosphorus removed due to iron dosing in R2 and R3 in all reoxidation tests.

sulfate concentration in both reactors, and the sulfate concentration continued to increase during the remaining period of the tests, likely due to the oxidation of FeS previously formed in wastewater. Concurrently, phosphate concentration decreased with time (Fig. 1B) in all reactors. The decrease was significantly higher in reactors R2 and R3 (where iron salts were added) than that in R1. P removal in R1, the control reactor, was likely due to bacterial P uptake for growth. The additional phosphate removal in R2 and R3, as compared to R1, should be due to chemical precipitation of phosphate with aerobically regenerated ferric ions from previously formed FeS.

P removal due to iron addition in R2 and R3 (i.e. P removal in R2 and R3 in excess of that in R1) in all the reoxidation tests are summarised in Fig. 2. The 6 h experiments showed that P precipitation was completed in approximately 2 h. It is likely that at this point all iron had been completely regenerated. In R2, the total sulfate production at this point averaged to 11.2 mgS/L. Assuming that 72% (a crude estimation based on R1 data) of the dissolved sulfide initially present in R2 was oxidised to sulfate, the amount of iron oxidised to ferric ions would be 16.1 mgFe/L, which corresponds to 80% of the

amount of ferrous ions initially added. Similar values of iron regeneration were estimated in R3.

A strong, positive correlation was found between the amount of iron salts dosed and the amount of phosphorus precipitated (Fig. 2). At 1.3 h, the amounts of P precipitated in the cases of iron salt addition at 5 and 10 mg Fe/L were approximately 1/4 and 1/2, respectively, of the amount precipitated with 20 mg Fe/L addition at 1.3 h. These ratios hold true for both ferrous and ferric ions.

It is observed in Fig. 2 that different iron species dosed produced slightly different degrees of P removal. The ratio between the amount of P precipitated and the amount of iron added was calculated as 0.44 and 0.37 mgP/mgFe for ferric and ferrous ions, respectively. The reason for the difference is not immediately clear, but could be related to the different stability of the precipitation products when Fe^{3+} and Fe^{2+} were used to precipitate sulfide. According to Nielsen et al. (2005) stable amorphous ferrous sulfide (FeS) is the final product when ferrous ions are used to precipitate sulfide under anaerobic conditions. In contrast, there are still uncertainties about the detailed mechanism involved in sulfide oxidation by ferric and the subsequent precipitation (Davydov et al., 1998). Compared to ferrous precipitation, more complex reactions and intermediate compounds are involved in this process (Firer et al., 2008). In this study, the use of ferric chloride seemed to create a pool of iron complexes more easily available during reoxidation, thereby resulting in higher phosphorus removal when aerobic conditions were maintained. More research needs to be conducted in order to reveal specific mechanisms involved in iron-sulfide reoxidation and to clarify the reasons of the ferric/ferrous differences in P removal.

3.2. FeS settling test – impact of iron dosing location and settling time

Fig. 3A shows the change of FeS concentration in the supernatant of the simulated primary settling tanks as a function of settling time, and the mixing time of the FeS containing wastewater prior to settling. A longer mixing time (representing a longer HRT of iron salt-receiving wastewater in a sewer) resulted in higher removal of FeS particles during settling. The FeS concentration in the supernatant dropped very fast in the sample subjected to 24 h mixing prior to

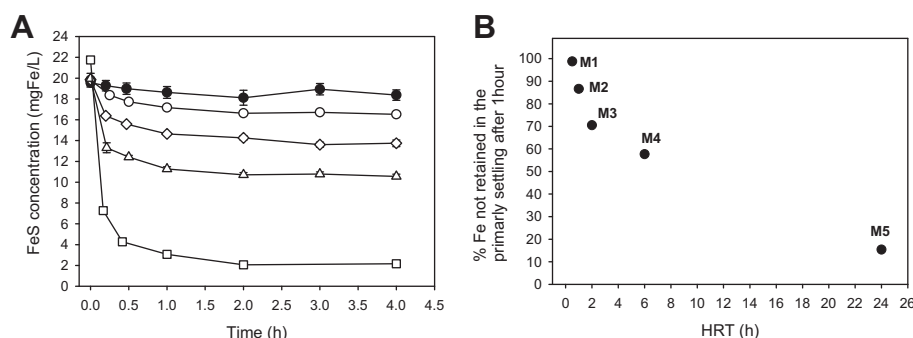


Fig. 3 – (A). Iron concentrations in the supernatant over 4h settling. Simulated HRT prior to settling was M1: 0.5 h (●), M2: 1 h (○), M3: 2 h (◇), M4: 6 h (△) and M5: 24 h (□). The 0.5 h, 2 h and 6 h experiments were done in triplicates (error bars given). (B) Fraction of FeS transferred from primary clarifier to aeration tank after 1h settling as a function of HRT in a sewer.

Table 3 – Stoichiometry and kinetics of the model describing FeS and S⁰ oxidation and the subsequent phosphate precipitation.

Reaction	S ²⁻	S ⁰	SO ₄ ²⁻	Fe ³⁺	FeS	O ₂	PO ₄ ³⁻	Fe _r PO ₄ (OH) _{3r-3}	Kinetics
Oxidation of sulfide	-1.00		1.00			-2.00			$k_{\text{oxi},\text{S}^{2-}} \times (\text{S}_{\text{S}^{2-}})^{0.82} \times (\text{S}_{\text{O}_2})^{0.20}$
Oxidation of FeS			1.00	1.00	-1.00	-2.25			$k_{\text{oxi},\text{FeS}} \times \text{S}_{\text{FeS}} \times \text{S}_{\text{O}_2}$
Oxidation of S ⁰		-1.00	1.00			-1.50			$k_{\text{oxi},\text{S}^0} \times \text{S}_{\text{S}^0} \times \text{S}_{\text{O}_2}$
Precipitation of PO ₄ ³⁻ with Fe ³⁺				-r			-1.00	1.00	$r_{\text{fmax},\text{P}} \times (\text{PO}_4^{3-})^{(1/4r-2)} \times \text{Fe}^{3+(r/4r-2)} \times \text{OH}^{-(3r-3/4r-2)} - K_{\text{sp}}^{(1/4r-2)} \big)^{2.0}$
Transfer of sulfide from liquid to gas phase	-1.00								$k_{\text{La}} \times (\text{S}_{\text{H}_2\text{S}} - 0^*)$
Unit					mol/L				

*Concentration of H₂S in gas phase is assumed to be zero resulting in 0 equilibrium concentrations.

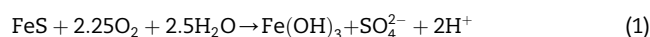
settling (M5). After 1 h settling, only 15% of the iron initially added was present in the supernatant and only 10% was detected after 4 h. In contrast, in the test with 0.5 h mixing (M1), 99% of the initial iron was still available in the supernatant after 1 h settling, and 95% was detected after a settling time of 4 h. The dependency of the supernatant FeS concentration after 1 h settling on the mixing time (or in-sewer HRT) is summarised in Fig. 3B. The non-settled FeS fraction dropped sharply when the mixing time increased from 0.5 h to 2 h from 99% to 70%, which was then followed by a slower decrease for mixing times between 2 and 24 h.

The results of the FeS settling tests demonstrate that the mixing time, which depends upon the location of iron dosing in the sewer and the wastewater flow rate, has a major effect on the transferability of FeS through the primary settling tank and therefore on the availability of FeS for iron regeneration in aeration tanks. Iron is a well known coagulant, which is able to create aggregates with sizes depending on the mixing times (Metcalf and Eddy, 2003). Iron salts have been used since the early days of wastewater treatment to improve settling characteristics of activated sludge and for phosphate and Biological Oxygen Demand (BOD) removal (Jenkins et al., 1971). When iron is dosed in upstream sections of a sewer main for sulfide control, larger aggregates are expected to form. In such a case, the precipitates get easily settled in the primary settling tank. As a consequence, only a small fraction of FeS would be available for phosphorus removal in aerobic tanks. Iron dosing at a location close to the WWTP would maximise phosphate precipitation in the aeration tanks. It should be recognised that many wastewater treatment plants do not use a primary settling tank in order to maximise the

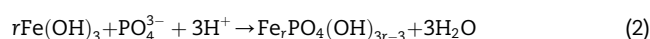
availability of organic carbon for biological nutrient removal. In these plants, all FeS is expected to be transferred to the biological reactors and hence available for P removal.

3.3. Formulation of a model describing FeS oxidation

The aerobic oxidation of FeS may be described by the following reaction according to Schippers and Jorgensen (2002).



Fe(OH)₃ formed can then combine with phosphate to produce ferric hydroxy-phosphate, which can be represented by a general formula of Fe_rPO₄(OH)_{3r-3} (Lueddecke et al., 1989). These authors suggested an r value of 1–2 for residual phosphate concentrations in the range of 1–5 mgP/L. Precipitation of phosphate with ferric hydroxide can thus be represented as:



A model describing the above oxidation and precipitation reactions is presented in Table 3. Also included in the model is the aerobic oxidation of sulfide and elemental sulfur to sulfate (elemental sulfur is expected to form during sulfide oxidation by ferric ions). The kinetics for phosphate precipitation is modelled according to Koutsoukos et al. (1980). The oxidation of sulfide is modelled according to Nielsen et al. (2003), while all other kinetic expressions are assumed to be first order with respect to each of the participating chemical species. The model also included H₂S transfer from liquid to gas phase.

Table 4 – Assumed and calibrated model parameters.

Parameter	Unit	Value	Reference
$r_{\text{fmax},\text{P}}$	1/h	1×10^{12}	Large value to ensure that precipitation occurs instantaneously
$K_{\text{sp},\text{FeIIIPO}_4}$		1.0×10^{-23}	Stumm and Morgan (1970)
$k_{\text{oxi},\text{S}^{2-}}$	(mg S/L) ^{0.18} /(mg O ₂ /L) ^{0.20} ·h	0.25	Nielsen et al. (2003)
$k_{\text{oxi},\text{S}^0}$	L/mg O ₂ ·h	$0.27 \pm 0.02^{\text{a}}$	This study
$k_{\text{oxi},\text{FeS}}$	L/mg O ₂ ·h	$0.54 \pm 0.03^{\text{a}}$	This study
r		$1.31 \pm 0.01^{\text{a}}$	This study
k_{La}	1/h	10.1	Foley et al. (2009)

a 95% confidence interval.

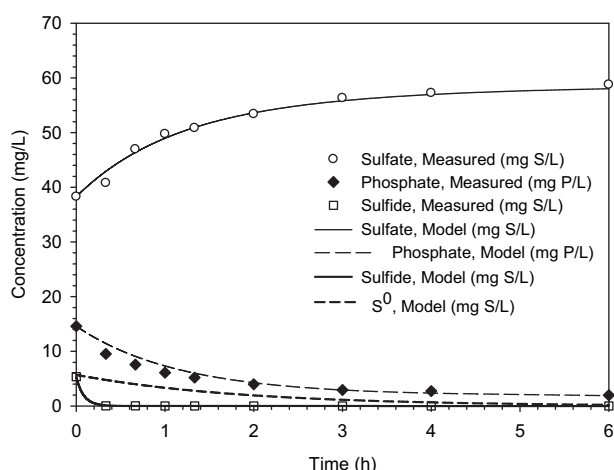


Fig. 4 – Comparison of model simulations with experimental results for Fe^{3+} dosing.

3.4. Model calibration

The above model was calibrated using the experimental results reported in Section 3.1. Parameter $r_{f\max,P}$ was chosen to have a high value so that it enables instantaneous phosphate precipitation when $\text{Fe}(\text{OH})_3$ is regenerated. $K_{sp,\text{FeIIIPO}_4}$ was assumed according to Stumm and Morgan (1970). Parameters

$k_{\text{oxi},\text{S}^0}$, $k_{\text{oxi},\text{FeS}}$ and r were estimated using experimental results obtained in the six sets of batch tests conducted in this study: three sets with Fe^{2+} addition and three sets with Fe^{3+} addition. The estimated model parameter values are presented in Table 4, along with the 95% confidence intervals of these estimates. The parameters for sulfide oxidation were taken from literature (Nielsen et al., 2003). The k_{La} value for modelling H_2S transfer was calculated as described in Foley et al. (2009). Based upon the superficial gas velocity of $0.0035 \text{ m}^3/\text{m}^2\cdot\text{s}$, k_{La} was estimated to be 10.1/h for the laboratory reactor with mixed liquor. The values of the model parameters taken from literature are also shown in Table 4.

Good fit was achieved between the experimental and simulated sulfate and phosphate profiles for all tests. An example of the fit is shown in Fig. 4. The results suggest that the proposed model structure well describes the experimental results.

3.5. Model-based optimisation of ferric chloride dosage for simultaneous sulfide control and phosphorus removal

The simulation results for the two cases of FeCl_3 dosing are compared in Fig. 5. By moving the injection of FeCl_3 from WWTP (current practice) to an upstream sewer location, sulfide entering the WWTP was reduced substantially with the average dissolved sulfide concentration decreased from 7.6 mgS/L to 0.1 mgS/L. In the mean time, the effluent phosphate concentration was maintained at the same level as in the case of FeCl_3 dosage at WWTP.

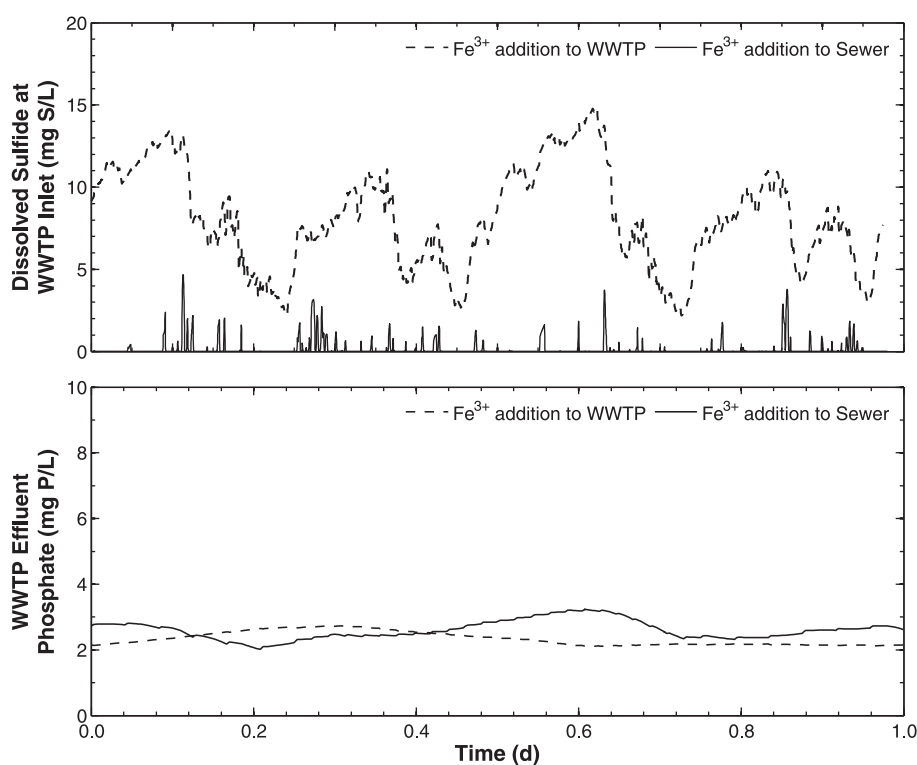


Fig. 5 – Comparison of model predicted sulfide and phosphate levels (average dissolved sulfide concentration is 7.6 mgS/L with Fe^{3+} addition to WWTP and 0.1 mgS/L with Fe^{3+} addition to sewer; average phosphate concentration is 2.6 mgP/L with Fe^{3+} addition to WWTP and 2.4 mgP/L with Fe^{3+} addition to sewer)

This case study demonstrated that, by moving the FeCl_3 dosing point from the current location (in WWTP) to the sewer line feeding the WWTP, both H_2S and phosphate can be controlled with the same consumption of FeCl_3 . This would eliminate the need of adding another chemical to sewers for sulfide control, resulting in substantial savings. de Haas et al. (2008) estimated the operational costs for sulfide control in this sewer network range between $\$0.03$ – $0.09/\text{m}^3$ wastewater treated depending on the type of chemical used. The study highlights the importance of integrated sewer and WWTP management. Integrated modelling of WWTP and sewers is a highly valuable tool for such integrated management.

In this study, the oxidation of FeS and the subsequent precipitation reaction between Fe^{3+} , PO_4^{3-} and OH^- creating $\text{Fe}_{1.3}(\text{PO}_4)(\text{OH})_{0.9}$ will produce H^+ with an $\text{FeS}:\text{H}^+$ ratio of approximately 0.6–1.2 (depending on the pH in the mixed liquor). See supplementary information section. Therefore, these reactions will consume alkalinity. For typical Fe dosing rates of 0.2–0.3 mmol per L of wastewater, the consumption of alkalinity due to Fe-related reactions in the bioreactor would be roughly 0.1–0.4 mmol/L. Given the typical alkalinity of 2–4 mmol/L in wastewaters, there should be no need to add alkalinity to compensate for the consumption. However, pH adjustment through the addition of e.g. NaOH may be needed for wastewaters with low alkalinity

4. Conclusions

The effects of iron salt addition to sewers for sulfide control on phosphorus removal in the downstream wastewater treatment plant were investigated through experimental and simulation studies. The following conclusions are drawn from this study:

- The addition of ferrous or ferric salts to sewers for sulfide control may substantially enhance phosphorus removal at the downstream wastewater treatment plant. Iron sulfide precipitates are oxidised in aeration tanks, regenerating ferric ions that precipitate phosphate.
- Ferric salts result in higher P removal than ferrous salts. For the sludge used, 0.44 and 0.37 $\text{mgP}-\text{PO}_4^{3-}$ was removed per mg Fe^{2+} and Fe^{3+} added.
- The retention time of FeS particles in sewers affects iron availability for phosphate precipitation in the WWTP. Dosing at a location close to the treatment plant reduces the settling of iron sulfide in the primary settling tank, and is therefore beneficial for phosphorus removal.
- The impact of chemical dosage for sulfide control in sewer networks on the performance of the downstream WWTP should be considered. Integrated sewer network and treatment plant modelling is an important tool for the integrated management.

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Appendix. Supplementary data

The supplementary data associated with this article can be found in the on-line version at doi: [10.1016/j.watres.2010.03.023](https://doi.org/10.1016/j.watres.2010.03.023).

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