

FERRIC CHLORIDE (FeCl_3) AS REGULATORY AGENT FOR THE REDUCTION OF HYDROGEN SULFIDE (H_2S) IN MUNICIPAL WASTEWATER

S. Aslanidou¹, N. Lydakis-Simantiris¹, C. Kotsifaki², D. Pentari³ and E. Katsivela^{1*}

¹ Laboratory of Environmental Chemistry and Biochemical Processes, Technological Educational Institute of Crete, Romanou 3, Halepa, 73133 Chania, Crete, Greece

² Municipal Enterprise for Water and Sewage of Chania (DEYACH), Crete, Greece

³ Department of Mineral Resources Engineering, Technical University of Crete, Polytechnioupolis, 73100 Chania, Greece

*Corresponding author: katsivela@chania.teicrete.gr

ABSTRACT

In the present study, the use of trivalent iron (Fe^{3+}), added as ferric chloride (FeCl_3), in untreated wastewater was investigated for the reduction of hydrogen sulphide (H_2S) concentration. The area under study was the Municipal Enterprise for Water and Sewage of Chania (DEYACH) (Crete, Greece). FeCl_3 , at concentrations varied from 0.5 to 5,930 mg FeCl_3 per liter wastewater, was added into wastewater, which it was previously passed through the coarse and fine screens. Experimental data that simulated the procedure of grit/oil removal for 15 minutes and the primary sedimentation for 3.5 hours indicated that the reduction of the dissolved H_2S was achieved up to nearly 100 % when the concentration of the added FeCl_3 increased from 0 to 296.5 mg per L of wastewater. Thereby, the pH of the Fe^{3+} -treated wastewater at the concentration of 296.5 mg FeCl_3 / L reached values which varied between 4.7 and 6.5. Atomic absorption spectroscopy was used to determine the partition of the iron between the primary treated wastewater (supernatant) and the primary waste sludge (sludge). Our results show that after the FeCl_3 treatment, the majority of iron (85 %) remained in the supernatant, whereas only 15 % of it was found in the sludge.

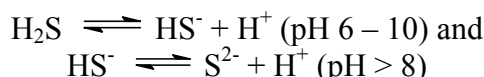
Keywords: wastewater, hydrogen sulfide, ferric chloride

1. INTRODUCTION

The removal of sulfur from wastewater is an important feature for every Municipal Wastewater Treatment Plant. This is due to its microbial conversion under anaerobic conditions to hydrogen sulfide (H_2S) which, at low concentrations is odorous and at relatively high concentrations toxic. In addition, H_2S is converted under aerobic microbial conditions to the corrosive sulfuric acid (H_2SO_4).

H_2S is the most commonly known and prevalent odorous gas associated with domestic wastewater collection and treatment systems, besides ammonia, indoles, skatoles, mercaptanes and nitrogen-bearing organics. H_2S has a characteristic rotten egg odor in concentrations higher than 0.2 ppm and it is extremely toxic and lethal at concentrations higher than 300 ppm [1].

Molecular H_2S dissolves in water and participates in equilibria described by the equations:



Thus, it is apparent that the concentration of S^{2-} ions is low within the normal pH range of municipal wastewater (pH 6.0 to 8.0). The non ionized H_2S is released in great potential from the liquid wastewater as gas [2].

The extent and the rate of the release of gaseous hydrogen sulphide, which is produced mostly in sewages and untreated wastewaters from the anaerobic microbial fermentation of organic sulphide containing substances, is mainly controlled by i) concentrations of dissolved oxygen greater than 1 mg/L; ii) basic pH values higher than pH 8.0; iii) decrease of the wastewater temperature; iv) optimisation of velocity of wastewater and the depth of flow; v) formation of insoluble metallic sulfides after reaction with metals, such as iron, zinc, copper, lead and cadmium [2].

The aim of the present study was to find the ideal concentration of FeCl_3 that should be added into untreated wastewater, which it was previously passed through the coarse and fine screens, for the reduction of H_2S through formation of ferric and ferrous sulfides (Fe_2S_3 , FeS).

2. MATERIALS AND METHODS

2.1 Sampling and experimental setup

The area under study was the Municipal Enterprise for Water and Sewage of Chania (DEYACH) (Crete, Greece). Experiments were performed from May 2006 until April 2007 using 1 L wastewater for each experiment, after it was passed through the coarse and fine screens, for every batch. The experimental setup simulated i) the procedure of grit/oil removal by stirring the untreated (controls) as well as the treated samples with FeCl_3 wastewater for 15 minutes at room temperature, 22-24°C, and ii) the primary sedimentation by precipitation of the sludge for 3.5 hours. For this purpose, the commercially available reagent “Ferrisol Cl 140” (Ferri Tri Company, Thessaloniki, Greece), with a concentration of FeCl_3 41% (w/v) and a density of 1.445 g/cm³ was used. Samples treated as mentioned above, without any addition of FeCl_3 , were used as controls. For FeCl_3 -treated samples, fourteen final concentrations of FeCl_3 from 0.5 to 5,930 mg/L were examined with different batches of wastewater. All the experimental conditions were repeated at least twice (2 to 16 times).

The daily mean inflow of wastewater during the investigation period varied from 16,850 until 18,890 m³/d, whereas during the summer 2006 the wastewater was pretreated by addition of 1 t/d of $\text{Ca}(\text{NO}_3)_2$ (reagent Nitrasbestol 50, Ferri Tri Company, Thessaloniki, Greece).

2.2 Determination of sulfide ions

Wastewater samples at 0h, after 15 min of stirring, and finally after 3h and 30 min sedimentation after stirring were centrifuged for 10 minutes at 3,000 rpm before the determination of sulfide. Samples without any addition of FeCl_3 were used as controls. Dissolved sulfide ions were determined photometrically at 665 nm using the methylene blue method (photometer Hach, DR 2000), after addition of the reagents Sulfide 1 and 2 (Company Hach) [3]. Samples containing distilled water and appropriate concentration of FeCl_3 after addition of the reagents Bromine Water and Phenol Solution (Company Hach) were used as blanks. According to Hach photometer instructions, the used method No 8131 is very sensitive, with detection limits in the order of ppb and very small inherent error.

2.3 Determination of iron by Atomic Adsorption Spectroscopy (AAS)

100 mL of supernatant as well as 6 mL of sludge (as they were measured by the volumetric climax of falcon tubes), originated from the centrifugation of five different batches of wastewater samples treated with 296.5 mg FeCl_3 / L were digested with 2 mL of concentrated HNO_3 (65%, Riedel de Haen, Germany) and 5 mL concentrated HCl (37% w/v, suprapur grade, Merck, Germany) at 100° C, on a heating plate, until nearly complete evaporation. This procedure was repeated for two times more. The final concentrates were dissolved in 1 mL of concentrated HCl and 5 mL of ultra pure water (Millipore), in which 5 drops of concentrated HNO_3 were added. The samples were filtered using Whatman 42 filter before analysis in AAS. The concentrations of iron were determined by atomic absorption spectroscopy (Perkin Elmer AAnalyst 100) using acetylene-air flame. The detection wavelength was 248.3 nm for Fe. Calibration curves for all the determinations were constructed using freshly prepared standards (Merck, Germany). Solutions prepared as mentioned above, without any addition of FeCl_3 were used as controls. Experiments were repeated five times using different batches of wastewater.

3. RESULTS AND DISCUSSION

3.1. Determination of the proper FeCl_3 concentration for maximum H_2S removal

Concentrations of FeCl_3 varied from 0.5 to 5,930 mg FeCl_3 per liter wastewater were examined in order to determine the proper concentration of FeCl_3 which results the highest reduction of dissolved H_2S . The concentrations 0.5 to 5,930 mg FeCl_3 per liter wastewater correspond to added volumes varied from 10 μL to 10 mL of the commercially available reagent “Ferrisol Cl 140” per liter wastewater. In the reducing conditions of the wastewater, a significant amount of ferric ions (Fe^{3+}) is expected to be reduced to ferrous (Fe^{2+}) ions.

The initial concentrations of dissolved sulfides in the wastewater during the whole study period were relatively low and varied from 0.1 to 0.66 mg/L.

The experimental data obtained from the sample treatments which simulated the procedure of grit/oil removal for 15 minutes as well as the following primary sedimentation for 3.5 hours indicated that a reduction of the dissolved H_2S concentration was achieved up to nearly 100 % when the concentration of FeCl_3 increased from 0 to 296.5 mg / L wastewater. Thereby, the pH of the Fe^{3+} -treated wastewater at the concentration of 296.5 mg FeCl_3 / L (0.5 mL reagent “Ferrisol Cl 140”/L) reached values which varied between 4.7 and 6.5.

Figure 1 shows that at FeCl_3 concentrations higher than 296.5 mg / L wastewater, the decrease of the dissolved H_2S concentration in the wastewater was lower. The increase of FeCl_3 concentrations is followed by decrease of pH at values lower than 3. Most likely at these pH values ferrous and ferric ions participate in different equilibria in the complex matrix of wastewater, and as a result, the concentration of the dissolved H_2S increases. The dissolved

H_2S participates also in the equilibrium $\text{H}_2\text{S}_{(l)} \rightleftharpoons \text{H}_2\text{S}_{(g)}$ which is pH dependent as well [3, 4].

Figure 1 shows the mean reduction of dissolved sulfides after addition of FeCl_3 in the range of 0 to 3,000 mg / L at different batches of wastewater.

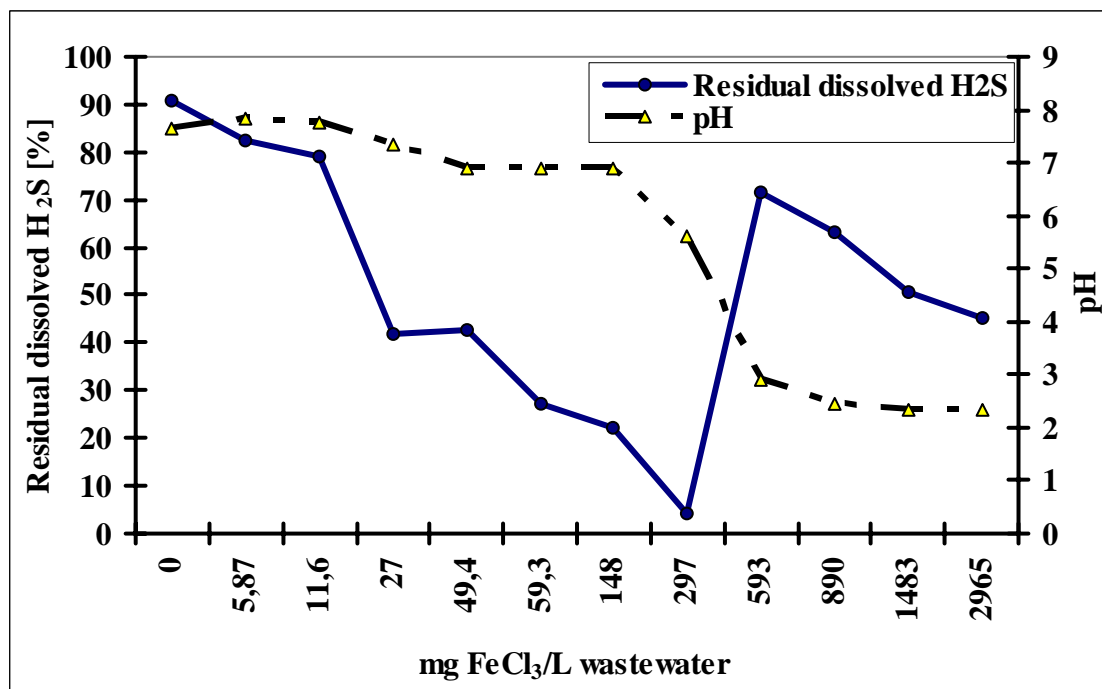


Figure 1: Residual dissolved H_2S in the wastewater versus added FeCl_3 concentration and corresponding pH values.

3.2. Partition of iron in the supernatant (primary treated wastewater) and in the sludge (primary waste sludge) of treated wastewater

Figure 2 shows the partition of iron in the supernatant (primary treated wastewater) and in the sludge (primary waste sludge) in wastewater samples treated with 296.5 mg FeCl_3 / L wastewater from five batch experiments, performed on 16/11/06, 20/11/06, 22/11/06, 17/04/07 and 18/04/07.

The initial concentration of iron in untreated wastewater varied in the sludge and supernatant from 0.05 to 0.24 mg/L and 0.24 to 1.89 mg/L, respectively, whereas the final concentration of iron in the sludge and supernatant of the treated with 296.5 mg FeCl_3 / L wastewater varied from 0.72 to 21.6 mg/L and 67.6 to 84 mg/L, respectively (Figure 2).

As shown in five different batch experiments, a mean partition of iron at values close to 85 % in the supernatant (primary treated wastewater) was observed in comparison to 15 % partition in the sludge (primary waste sludge). Thus, the majority of iron remains diluted in supernatant and flows to the secondary aerobic biological treatment of wastewater.

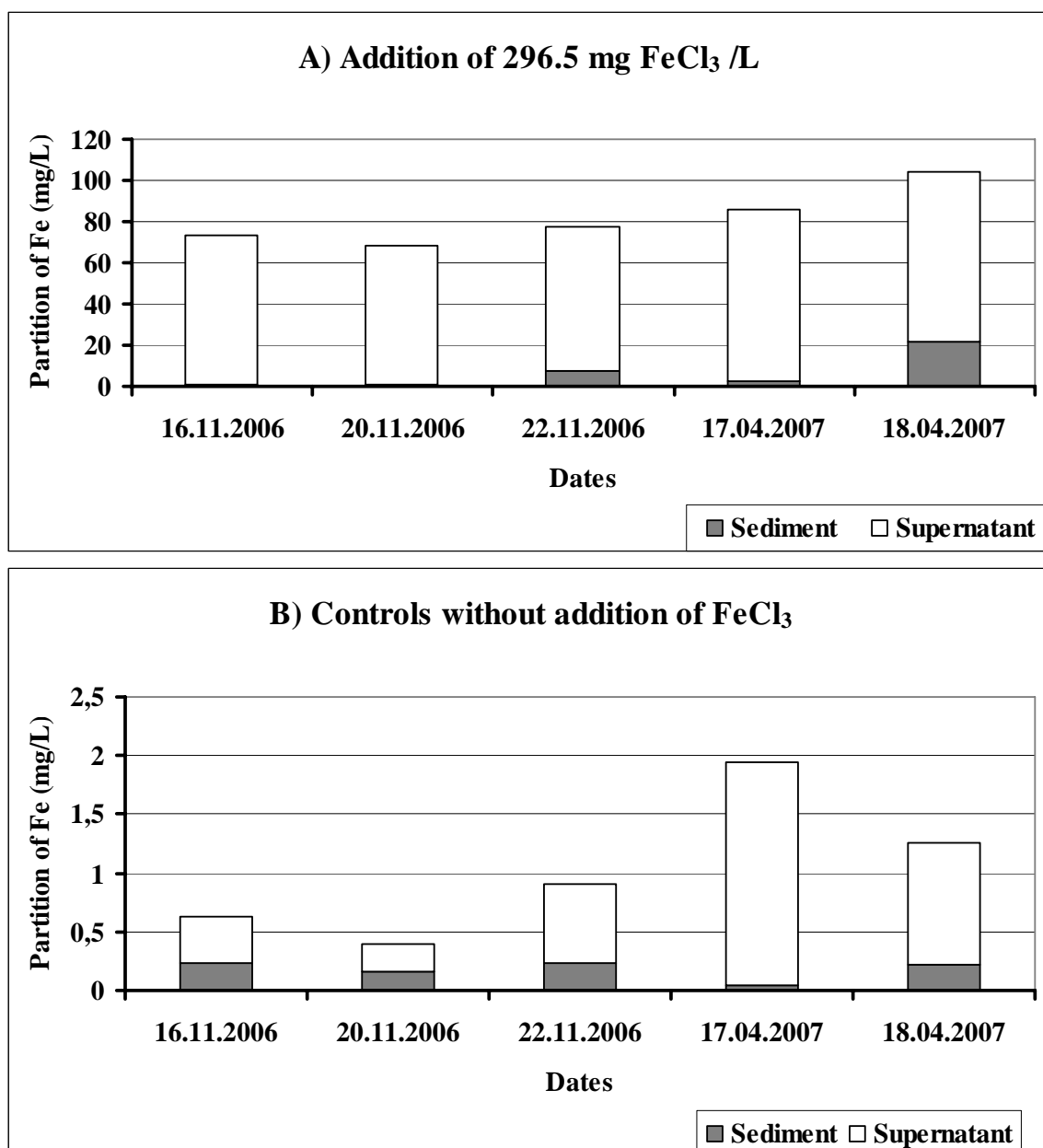


Figure 2: Partition of iron as mg/L wastewater in the supernatant (primary treated wastewater) and in the sludge (primary waste sludge) A) after addition of 296.5 mg FeCl₃/L of wastewater, and B) without any treatment of wastewater (control).

4. CONCLUSIONS

A reduction of dissolved sulfides (concentrations between 0.1 and 0.66 mg/L) was achieved up to nearly 100 % by addition of 296.5 mg FeCl₃ / L of crude wastewater. Thereby, the pH of the Fe³⁺-treated wastewater reached values which varied between 4.7 and 6.5. The majority of iron remains diluted in supernatant and flows to the secondary aerobic biological treatment of wastewater.

The used dose of 296.5 mg FeCl₃ / L of crude wastewater was not stoichiometrically related to the amount of sulfides present in the wastewater. This is totally expected, as ferrous and ferric ions should participate in several equilibria with the complex matrix of wastewater along with their interaction with sulfides.

Acknowledgements

Authors want to thank the chemist P. Maraka, the food engineer G. Pitsoulakis, and Mr. P. Bolioudakis at the Municipal Wastewater Treatment Plant of Chania for their kindly help.

REFERENCES

1. Tsobanoglous G., F. L. Burton, H. D. Stensel (2006) **“Wastewater Engineering”**, Tziolas Press, Thessaloniki, Greece.
2. Bowker, R.P.G., J.M. Smith and N.A. Webster (1985) **"Design Manual, Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants"**, EPA 625/1-85/018, October, 1985. Center for Environmental Research Information, U.S. EPA, Office of Research and Development, Cincinnati, OH 45268.
3. American Public Health Association, American Water Works Association, Water Environment Federation, (1998) **“Standard Methods for Examination of Water and Wastewater”** 20th Edition, American Public Health Association, New York, USA.
4. Dezhnam P, E. Rosenblum and D. Jenkins (1988) “Digester gas H₂S control using iron salts”, **Journal of Water Pollution Control**, Vol. 60, pp. 514-517.