Hydrogen sulfide removal from sediment and water in box culverts/storm drains by iron-based granules

J. L. Sun, C. Shang and G. A. Kikkert

ABSTRACT

A renewable granular iron-based technology for hydrogen sulfide removal from sediment and water in box culverts and storm drains is discussed. Iron granules, including granular ferric hydroxide (GFH), granular ferric oxide (GFO) and rusted waste iron crusts (RWIC) embedded in the sediment phase removed aqueous hydrogen sulfide formed from sedimentary biological sulfate reduction. The exhausted iron granules were exposed to dissolved oxygen and this regeneration process recovered the sulfide removal capacities of the granules. The recovery is likely attributable to the oxidation of the ferrous iron precipitates film and the formation of new reactive ferric iron surface sites on the iron granules and sand particles. GFH and RWIC showed larger sulfide removal capacities in the sediment phase than GFO, likely due to the less ordered crystal structures on their surfaces. This study demonstrates that the iron granules are able to remove hydrogen sulfide from sediment and water in box culverts and storm drains and they have the potential to be regenerated and reused by contacting with dissolved oxygen.

Key words | hydrogen sulfide, iron-oxide granules, odour control

J. L. Sun (corresponding author)
C. Shang
G. A. Kikkert
Department of Civil and Environmental Engineering,
the Hong Kong University of Science and Technology,
Clear Water Bay,
Kowloon,
Hong Kong
E-mail: *jlsun@ust.hk*

INTRODUCTION

The hydrogen sulfide odour emitted from box culverts and storm drains has raised frequent complaints in Hong Kong and other coastal cities. Box culverts and storm drains are designed for discharging storm water during heavy rain, however they may often be polluted with organics from misconnected sewers or illegal sewage discharges. Some of the organic pollutants co-settle with sand particles and accumulate in the form of sediments in the box culverts/storm drains, where sulfate-reducing bacteria then utilize the organics and sulfate provided from tidal seawater to form odorous hydrogen sulfide, which causes the odour nuisance. To solve the odour problem, sediment desilting which involves high operational costs is one solution that has been employed in Hong Kong for decades. But the accumulation of sediments and sulfide generation after desilting brings back the odour problem. The addition of chemical oxidants, such as hydrogen peroxide, chlorine, nitrate salts and ferric salts, is used for hydrogen sulfide removal in sewer systems by oxidizing odorous hydrogen sulfide to odourless compounds (Nielsen *et al.* 2005; Firer *et al.* 2008; Zhang *et al.* 2008). These chemical oxidants also provide a possible solution to eliminate the odour nuisance in box culverts and storm drains. However, this solution is rather temporary and of high cost in box culverts and storm drains, due to the loss of the soluble oxidants to the tidal and storm water. The technological shortfalls of these existing methods demand more sustainable solutions.

The addition of ferric (hydr)oxides in granular form can be one long-lasting method. Ferric (hydr)oxide granules embedded in or placed on the sediment phase are expected to remove aqueous hydrogen sulfide. Because of their solid form and high density it is much more difficult for the granules to be flushed away by tidal or storm water. Various ferric (hydr)oxide particles/powders such as hematite, goethite, ferrihydrite and lepidocrocite have been used to suppress hydrogen sulfide in various aqueous systems (Yao & Millero 1996; Poulton *et al.* 2004; Ritvo *et al.* 2004). The reaction between dissolved sulfide and ferric (hydr)oxides has been recognized as a surface-controlled process (Dos Santos Afonso & Stumm 1992). Iron sulfide (FeS), ferrous hydroxide ($Fe(OH)_2$) and elemental sulfur (S^0) were found as the major products of the reaction (Peiffer *et al.* 1992; Poulton *et al.* 2004), which may cover the surface and lead to exhaustion. The ferrous iron products including iron sulfide,

ferrous ion and ferrous hydroxide, which are produced from the ferric reduction by hydrogen sulfide, have been reported to be re-oxidized back into ferric (hydr)-oxides with oxygen or dissolved oxygen (Davydov et al. 1998; Ma et al. 2006). In addition, the tidal conditions in box culverts and storm drains in seafront areas provide an environment that allows the use of tidal energy (by installing a gate that is closed at low tide and opened rapidly at high tide) to periodically suspend and mix the exhausted iron granules with the dissolved oxygen-rich tidal water for regeneration. These previous findings and the proposed use of tidal energy suggest the possibility of the use, regeneration and reuse of iron in the granular form for sulfide removal, which deserves further investigation.

This paper discusses the evaluation of the potential of a renewable granular iron-based technology for aqueous hydrogen sulfide removal from sediment and water in box culverts and storm drains by lab simulations. Three types of iron granules including granular ferric hydroxide (GFH), granular ferric oxide (GFO) and rusted waste iron crusts (RWIC) were evaluated and compared. The regeneration and reuse of these iron granules were also investigated.

MATERIALS AND METHODS

Materials

GFH (GEH® 101) and GFO (Bayeroxide® E33) were obtained from GEH Wasserchemie and Severn Trent Services, respectively. RWIC was prepared by submerging the waste iron crusts (from Connelly-GPM) in seawater open to the atmosphere at $22 \pm 1\,°C$ for 3 days. Some physical and chemical properties of GFH, GFO and RWIC measured are listed in Table 1. The TRIS buffer was prepared with TRIS base (Trizma® base) and adjusted to pH 8.0 with 0.5 mol/L HCl. Sediment samples were collected from a box culvert at an odorous site in Hong Kong. Seawater

was obtained from the Coastal Marine Laboratory at HKUST after filtration through 0.45 μm filters.

Experimental procedures

The sulfide removal capacities of GFH, GFO and RWIC were first evaluated in the well-controlled water phase by daily feeding of 5.47 g iron granule with a 20-mg/L sulfide solution, which was deoxygenated by nitrogen gas purging and buffered at pH 8.0 (50-mmol/L TRIS), in a capped 1.05-L plastic bottle in the dark at room temperature ($22 \pm 1\,°C$). The bottle reactor was continuously mixed at 12 rpm in an end-over-end rotator (Environmental Express, Inc.). TRIS buffer was selected as it does not interfere with the reaction of dissolved sulfide with ferric (hydr)oxides (Yao & Millero 1996). The daily feeding was repeated until the remaining dissolved sulfide concentration of the mixture reached 0.5 mg/L or above, which was operationally defined as exhaustion. The sulfide removal capacity was then calculated from the cumulative amount of sulfide that had been removed before the exhaustion. The exhausted iron granules were regenerated by mixing the granules with a 50-mmol/L TRIS buffer saturated with dissolved oxygen by a mechanical mixer (BIBBY Stuart Scientific Flocculator SW1) at 200 rpm in a 500-ml beaker open to the atmosphere for 6 hours at pH 8.0 and $22 \pm 1\,°C$. The dissolved oxygen concentration in the buffered solution experienced a fast drop and then it gradually rebounded to the initial level after 6 h mixing, with the observation of red/brown granules. After settlement, the iron granules were collected for reuse tests, which were conducted in the same manner as above.

For studying hydrogen sulfide removal in the sediment phase, sediment samples were blended with aliquots of GFH, GFO and RWIC at a predetermined dosage of 2.18 or 4.36 g per litre of sediment and the mixtures completely filled 500-mL flow-through column reactors. The schematic presentation of the testing system is shown in Figure 1, where the column reactor was continuously fed upwards with deoxygenated seawater (providing 2,700 mg/L sulfate), spiked with glucose and sodium acetate (as carbon sources for biological sulfate reduction, 300 mg/L as chemical oxygen demand (COD)) at a flow rate of 6.6 mL/h and $22 \pm 1\,°C$. Effluent samples were taken daily and immediately subjected to sulfide analysis until the exhaustion occurred. After the exhaustion, the exhausted iron granules in the sediment-iron mixture were regenerated by rapidly mixing the 500-mL mixture at 200 rpm with a paddle mixer in a 30-L bucket of seawater open to the atmosphere for 2 or 4 hours. The sediment and iron granules were

Table 1 | The physical and chemical properties of GFH, GFO and RWIC

	GFH	GFO	RWIC
Effective component	β-FeOOH	α-FeOOH	Amorphous FeOOH
Porosity (v%)	46.5	82.1	65.8
Bulk density (g/cm³)	1.1	0.42	1.7
Grain size (mm)	0.075–2.0	0.075–2.0	0.075–2.0
Fe content (wt%)	35.1	62.0	72.8
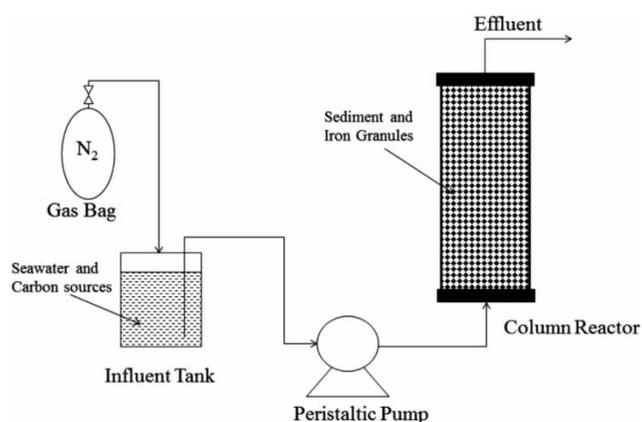
Figure 1 | Schematic presentation of the reactor setup for studying the aqueous hydrogen sulfide removal in the sediment phase.

Figure 2 | The sulfide removal capacities of virgin and regenerated iron-based granules (GFH, GFO and RWIC) in the water phase. Temperature = 22 ± 1 °C, pH = 8.0, Regeneration time = 6 h.

allowed to settle to collect the regenerated mixtures, which were then put back into the column reactor and subjected to reuse tests. A control reactor with the sediment sample in the absence of iron granules was also prepared and analysed for comparison. The sulfide removal capacity was then calculated from the cumulative amount of sulfide that had been produced in the control reactor during the corresponding period. It should be reemphasized that the continuous tests were conducted with small, laboratory-scale column reactors to allow continuous contact between seawater and sediments, the hydrodynamics and the conditions of which are very different from the reality.
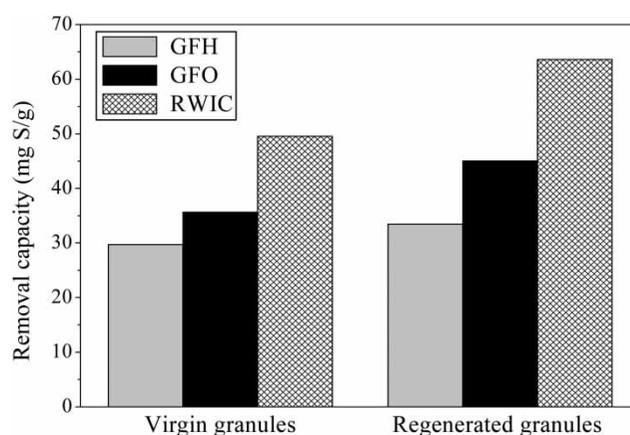
Analytical methods

The dissolved sulfide concentrations in all water samples were measured by the methylene blue method (APHA-AWWA-WEF 1998) after filtering through 0.45-μm filters. pH and dissolved oxygen concentrations were measured by a multi-parameter meter (WTW Multi 3420) equipped with pH and dissolved oxygen probes. The particle size distributions of virgin and regenerated iron granules were determined by a laser diffraction particle size analyser (Coulter LS 13 230).

RESULTS AND DISCUSSION

Hydrogen sulfide removal capacities of iron granules in the water phase

Figure 2 shows that, among the three virgin iron granules tested in the water phase, RWIC possessed the highest

sulfide removal capacity of 49.5 mg S/g, while the capacity of GFH was the lowest. The different sulfide removal capacities of the three iron granules may be attributed to their different surface properties, such as the quantities of reactive surface sites, porosity and iron content. Compared with GFH and GFO, RWIC is covered with a layer of freshly formed amorphous ferric hydroxide, which possesses the highest surface area, and thus provides the largest quantity of reactive surface sites (Cornell & Schwertmann 2003; Poulton *et al.* 2004). Despite the fact that GFH and GFO are both known for their porous structure and high surface areas (Chitrakar *et al.* 2006; Yusan & Erenturk 2011), the iron content and porosity of GFO are higher than those of GFH (Table 1), resulting in a larger sulfide removal capacity of GFO.

Figure 2 also displays the sulfide removal capacities of the iron granules regenerated by dissolved oxygen, which oxidized and recovered ferric (hydr)oxides on the granular surface. Increases in the removal capacities were found in all cases, suggesting the formation of higher quantities of reactive surface sites during the regeneration. The increases in the reactive surface sites may be partially attributed to the reduction of the granular size. As shown in Figures 3 and 4, the particle size distributions of the regenerated GFH and GFO granules shifted to smaller sizes after the 6-hour regeneration, due to the fracturing of the original granules during the mechanical mixing. The increases in the reactive surface sites may also be attributed to the formation of amorphous ferric hydroxide. The particle size distribution of RWIC could not be determined by the laser diffraction particle size analyser because of its magnetic metal core. The relative removal capacities among
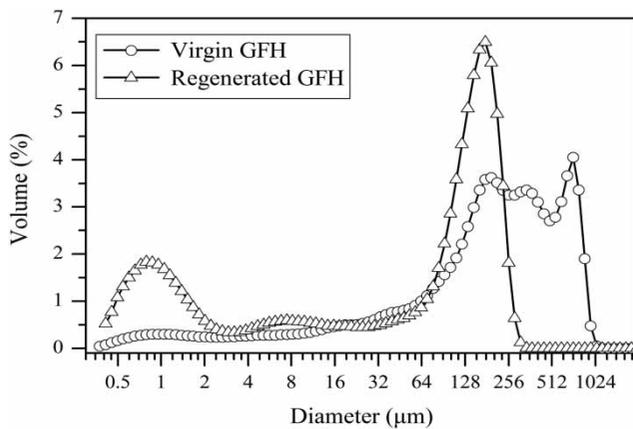
Figure 3 | The particle size distributions of virgin and regenerated GFH.
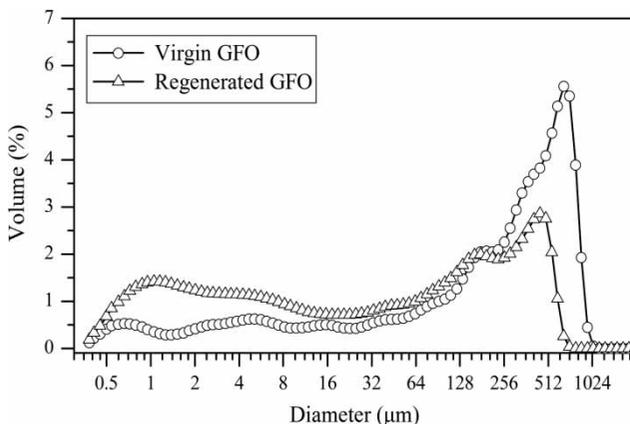
Figure 4 | The particle size distributions of virgin and regenerated GFO.

the three regenerated granules showed the same order as the virgin ones, likely due to the same reasons discussed above.

## Hydrogen sulfide removal by iron granules in the sediment phase

Figures 5 and 6 display hydrogen sulfide removal by the three iron granules in the sediment phase. As shown in Figure 5 by the results from the control test, the provision of deoxygenated seawater 2,700 mg/L sulfate and 300 mg/L COD produced and maintained a sulfide concentration of around 50 ± 11 mg/L as S as a result of biological sulfate reduction in the sediment phase. After GFH dosing on Day 9, nearly all dissolved sulfide produced in the sediment phase was removed until GFH approached its exhaustion on Day 23 and 24. Based on data presented in Figure 5, the sulfide removal capacity of virgin GFH was estimated to be

92.0 ± 4.2 mg S/g, which was approximately three times higher than that measured in the water phase.

The sulfide removal by regenerated GFH, after 2-h and 4-h mixing, is also presented and compared in Figure 5, with corresponding sulfide removal capacities of 118.7 and 188.6 mg S/g, respectively, after the first regeneration. The longer regeneration time allowed more time for iron oxidation by the dissolved oxygen to yield a higher recovery rate. Similar to the observation in the water phase (Figure 2), the regenerated GFH had a higher sulfide removal capacity than did the virgin GFH in the sediment phase.

Figure 6 displays the sulfide removal by GFO and RWIC embedded in the sediment in another batch of experiments. Similar to the GFH case, there was virtually no dissolved sulfide detected in the effluents from the column reactors containing virgin and 4-h regenerated GFO and RWIC before they became exhausted. Removal capacities of virgin GFO and RWIC were estimated to be 37.8 and 82.9 mg S/g, respectively, and the capacities of the regenerated GFO and RWIC increased to 45.4 and 104.6 mg S/g, respectively.

Two important similarities were observed from the data obtained in this study. Firstly, the capacities of virgin iron granules obtained in the sediment phase are all larger than those of the corresponding ones obtained in the water phase. This is partly related to the fracturing of iron granules caused by the high shear force exerted on the iron granules during the mixing with the sediment sample, which increased the available surface area for sulfide removal. The presence of organic ligands in the sediment phase may partially account for the increase as well. Several organic ligands such as ethylenediaminetetraacetate (EDTA), natural organic matter (NOM) and citrate are ubiquitous under organic-rich and anaerobic conditions and concentrations of several milligrams per litre in the sediments and sewage have been reported (Feijtel *et al.* 1996; Nielsen *et al.* 2005). These organic ligands formed complexes with iron and promoted the detachment of iron from the surface by ligand-induced dissolution (Bondietti *et al.* 1993; Liang *et al.* 2000; Cornell & Schwertmann 2003). Despite the fact that the ligand-induced dissolution of ferric (hydr)oxides is always slow, the contribution could be significant at the time scale of months of the current study. The ligand-induced dissolution formed ferric-containing complexes that also reacted with sulfide and could deposit a portion of the products (ferrous iron and S^0 precipitates) in the solution or on the surface of the surrounding sand particles. As a result, fewer precipitates were deposited on the surface of the iron granules, resulting
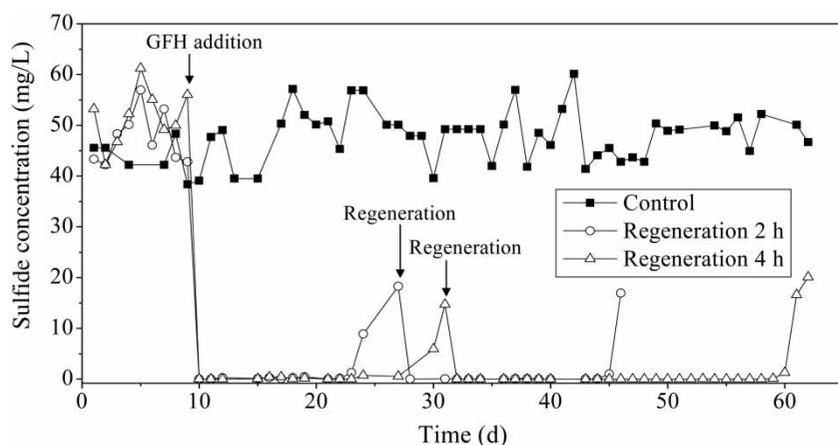
Figure 5 | Concentrations of sulfide in the effluents from the reactors with GFH embedded in the sediment phase. GFH dosage = 2.18 g/L, Flow rate = 6.6 mL/h, $[SO_4^{2-}]$ = 2,700 mg/L, COD = 300 mg/L, Temperature = 22 ± 1 °C, Sediment volume = 500 mL, GFH was added on Day 9.
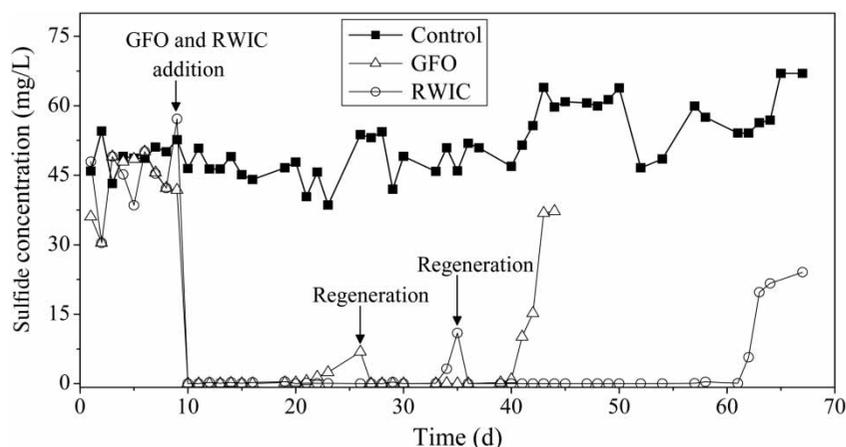
Figure 6 | Concentrations of sulfide in the effluents from the reactors with GFO and RWIC embedded in the sediment phase. GFO and RWIC dosage = 4.36 g/L, Flow rate = 6.6 mL/h, $[SO_4^{2-}]$ = 2,700 mg/L, COD = 300 mg/L, Temperature = 22 ± 1 °C, Sediment volume = 500 mL, iron granules were added on Day 9.

in a delay of the exhaustion. It should be noted that there may be other reasons that also contribute to the higher capacities observed in the sediment phase. For example, iron-reducing bacteria may compete for the carbon source with the sulfate-reducing bacteria to interfere with the sulfide production, which cannot be excluded here and requires further study.

The second similarity observed is the higher capacities of the regenerated iron granules compared to those of the corresponding virgin ones. In addition to the contributions by the particle fracturing and the freshly formed amorphous ferric hydroxides aforementioned, the ferrous iron precipitates deposited on the surface of sand particles as discussed above could also be oxidized by dissolved oxygen during regeneration and form new reactive surface sites that are later available for sulfide removal. The

mechanistic study on the transport and transformation of Fe(II)/Fe(III) during sulfide removal, regeneration and reuse is on-going.

However, among the three iron granules tested, the order of their relative capacities in sulfide removal is inconsistent in the water and sediment phases. The inconsistency is likely attributed to their different mineral properties. Ferric (hydr)oxides with highly ordered crystal structure are more stable and their ligand-induced dissolution has proved to be more difficult, compared to the less ordered minerals (Bondietti *et al.* 1993; Liang *et al.* 2000). In addition, the highly ordered crystals are harder and stronger (Cornell & Schwertmann 2003) and are less susceptible to breakage by mechanic forces than the less ordered ones. The crystallinity degree of the three materials tested in the current study follows the order of GFO ≫ GFH > RWIC

(Poulton *et al.* 2002; Cornell & Schwertmann 2003). Thus, GFH is expected to be more susceptible to breakage in the sediment phase, to provide more surface sites for sulfide removal and to increase the removal capacity. Although RWIC is known to have the least ordered crystalline structure on the surface, the metal core of RWIC granules restrains the breakage, leading to its slightly lower capacity than that of GFH in the sediment phase.

CONCLUSIONS

The results of this study demonstrated that the granular iron-based technology is a solution to remove hydrogen sulfide from sediment and water in box culverts and storm drains. Various granular iron-based materials, including GFH, GFO and WRIC, removed hydrogen sulfide both in the water and sediment phases. Higher sulfide removal capacities were observed in the sediment phase, compared to those obtained in the water phase. The exhausted iron granules were regenerated by dissolved oxygen and higher removal capacities were achieved in the regenerated iron granules. This may be attributed to the reduction of particle sizes of iron granules and generation of new ferric hydroxide surface sites on the granules and the surrounding sand particles. This study demonstrates that the iron granules are able to remove hydrogen sulfide from sediment and water in box culverts and storm drains. By making use of the iron-sulfide redox cycle and the natural tidal energy, they have the potential to be regenerated and reused by contacting with dissolved oxygen.

ACKNOWLEDGEMENTS

REFERENCES

APHA-AWWA-WEF 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

Bondietti, G., Sinniger, J. & Stumm, W. 1993 The reactivity of Fe(III) (hydr)oxides: effects of ligands in inhibiting the dissolution. *Colloids Surf. A* **79**, 157–167.

Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K. & Hirotsu, T. 2006 Phosphate adsorption on synthetic goethite and akaganeite. *J. Colloid Interface Sci.* **298**, 602–608.

Cornell, R. M. & Schwertmann, U. 2003 *The Iron Oxides: Structure, Properties, Reactions, Occurrences and uses*, 2nd edn. Wiley-VCH, Weinheim, Germany, pp. 1–339.

Davydov, A., Chuang, K. T. & Sanger, A. R. 1998 Mechanism of H_2S oxidation by ferric oxide and hydroxide surfaces. *J. Phys. Chem. B* **102**, 4745–4752.

Dos Santos Afonso, M. & Stumm, W. 1992 Reductive dissolution of iron (III) (hydr)oxides by hydrogen sulfide. *Langmuir* **8**, 1671–1675.

Feijtel, T., Vits, H., Murray-Smith, R., Van Wijk, R., Koch, V., Schroder, R., Birch, R. & Berge, W. T. 1996 Fate of LAS in activated sludge wastewater treatment plants: a model verification study. *Chemosphere* **32**, 1413–1426.

Firer, D., Friedler, E. & Lahav, O. 2008 Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications. *Sci. Total Environ.* **392**, 145–156.

Liang, L., Hofmann, A. & Gu, B. 2000 Ligand-induced dissolution and release of ferrihydrite colloids. *Geochim. Cosmochim. Acta* **64**, 2027–2037.

Ma, S. F., Noble, A., Butcher, D., Trouwborst, R. E. & Luther III, G. W. 2006 Removal of H_2S via an iron catalytic cycle and iron sulfide precipitation in the water column of dead end tributaries. *Est. Coast. Shelf Sci.* **70**, 461–472.

Nielsen, A. H., Lens, P., Vollertsen, J. & Hvitved-Jacobsen, T. 2005 Sulfide–iron interactions in domestic wastewater from a gravity sewer. *Water Res.* **39**, 2747–2755.

Peiffer, S., Dos Santos Afonso, M., Wehrli, B. & Gachter, R. 1992 Kinetics and mechanism of the reaction of H_2S with lepidocrocite. *Environ. Sci. Technol.* **26**, 2408–2413.

Poulton, S. W., Krom, M. D., Van Rijn, J. & Raiswell, R. 2002 The use of hydrous iron (III) oxides for the removal of hydrogen sulphide in aqueous systems. *Water Res.* **36**, 825–834.

Poulton, S. W., Krom, M. D. & Raiswell, R. 2004 A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulphide. *Geochim. Cosmochim. Acta* **68**, 3703–3715.

Ritvo, G., Shitumbanuma, V. & Dixon, J. B. 2004 Soil solution sulfide control by two iron-oxide minerals in a submerged microcosm. *Aquaculture* **239**, 217–235.

Yao, W. S. & Millero, F. J. 1996 Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Mar. Chem.* **52**, 1–16.

Yusan, S. D. & Erenturk, S. A. 2011 Sorption behaviors of uranium (VI) ions on α-FeOOH. *Desalination* **269**, 58–66.

Zhang, L. H., Schryver, P. D., Gusseme, B. D., Muynck, W. D., Boon, N. & Verstraete, W. 2008 Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. *Water Res.* **42**, 1–12.