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Removal of Pharmaceuticals and Illicit Drugs from Wastewater Due to Ferric Dosing in Sewers

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Removal of Pharmaceuticals and Illicit Drugs from Wastewater Due to Ferric Dosing in Sewers

Abstract

Ferric (Fe3+) salt dosing is an efficient sulfide control strategy in the sewer network, with potential for multiple benefits including phosphorus removal in the biological reactors and sulfide emission control in the anaerobic digesters of wastewater treatment plant (WWTP). This paper extends the knowledge on the benefit of iron dosing by exploring its impact on the fate of organic micropollutants (MPs) in the wastewater using sewer reactors simulating a rising main sewer pipe. The sulfide produced by the sewer biofilms reacted with Fe3+ forming black colored iron sulfide (FeS). Among the selected MPs, morphine, methadone, and atenolol had >90% initial rapid removal within 5 min of ferric dosing in the sewer reactor. The ultimate removal after 6 h of retention time in the reactor reached 93-97%. Other compounds, ketamine, codeine, carbamazepine, and acesulfame had 30-70% concentration decrease. The ultimate removal varied between 35 and 70% depending on the biodegradability of those MPs. In contrast, paracetamol had no initial removal. The rapid removal of MPs was likely due to adsorption to the FeS surface, which is further confirmed by batch tests with different FeS concentrations. The results showed a direct relationship between the removal of MPs and FeS concentration. The transformation kinetics of these compounds in the reactor without Fe3+ dosing is in good agreement with biodegradation associated with the sewer biofilms in the reactor. This study revealed a significant additional benefit of dosing ferric salts in sewers, that is, the removal of MPs before the sewage enters the WWTP.

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Removal of pharmaceuticals and illicit drugs from wastewater due to ferric dosing in sewers

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ABSTRACT. Ferric (Fe^{3+}) salt dosing is an efficient sulfide control strategy in the sewer network, with potential for multiple benefits including phosphorus removal in the biological reactors and sulfide emission control in the anaerobic digesters of wastewater treatment plant (WWTP). This paper extends the knowledge on the benefit of iron dosing by exploring its impact on the fate of organic micropollutants (MPs) in the wastewater using sewer reactors simulating a rising main sewer pipe. The sulfide produced by the sewer biofilms reacted with Fe^{3+} forming black coloured iron sulfide (FeS). Among the selected MPs, morphine, methadone and atenolol had >90% initial rapid removal within five minutes of ferric dosing in the sewer reactor. The ultimate removal after 6 h of retention time in the reactor reached 93-97%. Other compounds, ketamine, codeine, carbamazepine and acesulfame had 30-70% concentration decrease. The ultimate removal varied between 35 and 70 % depending on the biodegradability of those MPs. In contrast, paracetamol had no initial removal. The rapid removal of MPs was likely due to adsorption to the FeS surface, which is further confirmed by batch tests with different FeS concentrations. The results showed a direct relationship between the removal of MPs and FeS concentration. The transformation kinetics of these compounds in the reactor without Fe^{3+} dosing is in good agreement with biodegradation associated with the sewer biofilms in the reactor. This study revealed a significant additional benefit of dosing ferric salts in sewers, that is the removal of MPs before the sewage enters the WWTP.

INTRODUCTION. Hydrogen sulfide in sewers causes serious cracking and failure of the concrete structure, malodor and human health problems [1,2]. Billions of dollars are expended every year due to the need for rehabilitation or replacement of the corroded sewer pipes [3]. The anaerobic condition in the rising main induces the growth of stratified biofilms comprising of sulfate-reducing bacteria (SRB) and methanogenic archaea (MA)[4]. The SRB reduce sulfate in the wastewater and produce sulfide that subsequently transfers to the gas phase in the gravity sewers. The H_2S gas induces sewer corrosion by forming sulfuric acid on the concrete surface [5].

Chemicals are commonly used for the control of sulfide, including i) chemical oxidation of sulfide by the injection/addition of air, pure oxygen, nitrate salts [1, 6-8], ozone, hydrogen peroxide, hypochlorites, chlorine and potassium permanganate [9, 10] ii) pH elevation by the addition of alkali such as $Mg(OH)_2$ and iii) precipitation of sulfide by forming insoluble metal particles through the addition of metal salts such as iron, zinc, lead and copper salts [2]. Among the various metal salts used, iron based salts were shown to be most efficient because of its specificity to H_2S [11]. In Australia iron salts accounted for 66% of the sewage flow dosed with chemicals for sulfide control [12].

The iron salt dosing in the sewers is effective in the control of dissolved sulfide by the formation of iron sulfide particles [2, 13-15]. These studies showed that the mechanism responsible for the removal of sulfide includes the precipitation reaction of Fe^{2+} ions with sulfide forming ferrous sulfide (FeS), while Fe^{3+} ions oxidizes sulfide chemically to elemental sulfur, with itself being reduced to Fe^{2+}, which subsequently precipitates sulfide (Equation 1&2). The continuous dosing of iron salts for two months significantly inhibits the SRB and MA production in the long run, leading to reduced demand for iron salts [2].

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^{0} \qquad (1)$$

$$Fe^{2+} + HS^{-} \rightarrow FeS \downarrow + H^{+} \qquad (2)$$

Further studies found that FeS particles formed in the sewer network can be oxidized in the aerobic activated sludge reactor. This enables phosphorus removal at a ratio of 0.44 and 0.37 mg P/mg of Fe^{2+} and Fe^{3+} added to the sewer network [13]. The iron dosing (e.g. 5–20 mg-Fe/L) to the sewer network was also demonstrated to provide iron for H_2S emission control in the anaerobic digester by forming iron sulfide particles [16]. Previous studies have demonstrated the multiple benefits of iron salts dosed into sewers, including sewer corrosion and odour control, phosphorus removal and biogas desulfurization [17].

Iron salt was shown to be an effective coagulant for the removal of MPs such as pharmaceuticals and personal care products (PPCPs) in the drinking water treatment systems and WWTPs [18-20]. Organic MPs are ubiquitous in wastewater, and are recalcitrant to the traditional secondary treatment processes. The MPs thus find their way in the aquatic environment and can have adverse effects on aquatic organisms [21, 22]. Before entering the WWTP, MPs go through the sewers with sewage flow and there is very limited understanding about their fate and transformation in the sewers. Some recent studies focused on the biological transformation of organic MPs in the sewer network due to the presence of biofilms [23-25]. Also, there are a couple of studies focused on the biodegradation of pharmaceuticals and illicit drugs in the sewer network [26, 27].

However, no study has systematically investigated the impact of iron salt dosing on the removal of MPs in the sewer network. Considering the coagulating nature of iron salt and the adsorbing nature of iron sulfide particles [28], it is hypothesized that there can be additional removal of some MPs due to iron dosing on top of in-sewer biodegradation.

Collectively speaking, ferric dosing is one of the most widely used strategy to control sewer odor corrosion and odor, with additional beneficial effects on the downstream WWTP. The main objective of this study is to investigate the fate and removal of selected organic MPs from wastewater due to ferric dosing and biological processes in the sewer network. Experiments using laboratory-scale rising main sewer reactors were carried out with selected MPs, including pharmaceuticals and illicit drugs in the wastewater. To understand the removal mechanisms of MPs, batch tests were conducted with different levels of iron sulfide precipitate that was identified and characterized with advanced electron microscopic analysis.

2. MATERIALS AND METHODS

2.1. CHEMICALS. The reagent grade ferric chloride ($FeCl_3.6H_2O$) was purchased from Sigma Aldrich (NSW, Australia). All the drugs and pharmaceuticals were purchased from Cerilliant (Texas, US) and Sigma Aldrich (NSW, Australia). The selected MPs include ketamine, methadone, morphine, codeine, carbamazepine, atenolol, paracetamol and acesulfame and their properties are presented in Table S1. The compounds were selected to represent the hydrophobic and hydrophilic MPs in the wastewater. The octanol-water partition coefficient is arranged in the ascending order in table S1 (Acesulfame being hydrophilic and methadone hydrophobic). Spiking solutions were prepared in Milli-Q water before being spiked in to the reactors. Liquid Chromatography grade methanol was purchased from Merck, Germany. Deionized water was produced by a Milli-Q system (Millipore, 0.22 μm filter, 18.2 $m\Omega \cdot cm^{-1}$).

2.2. WASTEWATER CHARACTERISTICS. The wastewater used in this study was collected from a local sewer wet well (St. Lucia, Brisbane, Queensland) every week and was stored in the cold room at -4 °C. The sewage typically contained sulfate at concentrations of 10-25 mg-S/L, sulfide at <3 mg-S/L, soluble chemical oxygen demand (sCOD) at 200-300 mg/L, volatile fatty acids at 50 - 120 mg-COD/L and ammonium at approximately 50 mg-N/L. Negligible amounts of sulfite, thiosulfate (<1 mg-S/L), nitrate and nitrite (<1 mg-N/L) were present. The background micropollutant concentration in the feed wastewater includes methadone (<0.1 μg/L), morphine (0.15-2 μg/L), atenolol (0.8-1 μg/L), ketamine (<0.1 μg/L), codeine (0.6-2 μg/L), carbamazepine (0.5 μg/L), acesulfame (10-12 μg/L), paracetamol (75-130 μg/L). The paracetamol was not spiked into the reactor considering its high background concentration.

2.3. LABORATORY-SCALE SEWER REACTORS. Two parallel lines, one control and one experimental, of laboratory-scale sewer reactors were designed and set up to simulate rising main sewers (Figure S1). The reactors were made of Perspex^{TM} with a volume of 0.75 L (diameter 80 mm and height 149 mm) and an A/V ratio of 70.9 m^{-1}[1]. Mixing was continuously provided by a magnetic stirrer (Heidolph MR3000) at 250 rpm.

The wastewater described in section 2.2 was heated to 20°C using the heating coil before being pumped into the reactor. The feed pumping event occurred for 2 min at a flow rate of 350 mL/min for every 6-hr. The reactors were operated continuously for more than a year allowing for the development of biofilms. The biological activities of the reactors were monitored by the dissolved sulfide and methane production. Baseline monitoring of the systems showed consistent sulfide, sulfate, and methane profiles over days for four months, suggesting that the pseudo-steady state conditions were established in the systems.

The experimental line was dosed with $FeCl_3$ in the sewer reactor to study its impacts on the sulfide and methane production in sewers. From this point, the experiment reactor will be represented as ferric dosed reactor. The addition of $FeCl_3$ was initiated upon the establishment of pseudo-steady state of the reactors. Fe^{3+} was added from a stock solution prepared from reagent-grade ferric chloride ($FeCl_3 \cdot 6H_2O$). The stock solution was prepared weekly by dissolving appropriate amounts of ferric salts in deoxygenated water containing 0.01M HCl (to prevent ferric hydroxide precipitation). The deoxygenated water was prepared by bubbling purified N_2 in Milli-Q water for 1-hr. The Fe^{3+} stock solution was added into experimental rising main reactor during each pumping event resulting in a theoretical Fe^{3+} concentration of 10 mg-Fe/L.

2.4. EXPERIMENTS OF MICROPOLLUTANTS REMOVAL IN SEWER REACTORS.

Cycle experiments (6-hr) were conducted in the two lines of sewer reactors to investigate the impact of ferric dosing on the selected MPs (Figure S1). Fresh wastewater was used for each experiment. After the pumping event, the targeted MP compounds were spiked separately in both the control and experimental reactors and a thorough mixing was provided. The background concentration of the spiked compounds was also analysed to quantify the exact concentrations spiked. Wastewater samples were taken at a time interval of 1-hr throughout the cycle time of the reactor (6-hr) after the experiment started. For each time point, 2 mL of sample was filtered into a vial using 0.22 μm PES membrane syringe filter (Tullagreen, Ireland) and 20 μL of 2M HCl was added to adjust each of the samples to pH 2. The acidified samples were then frozen at − 20°C until analysis. Hourly samples were taken for the analysis of sulfur compounds (sulfate, sulfide, thiosulfate and sulfite) and dissolved methane. The total metal concentration of the samples was also taken on an hourly basis. Duplicate experiments were performed for each cycle test.

2.5. BATCH TESTS WITH DIFFERENT FeS CONCENTRATIONS. The scope of the batch tests is to reduce the complexity by avoiding biodegradation due to sewer biofilms and to find out the sorption behavior of selected MPs on the suspended iron sulfide particles. The batch experiments were conducted with serum bottles enclosed tightly with a rubber stopper to maintain the anaerobic condition. Before the experiment, the wastewaters were flushed with N_2 until the dissolved oxygen becomes negligible.

The wastewater containing iron sulfide particles formed in the ferric dosed sewer reactor was taken and mixed with fresh sewage, either filtered or unfiltered, at three different ratios (1:2, 1:10 and 1:50). The filtration was done with 5 micron water cartridge filter, to remove suspended solids. Selected MPs were then spiked in the wastewater mixture in the serum bottles. The bottles were mixed in an orbital shaker (Lab-line instruments model 3520 and at 150 rpm) covered with aluminum foil to avoid potential photo-transformation process. The batch tests were carried out for 1-hr with the sampling interval of 15 min. Wastewater samples were taken as described in 2.4 for the analysis of selected MPs.

2.6. CHEMICAL ANALYSIS. The analysis of organic MPs in this study was based on a previously developed analytical method [24]. Briefly, analysis was performed using liquid chromatography (Shimadzu Prominence) coupled to a tandem mass spectrometer (AB-SCIEX 5500® QTrap) with electrospray ionization source in positive mode. Chemical separation was achieved on a Kinetex Biphenyl column (Phenomenex, 50 × 2.1 mm, 2.6 μm) using the mobile phase of (A) 1% methanol and 99% Milli-Q water and (B) 95% methanol and 5% Milli-Q water; both with 0.1% acetic acid, at the gradient: 5% B, 0–1 min; 100% B at 7.5 min for 3 min; 5% B at 9.6 min for 3.4 min. The flow rate was set at 0.3 mL/min and the injection volume was 8 μL. The MS was operated in multiple reaction monitoring (MRM) mode for data acquisition [23]. The matrix spike samples were used in the analytical batch and the recovery % ranged between 90-105%.

Dissolved inorganic sulfur species (i.e. sulfide, sulfate, sulfite, and thiosulfate) were measured using ion chromatography (IC) coupled with a UV and conductivity detector (Dionex ICS-2000). The methane analysis was performed using BD vacuum tubes. The samples were allowed to reach gas/liquid equilibrium overnight and the gas phase methane was analysed using a Shimadzu GC-9A gas chromatography equipped with flame ionization detector. The concentrations of methane in the wastewater were calculated using mass balance and Henry's law. The metal concentration of the samples were analysed using Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES optima 7300 DV). The samples were digested using 10% nitric acid before being analysed.

2.7. CHARACTERIZATION OF PARTICLES FORMED BY FERRIC DOSING. To characterize the suspended particles in the ferric dosed sewer reactors, wastewater was sampled with a syringe and filtered immediately using a vacuum filter to avoid the interference of oxygen during the sample preparation. The precipitate samples were dried overnight in a vacuum oven

(SEMSA OVEN 718). These particles were then tested for its properties using scanning electron microscopy-Energy dispersive X-ray spectrometry (SEM-EDS). The chemical composition of the particles was further analysed using X-ray diffraction technique (XRD).

The vacuum dried particles were coated twice by the carbon coater (Quorum Q150T, UK), following the three heavy-burst model to obtain the carbon thickness of 30-40 nm. The microstructure and elemental composition of the particles were examined by SEM (JEOL JSM-6610, America) equipped with a detector (Oxford 50 mm^2 X-Max SDD x-ray) that enables simultaneous imaging and elemental analysis at high count rates with 125 eV energy resolutions. The EDAX software (EDAX, AMETEK Inc.) was utilized, at a frame resolution of 1024×800, with a dwell time of 200 s/frame, to collect 16 frames for each region of interest. The locations for spot analyses were chosen by examining features of the back scattered electron image. The mineral compositions of the particles were tested by XRD (Bruker D8 Advance MKII). X-rays were generated at 40 kV and 40 mA, with a scanning speed of 2.0 deg/min, and a scanning range of 10–100°. The composition identifications were carried out using Jade software (version 5) and pdf-2 crystal structure database.

2.8. TRANSFORMATION MODEL. First-order kinetics (equation 3) was used to simulate the transformation of the investigated compounds in the sewer reactors. For control reactor, simulation starts at the time right after spiking (t_0). For the ferric dosed reactor, simulation starts at 5 min after spiking (t_5), due to the rapid initial removal of some investigated compounds.

$$C_t = C_0 \cdot e^{-k_{bio} \cdot t} \qquad (3)$$

where C_t is concentration (ppb) at time t, C_0 is initial concentration (ppb), k_{bio} (h^{-1}) represents the overall biomarker transformation in control and ferric dosed reactor with anaerobic condition and biofilm. Determinations of k_{bio} use the Bayesian statistic method [29]

3. RESULTS AND DISCUSSION

3.1 EFFECT OF FERRIC DOSING ON THE BIOLOGICAL PERFORMANCE OF THE SEWER REACTORS. Typical concentration profiles of dissolved sulfide, sulfate and methane during a 6-hr batch test are shown in Figure 1. The wastewater in the reactors had a pH around 6.7 – 6.9. The sulfate reduction rates were 1.6 ± 0.7 and 1.7 ± 0.7 mg-S L^{-1} h^{-1} for the control and ferric dosed reactor, respectively. The dissolved sulfide concentration in the ferric dosed reactor was notably lower than the control reactor, with effluent concentration at 3.6 ± 0.1 compared to 19.7 ± 0.2 mg-S L^{-1} h^{-1} for the control reactor without ferric dosing. Considering similar sulfate reduction in both reactors, the sulfide removal due to the dosing of $FeCl_3$ happened simultaneously with sulfide production in the ferric dosed sewer reactor. The methane production rates were 12.3 ± 3.4 and 7.3 ± 1.5 mg-COD L^{-1} h^{-1} for the control and ferric dosed reactor, respectively. The methane production in the ferric-dosed reactor had been reduced by 38%. The microbial community analysis of the sewer biofilms also emphasize the reduction in the relative abundance of MA in the ferric dosed reactor compared to the control reactor. The SRB community was not affected by the ferric dosing (Section S4). The sulfate reduction and methanogenesis in the control reactor are comparable to the previous reported values [23, 25, 30-32].

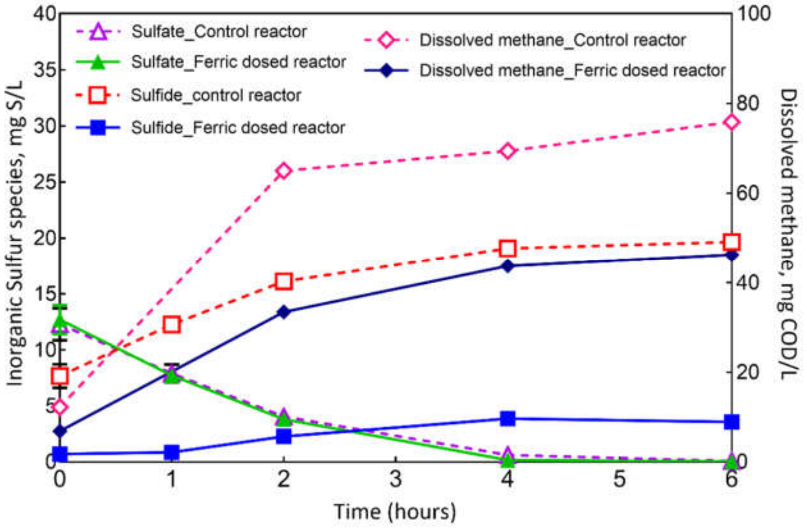

Figure 1. Concentration profiles of sulfur compounds and dissolved methane in the control and ferric dosed rising main sewer reactors (error bars are the error calculated from triplicates. For some points, the error bars are shorter than the height of the symbol and thus are not shown)

The ferric dosing in the rising main sewer reactor leads to the removal of dissolved sulfide, forming iron sulfide particles [2]. The total suspended solids in the ferric dosed reactor were 550 ± 90 mg/L, which is about 4 times higher than the control reactor due to the formation of particles. Zhang, et al.[2] observed the inhibition of methanogenic activity of the rising main reactor by about 52-80% after two months of Fe^{3+} addition. Utgikar, et al. [33] hypothesized the deposition of metal sulfides on the surface of SRB and MA could cause the inhibition of these cells. The ferrous sulfide particles in close vicinity to the cells may reduce the access of reactants such as volatile fatty acids to the necessary enzymes. This could be the likely cause for the reduced methane production in the ferric-dosed reactor. In contrast, the SRB activity of the ferric dosed reactor in this study was not affected, contrary to what reported by Zhang, et al.[2] which may due to the high ferric dosing concentration (21 mg Fe^{3+}/L) used in the previous study.

3.2 IRON SULFIDE PARTICLES. The EDS elemental mapping analysis was performed on particles collected from ferric-dosed sewer reactor to find the composition of the particles (Figure S2a). The atomic % and the atomic ratio was calculated between iron and sulfide. The atomic ratio between 0.8 – 1.1 (Table S4) suggests the speciation of the particles as FeS. Analysis of the wastewater samples in the ferric-dosed reactor with ICP-OES also identified a molar ratio of Fe:S to be around 1 (Table S5).

The SEM images (Figure S3) of the particles showed intergranular porous structure, likely due to the formation of nanocrystalline mackinawite (FeS) particles that stacked irregularly [34, 35]. To further confirm this, XRD was used to identify the mineral forms of iron sulfide particles. Clearly, theta-angle positions of the peaks from 10° to 100° as depicted in Figure S2b corroborate mackinawite (FeS) as the main form of iron sulfide particles. The precipitation of mackinawite might be a result of the reaction between Fe^{2+} and HS^{-}, owing to the reduction of Fe^{3+} and sulfate in the ferric dosed reactor, as shown in equation (1) & (2)

3.3. REMOVAL OF ORGANIC MPS BY FERRIC DOSING IN THE SEWER REACTORS.

The concentration profiles of selected organic MPs over the 6-hr cycle time in the control and ferric-dosed sewer reactors are shown in Figure 2-Figure 4. For most MPs, a fast initial removal was observed immediately after the spiking in the ferric dosed reactors followed by slower biodegradation. The behavior and removal patterns of different compounds were thus discussed in three groups distinguished by the different levels of initial removal. Group 1-3 organic MPs showed high (>90%), medium (30-70%) and low (0%) levels of initial removal.

3.3.1. GROUP 1. METHADONE, MORPHINE AND ATENOLOL. The group 1 compounds are classified as biodegradable organic MPs and also highly susceptible to the ferric dosing in wastewater. The removal of methadone in the control reactor was 77 ± 3 % at the end of 6-hr retention time. In the ferric dosed reactor, the removal of methadone within five minutes was 97.5 ± 0.1 % and after 6-hr it reached 99 ± 0.1 %. The removal obtained in control reactor is similar to a previously reported removal of 76 ± 9 % in the rising main reactor over 12-hr [23]. This removal has been attributed to the biological degradation due to sewer biofilms, as confirmed by the simulated biological transformation (Figure 2) with coefficients shown in Table S7. Formation of 2-ethylidene-1, 5-dimethyl-3, 3-diphenylpyrrolidine (EDDP), the human metabolite of methadone was not observed in the control reactor, suggesting the complete degradation of methadone. The in-sewer transformation pathway of methadone could also be different to human metabolism ending up with different transformation product [23, 36].

For morphine and atenolol, the initial removal was 90 ± 0.3% and 87.8 ± 0.3% within five minutes of spiking the compounds respectively in the ferric dosed reactor. At the end of the 6-hr cycle, the overall removal reached 97 ± 0.2% and 93.4 ± 0.8% for these two compounds. The further removal was well simulated by the first order kinetics. Morphine might be formed from its glucuronides as it increased with time in the control reactor, as shown before [23]. The atenolol removal after 6-hr in control reactor was 52.7 ± 5.5 %, which is higher than a previous report (i.e. 20% transformation within 24-hr) [26]. This might be due to the high A/V ratio of the sewer reactors (8 times higher) used in this study.

The removal of these group-1 compounds in the ferric dosed reactor after the initial rapid adsorption has been shown in Figure S4. The removal % was plotted against the concentration of these compounds left after the adsorption. The removal trend of methadone and atenolol remains the same as the control reactor suggesting the biological degradation after adsorption. But, in the case of morphine the removal trend after the initial rapid removal was also higher compared to the control. This could be due to the adsorption of morphine glucuronides avoiding its back transformations or could be due to the adsorption of codeine. About 30% of codeine was observed to be transformed to morphine in the rising main sewer condition[23]

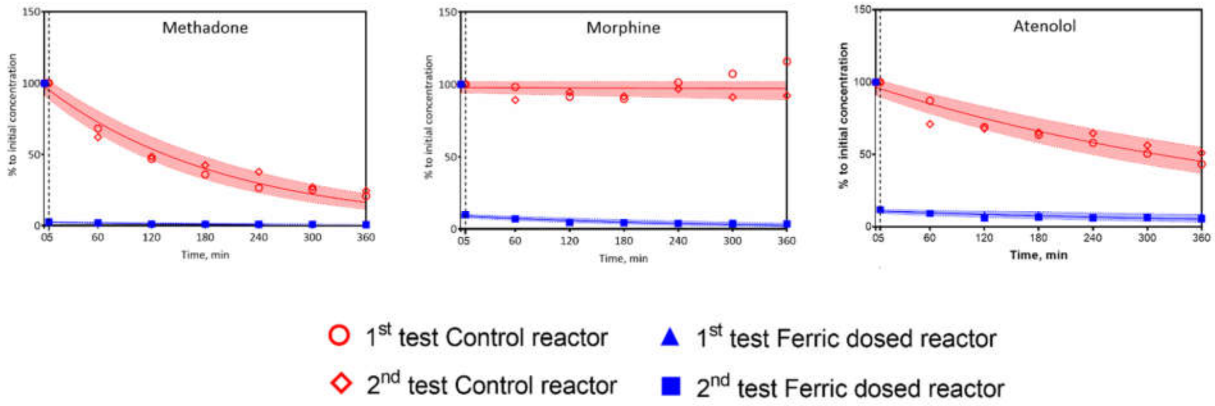

Figure 2. Stability of Group – 1 compounds in the ferric dosed and control sewer reactors. 1st and 2nd test represents the experiment performed at two different days. The middle line represents the simulated transformation with 95% confidence bounds (upper and lower lines).

3.3.2. GROUP 2. KETAMINE, CARBAMAZEPINE, ACESULFAME AND CODEINE. The group-2 organic MPs are classified as slightly biodegradable and less susceptible to iron sulfide particles. For ketamine up to 72.8 ± 0.5% was removed rapidly in the ferric dosed reactor within five min after spiking the compound. At the end of 6-hr retention time, the accumulated removal due to biological degradation and the fast initial removal reached 90.8 ± 0.2%. Although ketamine was also found to be biodegradable in the control sewer reactor, the removal was only 51.9 ± 0.6% at the end of 6-hr. This biological removal of ketamine by sewer biofilms was similar to previous studies, e.g. 63 ± 10% for 12-hr retention time [23]. The removal in the raw wastewater was about

11% up to 72-hr without biofilm [37, 38]. Norketamine, a major metabolite of ketamine, was not observed in both reactors.

Carbamazepine is the most prominent drugs with a long history of clinical usage and it is frequently found in the environment [39]. The carbamazepine removal was 40 ± 0.2% within five minutes of spiking the compound and at the end of 6-hr, the removal was 70 ± 3.5%. In comparison, the ultimate carbamazepine removal in control reactor was 36 ± 19%. However, carbamazepine was reported to be relatively stable in sewers and wastewater treatment plants[23, 40].

Similar to carbamazepine, acesulfame has been found to be one of the most stable and hydrophilic compound and has been suggested as a suitable biomarker in the population estimation [24, 41]. The initial removal of acesulfame was 32.1 ± 0.9% within five minutes and ultimately reached 34.7 ± 1.2%. Interestingly, the removal in the control reactor was 26.6 ± 8.4 %, likely due to the diversity of microorganisms in the sewer biofilms (Section S4) as a recent study found some species are capable of biodegrading acesulfame [42].

The initial and ultimate removal of codeine was 64 ± 1.4% and 70 ± 10% in the ferric dosed reactor. In contrast, the control reactor showed negative removal at the end of 6-hr. This may due to the back-transformation from its glucuronides or morphine to its original form. The codeine glucuronides was highly unstable in rising main sewers [23].

The better demonstration of biological degradation of these compounds in the ferric dosed reactor after rapid initial adsorption has been shown in Figure S4. The comparison of biological degradation in both the reactors has been discussed in section 3.4.

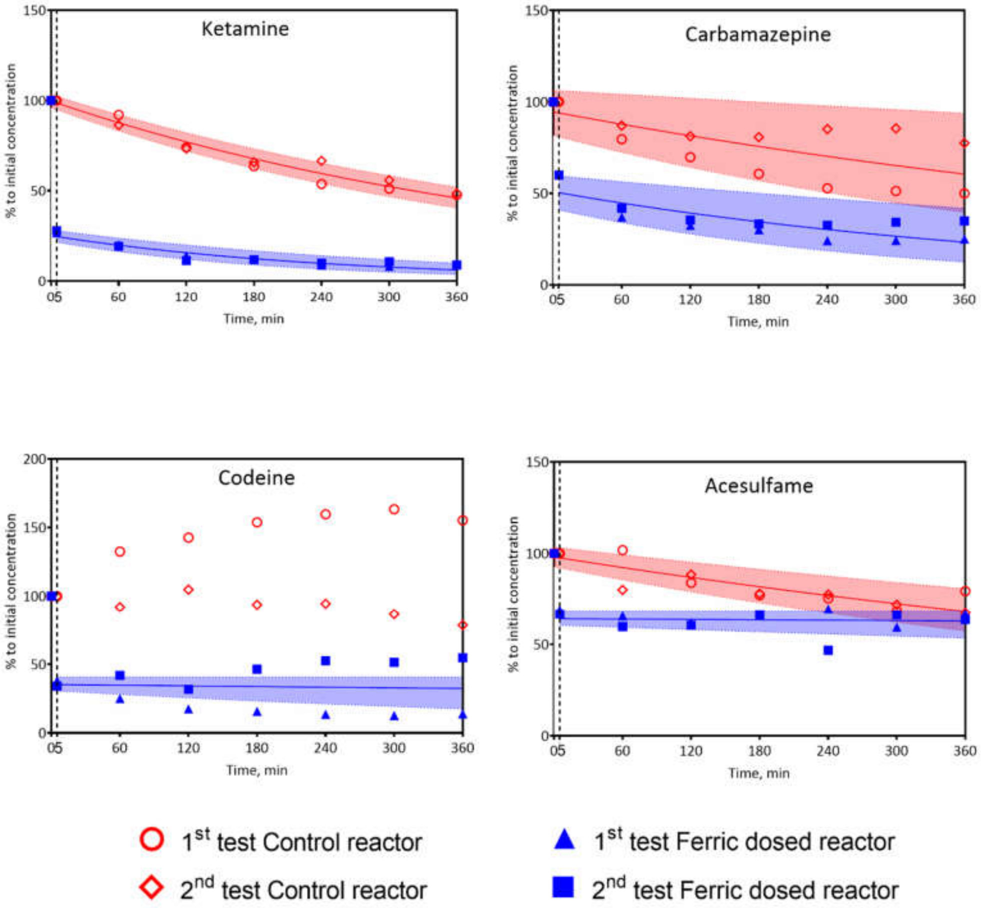

Figure 3. Stability of Group – 2 compounds in the ferric dosed and control sewer reactors. 1st and 2nd test represents the experiments performed at two different days. The middle line represents the simulated transformation coefficient with 95% confidence bounds (upper and lower lines)

3.3.3 GROUP 3. PARACETAMOL. As a singular case, ferric dosing did not induce an initial removal to paracetamol in the ferric dosed reactor. Considering the high paracetamol concentration of the wastewater (section 2.2), the surface of FeS particles might have reached its adsorption equilibrium for this specific compound. The biological degradation in both control and ferric dosed reactor was comparable, leading to the ultimate removal around 93.1 ± 1.3% and 78.4 ± 0.2% in the control and ferric dosed reactor, respectively. The relatively lower biodegradation in the ferric-dosed reactor could be due to the decreased biofilm activity, e.g. methanogenesis (Figure 1& Section S4). The co-metabolism of methanogenesis was reported to account for the removal of organic MPs such as the antibiotics (sulfamethaxazole, trimethoprim), neuro-drug (fluoxetine), endocrine-disrupting compounds (4-octyl phenol, 4-nonyl-phenol, 17α-ethinylestradiol, triclosan), anti-inflammatory drug (naproxen) and the musk fragrances (galaxolide, tonalide, celestolide) [43].

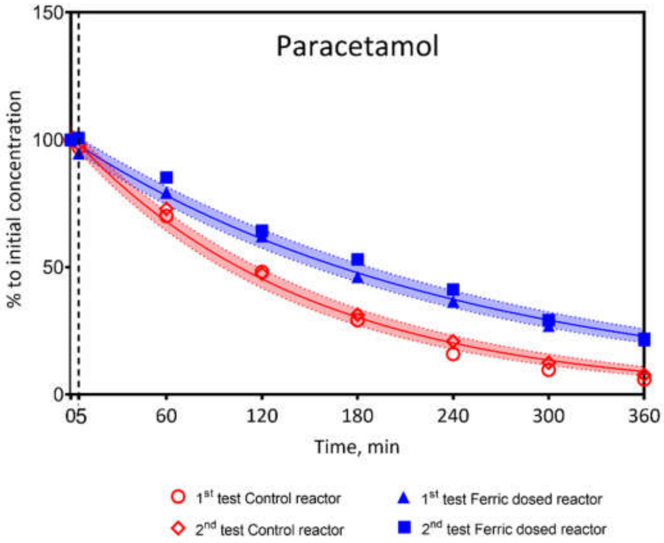

Figure 4. Stability of Group – 3 compounds in the ferric dosed and control sewer reactors. 1st and 2nd test represents the experiment performed at two different days. The middle line represents the simulated transformation coefficient with 95% confidence bounds (upper and lower lines)

It was clear that biological transformation can lead to different ultimate removal of MPs after 6-hr in the control reactor, and on top of the initial removal in the ferric-dosed reactor. The complete removal of compounds from the wastewater for group 1 can be achieved (methadone, morphine, atenolol). Without ferric dosing, the ultimate removal is limited (ketamine, carbamazepine) due to biological transformation alone or even formation (morphine, codeine) through back-transformation from glucuronides forms. The removal of these MPs in the sewer reactors were compared with previous studies and is shown in Table S5. The removal of methadone, ketamine and codeine in control reactor of this study are comparable to other studies and is due to the biological degradation. The difference in removal % observed could be due to change in microbial composition of the sewer biofilms grown in different sewer environments (Section S4).

3.4 ADSORPTION AND BIODEGRADATION OF MICROPOLLUTANTS. The majority of MP removal in the control reactor is mainly due to the biological transformations by microorganisms in the biofilms. On top of biological degradation, this study found a fast removal within minutes due to ferric dosing. Group 1 MPs are highly sensitive to the ferric dosing with an initial removal >90% within 5 minutes. In contrast, limited (30-70%) and no (0%) removal immediately after the dosing was observed for group 2 and 3 MPs, respectively. This fast initial removal was likely due to adsorption, whose kinetics is much faster than the chemical or biological degradation. For example, it was found that the sorption of methadone to the suspended solids in the wastewater accounted for 11% of the total removal [37]. In this study, the nearly complete removal within minutes for methadone could be due to the quick adsorption on to the surface of the FeS particles, which can be formed in the ferric dosed reactor. Quick removal of these MPs were not observed when iron was dosed into the sewer reactor without any preformed sulfides. This shows that any other iron species formed due to the hydrolysis of Fe^{3+} is not contributing to the removal of these MPs (Section S5). Batch tests with different ferric concentration (10, 5 and 1 mgFe/L) in the filtered wastewater also showed the negligible impact of other iron species on the MPs removal (Section S.5.2.2). Further, the Fourier transform infrared-Attenuated Total reflectance spectroscopy (FTIR-ATR) analysis of FeS particles before and after treating with MPs showed some shift in the characteristic peaks of FeS particles (Section S3). The stretching of both normal ‘polymeric’ –OH and aliphatic primary amine –NH functional groups showed a shift to lower numbers. The symmetric vibration of aryl sulfides and polysulfides shifted to lower wave numbers probably an indicative of hydrogen bonding. This further suggests that the initial fast removal of these MPs could be due to the adsorption on the suspended FeS particles. For instance, in group-1 compounds methadone (log K_{ow}=3.93) being the non-polar compound, the sorption could be due to the physical processes. In the case of morphine (log K_{ow}=0.89) and atenolol (log K_{ow}=0.16) which are polar compounds, the quick removal could attribute to the chemisorption on to the surface of FeS particles.

It is also important to note that, the metal ions such as zinc, copper (Cu) and iron in the wastewater could lead to the formation and accumulation of metal sulfides such as FeS or CuS on the sewer biofilms[44]. But, in the control reactor and in additional experiment with iron dosing (section S5), no rapid initial removal similar to ferric dosed reactor was observed. This indicates that the freshly formed FeS, in the form of suspended particles, was responsible for the adsorption of micropollutants. FeS precipitates accumulated in sewer biofilm was not as active likely due to the interaction and coverage by bacteria and extra cellular polymeric substances.

The degradation kinetics of these compounds in the control and ferric dosed reactor were well simulated using the first order kinetics [27]. Although both SRB’s and MA’s in sewer biofilms are capable of degrading the MPs it is still unclear how the change in microbial community due to ferric dosing (section S4) will specifically impact the removal of each MPs. The simulated transformation coefficients are shown in Table S6. The k_{bio} coefficients of some compounds like methadone and atenolol, are almost the same in the control and ferric dosed reactors. This implies that the microbes responsible for the biodegradation of those compounds were not impacted by the ferric dosing. The k_{bio} coefficient of acesulfame & paracetamol are lower in the ferric dosed reactor comparing to the control reactor which might be due to the co-metabolism of these compounds by methanogens were inhibited, as discussed in the previous section.

For other compounds (morphine, ketamine, carbamazepine, codeine), the k_{bio} coefficient in the ferric dosed reactor is higher than the control reactor. The iron sulfide with the adsorbed MPs can precipitate inside the biofilm matrix or deposit on its surface (Figure S8). The MPs were thus in a close vicinity and readily available for microbial biodegradation. This might be the reason for higher k_{bio} coefficient in ferric dosed reactor. The change of microbial community structure due to ferric dosing could be another potential reason for the enhanced biological degradation of MPs.

3.5 EFFECTS OF FeS CONCENTRATION ON THE MICROPOLLUTANTS REMOVAL.

Batch tests were conducted with different FeS concentration to further confirm the fast initial removal of MPs was due to the adsorption to suspended FeS particles. As shown in Figure 5, comparing the median, it is observed that the removal of Group-1 compounds was high at high concentration of FeS (1:2) in both unfiltered (methadone-59.7%, morphine-34.36% & atenolol – 2.7%) and filtered wastewater (methadone-85.79%, morphine-48.86% & atenolol – 26.21%). However, the removal in the unfiltered wastewater is comparatively lower than the filtered wastewater. This could be due to the interference of suspended particles for the adsorption sites on the FeS particles. The methadone removal in unfiltered and filtered WW is c.a. 18 times and 4 times lower at 1:10 dilution ratio compared with a with 1:2 dilution ratio and no removal was observed at lower FeS concentration (1:50 dilution ratio). Similar results were obtained in the case of morphine and atenolol at lower FeS concentrations.

These results clearly emphasize that the removal obtained is mainly correlated to the amount of iron sulfide particles and the result of rapid adsorption. There is no biofilm present in these batch experiments. The removal of these compounds due to presence of suspended particles in wastewater is negligible [37]. The metabolites due to their biological transformation such as EDDP were also not observed in this study.

Similar to group – 1, the group-2 compounds also showed less removal at lower FeS concentration (1:50 and 1:10) in comparison to the higher FeS concentration (1:2), with different ultimate removal of ketamine (23.91%, 49.18%), codeine (4.14%, 38.38%) and carbamazepine (58.85%,73.44%) observed in unfiltered and filtered WW respectively. In the case of codeine, the big variation of the data could be due to the abiotic backformation from its metabolites[45]. In contrast, the removal of carbamazepine was higher in the unfiltered wastewater than filtered wastewater, suggesting the mediating role of suspended solids in wastewater for the adsorption of carbamazepine to iron sulfide. Acesulfame, the more hydrophilic compound, showed no adsorption at all FeS concentrations while comparing the medians and ultimately, no removal was observed at the end of 1 hr.

Interestingly, we observed some removal of paracetamol in both unfiltered and filtered wastewater at all FeS dilutions. These results were different from the sewer reactors. It could be due to the continuous exposure of FeS particles with background wastewater paracetamol concentration in the sewer reactors as discussed in section 3.2.3. Comparing the medians, the highest removal of paracetamol was 48% and 49% at 1:50 FeS dilution ratio in unfiltered and filtered wastewater.

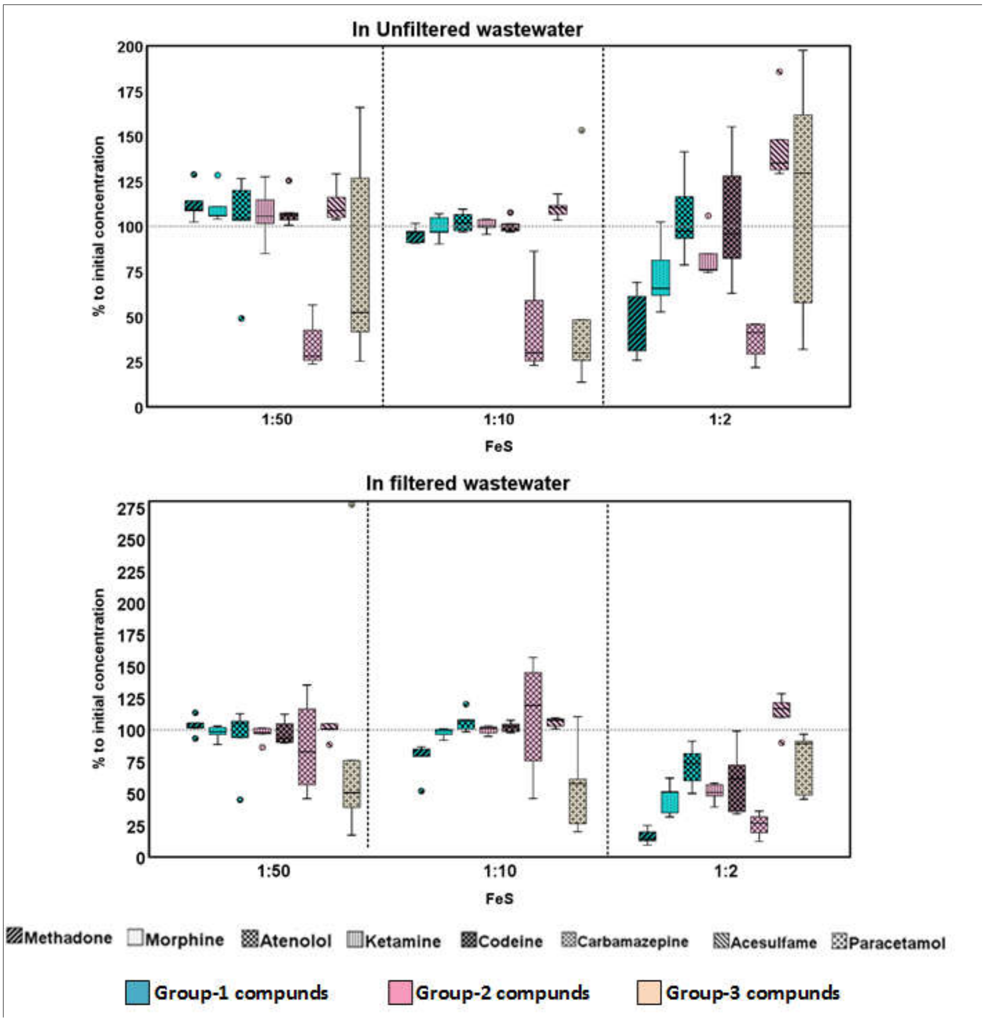

Figure 5. Box and whiskers plot showing the removal of MPs at different FeS concentrations (Middle line of the box represents the median, the upper and lower lines represents the 25th and 75th percentile, the whiskers extending the box and the outliers represents the data outside the inter quartile range. The data represents different measurements during the 1hr test)

4. IMPLICATIONS FOR WASTEWATER TREATMENT. This study showed that the biological degradation of MPs is limited in sewers. Due to their recalcitrant nature, the typical wastewater treatment process is also incapable of removing MPs from wastewater unless using the advanced treatment technologies. For the first time, the data supported that the removal of MPs in the sewer network due to ferric dosing could significantly reduce the MPs load in the liquid phase of the WWTPs. For nearly all the selected illicit drugs and pharmaceuticals, ferric dosing significantly enhanced the removal from wastewater in a time scale of minutes. As a popular chemical dosing strategy in rising main sewers, the dosing concentration required to remove sulfide is higher than that required to achieve a reasonable removal of MPs. Therefore, the ferric dosing in sewers is adding value to the downstream WWTP by removing the MPs from the influent wastewater.

Previous studies have shown that iron sulfide formed in sewers can be reactivated in the treatment plant for the phosphorus removal and the hydrogen sulfide emission control in the anaerobic digester. This study demonstrated another additional benefit of ferric dosing in the sewers. However, future research should focus on the diverse compounds of MPs and the mechanism behind the adsorption of these compounds with the FeS particles. Also, it is essential to understand the fate and transformation of FeS attached MPs when entering the WWTPs.

The usage of iron salts in drinking water treatment systems produces a huge amount of sludge as a by-product. The iron content in the sludge varies from 133 – 268 g Fe/kg of sludge [46-48]. The iron-rich drinking water treatment sludge has been used successfully to control the sulfide in the sewer reactor [48]. In addition, the complexing nature of natural organic matter (120 – 400 g/kg as organic carbon) presented in drinking water sludge might enhance the removal of MPs from wastewater [49, 50]. Future studies should further delineate the fate of MPs in sewers dosed with iron-rich drinking water sludge.

SUPPORTING INFORMATION

Rising main sewer setup. Properties of selected organic MPs. Chemical spiking in batch tests. Characteristics of particles formed in ferric dosed reactor. Atomic ratio of iron and sulfide based on weight % obtained from EDS and ICP-OES. Biodegradation of compounds in the control and ferric dosed reactor. Comparison of biodegradation results with previous studies. Simulated transformation coefficients of the investigated compounds with/without iron dosage. FTIR-ATR analysis depicting adsorption of MPs on the FeS particles.

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