Ferric chloride for odour control: studies from wastewater treatment plants in India

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Abstract

This study was about the feasibility of using ferric chloride as an agent for odour control in wastewater treatment plants (WWTPs) due to hydrogen sulphide emission. Total inlet sulphide concentrations at 11 WWTPs in Delhi were measured and ranged between 1.1 and 14.8 mg/L. Wastewater samples from Najafgarh drain were used in jar tests to estimate the ferric chloride concentration required to obtain acceptable treatment. Ferric chloride was effective in removing sulphide, phosphate and total suspended solids (TSS), and gave significant biological oxygen demand (BOD) reduction. It was ineffective, however, in removing ammoniacal-nitrogen. A dose of 40 mg/L removed 76% of total sulphide, which corresponds to a significant reduction in hydrogen sulphide emission. The study demonstrated that ferric chloride can be used as a cost-effective pre-treatment step in WWTPs to reduce sulphur-related odours significantly, as well as TSS, BOD and phosphate from wastewater.

Key words: ferric chloride, hydrogen sulphide, pre-treatment, wastewater

Highlights

- Foul odours at WWTPs are due mainly to hydrogen sulphide emission.
- This study explores the application of the commonly-used coagulant ferric chloride to remove sulphides from wastewater.
- Dosage of 40 mg/L ferric chloride was effective in removing sulphides, phosphates, TSS and BOD.
- Ferric chloride can provide cost-effective treatment in WWTPs to reduce foul odour emissions.

INTRODUCTION

Wastewater treatment plants (WWTPs) are integral in wastewater management and maintaining urban sanitation. A major issue encountered in WWTPs is foul odour emissions (Al-Shammiri 2004). Anaerobic microbial reactions in WWTPs and odorous volatile organic compounds (VOCs) produce hydrogen sulphide (Carrera *et al.* 2014), the target of this study. Hydrogen sulphide has a distinct, rotten egg smell and concentrations as low as 0.00047 mg/L can be detected (Crites & Tchobanoglous 1998) and it is produced by sulphate-reducing bacteria.

Hydrogen sulphide emissions at WWTPs can: (i) emanate foul odour; (ii) corrode exposed metal surfaces; (iii) lead to health issues among workers (Esswein *et al.* 2016), and (iv) cause fires if the gas comes into contact with strong oxidising agents (Nielsen *et al.* 1992). Strategies must be devised, therefore, to mitigate hydrogen sulphide emissions at WWTPs for both public health and safety. Odour neutralizers or masking agents are often used to neutralize odours, and industrial grade

covers are used, in some cases, to prevent odour diffusion into the atmosphere (Ando 1980). These methods only mask the problem and do not treat the odour's source. Other technologies are available but are not economically feasible for use in developing countries. In addition to higher maintenance costs, biological odour control methods such as biofilters and bio-trickling filters have a large footprint and high water consumption, respectively (Estrada *et al.* 2011).

Previous studies have analysed the efficacy of chemical oxidants such as hydrogen peroxide, sodium hypochlorite and potassium permanganate in wastewater samples from WWTPs. Studies with hydrogen peroxide showed that 20–30 minutes of reaction time was required for H_2S control at 50% (v/v) concentration. However, there are safety issues with handling hydrogen peroxide at the concentration used (Thomas 2007). The concentration of H_2S in WWTP influents is directly related to the sulphide concentration in the wastewater (Al-Shammiri 2004), so the use of strategies to reduce the influent sulphide concentration at WWTPs is expected to lower hydrogen sulphide emissions proportionally.

Iron salts are commonly used both for phosphorus removal and as coagulants for removing suspended solids (Metcalf & Eddy 2003). The potential of sludge containing ferric and alum salts for hydrogen sulphide removal has been explored by Wang & Pei (2012). The sludge that they used contained twice as much iron as aluminium (w/w) and demonstrated significant H_2S removal at neutral pH. Previous studies have shown the use of ferric salts in sewer systems for sulphide and phosphate removal from wastewater (Gutierrez *et al.* 2010). However, this model might not be feasible in all developing countries since not all areas have a centralized sewer system. For example, raw sewage in most unsewered areas in Delhi is currently trapped from open drains, via the Interceptor Sewer Project, and diverted to the nearest WWTP.

The effectiveness of ferric chloride dosing on sewage sludge in controlling malodourous sulphur gas emissions was also reported by Devai & Delaune (2002). As far as is known, however, there are no current studies on the application of ferric chloride as a pre-treatment step in WWTPs for potential odour control in relation to sulphurous gases.

The major objective of this study was to explore the potential of ferric chloride dosing in WWTP inlets to reduce sulphide concentrations substantially in the presence of TSS and phosphorus. Significant sulphide and TSS removal at WWTP inlets can potentially mitigate odour nuisance due to hydrogen sulphide emission and reduce oxygen demand during further treatment in the plant.

MATERIALS AND METHODS

Materials

1,000 mg of ACS reagent grade Iron (III) chloride hexahydrate (Sigma-Aldrich, Assay 97%, CAS No. 10025-77-1), molecular weight 270.30, was dissolved in 1,000 ml of deionized water (Milli-Q) to make the stock ferric chloride solution. Different concentrations of ferric chloride were prepared by further dilution of aliquots. Deionized water from Milli-Q was used throughout.

Methods

Sulphide concentration measurement at WWTP inlets

Samples of influent wastewater at WWTPs in Delhi were withdrawn and the sulphide concentrations determined by the iodometric method (APHA 1999). Influent wastewater samples were collected from the WWTPs at Kondli (phases II and IV), Chilla, Coronation Pillar (phases I, II and III),

Yamuna Vihar (phases I, II and III), Okhla (phases I, II and III), Keshopur (phases I and II), Najaf-garh, Nilothi (phases I and II), Pappankalan (phases I and II), Rithala (phase I and II) and Rohini.

Jar tests

Experiments were carried out in a jar test apparatus (Model 1924, Electronics India Pvt Ltd) with a speed range of 25–200 rpm. Raw sewage from Najafgarh drain was used – see Table 2 for its physico-chemical characteristics. The raw sewage samples were dosed with between 5 and 50 mg/L of ferric chloride, and stirred for 30 minutes at room temperature. The concentrations of sulphide, ammonia, phosphate, TSS (total suspended solids), BOD (biological oxygen demand) and COD (chemical oxygen demand) were measured following the APHA protocol (APHA 1999). The percentage removal of pollutants was calculated using Equation (1):

$$\%removal = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final concentration of the pollutant respectively. All experiments were performed in triplicate to check reproducibility, and average values are used in the tables.

RESULTS AND DISCUSSION

Generation and emission of hydrogen sulphide in WWTPs

The generation and emission of hydrogen sulphide in WWTPs depend on the wastewater's physical, chemical and biological constituents (Park *et al.* 2014). In addition to the problem of corrosion, hydrogen sulphide is a serious health and environmental hazard with high concentrations being fatal (Hvitved-Jacobsen *et al.* 2002; Nielsen *et al.* 2008). H_2S emission is related to the wastewater's free sulphide concentration (Al-Shammiri 2004). Typically, total sulphide concentrations in waste-water are between 0.1 and 10 mg/L (Henze & Comeau 2008), while sulphate ranges between 20 and 50 mg/L (Metcalf & Eddy 2003). Anaerobic regions in WWTPs, etc, facilitate the generation and emission of H_2S with the help of sulphate-reducing bacteria (SRBs). Maintaining the pH above the neutral range (the optimum pH for SRB growth is between 6 and 8) (Lopes 2007; Ayangbenro *et al.* 2018) and dissolved oxygen levels above 1 mg/L, can inhibit SRB growth and reduce foul odours at WWTPs.

Odour emission from WWTPs in Delhi

A study undertaken at 11 WWTPs in Delhi, all of which used the activated sludge process, showed that most had odour nuisance problems due to H_2S emission. A few plants also reported equipment corrosion thought to be due to high sulphide levels. Influent sulphide levels were measured (June 2020) in the WWTP inlets, therefore, and the results are shown in Table 1. The sulphide levels varied between 1.1 and 14.8 mg/L. Total sulphide concentrations can vary through the year depend-ing on both the influent wastewater's characteristics and external factors like temperature. Studies at the Ardiyah WWTP, Kuwait, which reported odour emissions, with measured annual median total sulphide levels in the raw influent of about 10 mg/L (Al-Shammiri 2004), consistent with the results obtained for this study.

Table 1 | Influent sulphide in selected Delhi WWTPs

WWTP	Sulphide concentration (mg/L)
Kondli Phase II	5.81 ± 0.37
Kondli Phase IV	5.19 ± 0.09
Chilla	4.81 ± 0.21
Coronation Pillar Phase I	11.45 ± 0.23
Coronation Pillar Phase II	14.8 ± 0.33
Coronation Pillar Phase III	9.4 ± 0.09
Yamuna Vihar Phase I	1.99 ± 0.22
Yamuna Vihar Phase II	1.99 ± 0.14
Yamuna Vihar Phase III	3.25 ± 0.41
Okhla Phase I	1.6 ± 0.23
Okhla Phase II	1.33 ± 0.13
Okhla Phase III	1.33 ± 0.13
Keshopur Phase I	4.2 ± 0.18
Keshopur Phase II	4.8 ± 0.23
Najafgarh	4.4 ± 0.11
Nilothi Phase I	2.9 ± 0.18
Nilothi Phase II	3.2 ± 0.19
Pappankalan Phase I	6.0 ± 0.13
Pappankalan Phase II	7.2 ± 0.26
Rithala Phase I	1.1 ± 0.21
Rithala Phase II	1.1 ± 0.08
Rohini	1.5 ± 0.03

Use of Iron (III) chloride for odour control

If the influent wastewater sulphide can be precipitated at the WWTP inlet by pre-treatment, further wastewater treatment will be eased, H_2S emission during treatment reduced, and, potentially, treatment costs reduced if the installation of odour control equipment is not needed. Previous studies have shown the ability of soluble sulphides to react with Fe salts and precipitate as insoluble iron sulphide (Grady *et al.* 1999), and the use of Fe salts to minimize sulphide generation in gravity sewers was studied by Cao *et al.* (2019). The latter used Fe salt concentrations in the range 30–60 mg/L, with different dosing frequencies, in their study and found that the microbial diversity and SRB function in the sewer were altered.

Jar tests on wastewater

Jar tests were carried out using raw wastewater from the Najafgarh drain, one of the major drains discharging into the River Yamuna. The sulphide concentration of the wastewater was 3.61 mg/L, and its TSS and BOD concentrations were 105 and 74 mg/L respectively (Table 2). Initial studies were carried out with 5, 10 and 15 mg/L FeCl₃ doses. While 25% of the phosphate – from 2 mg/L – was removed at all dosing concentrations, however, there was no significant removal of TSS, sulphide or BOD. Because of this, the dosing concentration was increased and 20, 30, 40 and 50 mg/L concentrations were used and determined.

Table 2 shows that increasing the ferric chloride concentration produces an increase in the proportional removal of sulphide – e.g. from 64 to 76% as the dosing concentration was raised from

Table 2 | Effect of FeCl₃ concentration on sulphide removal

Parameter	Reporting units	Raw sewage	Concentration of Ferric chloride (mg/L)			
			20 % removal	30	40	50
pH	–	7.65 ± 0.05	7.30 ± 0.15	7.17 ± 0.12	7.10 ± 0.11	7.11
Ammoniacal-nitrogen	mg-NH₃/L	30	0	0	0	25
Phosphate	mg-PO₄/L	3.25 ± 0.62	40	41.11	52.22	50
Sulphide	mg-S/L	3.61 ± 0.87	64	74	76	76
TSS	mg/L	105 ± 11.7	33	53	62	70
BOD	mg/L	74 ± 11.3	44	46	52	52

20 to 50 mg/L respectively. The elimination of hydrogen sulphide from sewer systems using iron salts depends on the precipitation of the sulphide present, thus lowering the soluble sulphide concentration (Park *et al.* 2014). The presence of FeCl₃ has also been shown to inhibit SRB activity significantly in anaerobic zones (Zhang *et al.* 2009) and so reduce hydrogen sulphide emissions.

FeCl₃ dosing had almost no effect on removing ammoniacal nitrogen removal until 40 mg-FeCl₃/L was achieved. A further increase to 50 mg-FeCl₃/L removed 25% of the raw wastewater's ammonia. Increases in the ferric chloride dose led to increased TSS removal, nearly 70% TSS removal being observed at 50 mg-FeCl₃/L and natural pH. Other studies have shown that ferric chloride is most effective as a coagulant between pH 4 and 12, with maximum TSS removal at pH 4.9 (Reynolds & Richards 1996; Amokrane *et al.* 1997; Selcuk 2005; Aziz *et al.* 2007). Sarparastzadeh *et al.* (2007) showed a 48% reduction in TSS levels when raw wastewater was treated with an optimum ferric chloride dose of 70 mg/L. COD concentrations were determined and ~35% removal was observed at 40 mg-FeCl₃/L dosing. Precipitation of soluble organic species with ferric chloride can be attributed as a factor in COD removal (Tebbutt 1998).

Increases in ferric chloride dosing also led to increased phosphorus removal from the wastewater. Proportional removal increased from 40 to 52% as dosing increased from 20 to 40 mg-FeCl₃/L. Park *et al.* (2014) reported precipitated phosphorus using iron salts. Iron salt addition to wastewater causes sulphide to precipitate as iron sulphide and the larger aggregates settle in the primary settling tank. Gutierrez *et al.* (2010) indicate the need for ferric chloride dosing at locations close to WWTPs to maximize phosphate precipitation in the aeration tanks. Similar trends were observed in BOD removal and are consistent with reports by Mostafa & Peters (2016) indicating a gradual improvement in BOD removal with increased ferric chloride dosing. The lowering of BOD concentrations may be due to the corresponding precipitation of phosphorus together with the coagulation-flocculation of suspended particles. The dosing concentration and frequency required depend on the wastewater's characteristics as the proteinaceous components of the organic matter affect iron species precipitation from wastewater (Kiilerich *et al.* 2017).

Cost-benefit considerations

The jar test results indicate that a dosing concentration of 40 mg-FeCl₃/L can remove 76% of sulphide in addition to significant reductions in BOD and TSS levels. The main objective of this study was to remove sulphide from wastewater to reduce WWTP odour emission arising from hydrogen sulphide. Lowering of BOD in TSS concentrations would potentially simplify downstream aeration requirements during treatment as well as being cost-effective for odour control. Use of 30 mg-FeCl₃/L removes around 74% of influent sulphide and a 25% increase in dosing rate from 30 to 40 mg/L yields a 25% operating cost (chemical purchases) increase but only 2–3% sulphide removal

improvement. Assuming that 40 mg-FeCl$_3$/L were used at a 10 MLD WWTP, 0.4 tonne/day of ferric chloride would be required at a cost of 10,000 INR/day (about USD 140/day). Dosing at 30 mg/L would lead to a saving, against 40 mg/L, of around 2,500 INR/day and can be taken into consideration as it can reduce the number of haulage journeys, materials handling required and so on. The long-term environmental impact must also be included when considering cost and benefits. Ferric chloride addition as a pre-treatment step is highly efficient in reducing odour and has low environmental impact. It can also improve the health of workers and local residents significantly.

SUMMARY AND CONCLUSIONS

1. Foul odours from WWTPs arise mainly from hydrogen sulphide emissions. Many WWTPs use odour masking agents or covers to deal with the issue.
2. Since hydrogen sulphide emissions relate directly to the presence of sulphide in wastewater, the feasibility of using ferric chloride to lower the wastewater sulphide concentration was studied.
3. Influent sulphide concentrations at 11 WWTPs in Delhi were measured and jar test studies performed on raw wastewaters. The results indicated that dosing 40 mg-FeCl$_3$/L led to significant proportional removal of sulphide, in addition to removal of TSS, BOD, phosphate and COD.
4. Ferric chloride dosing as a pre-treatment step at WWTP inlets can lower sulphide and other contaminant concentrations substantially, reducing downstream aeration requirements in treatment while providing cost-effective odour control.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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