ANALYSIS OF FLOWRATE, SULFATE, AND TOTAL SULFUR PATTERN IN WASTEWATER INLET TANKS FOR H₂S MANAGEMENT

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Hydrogen sulfide (H₂S) is a major source of concrete corrosion in a wastewater treatment plant (WWTP) that causes significant financial losses. Variations in the flow rate and composition of incoming wastewater have significant impact on H₂S generation. During anaerobic conditions, sulfur present in excreta and sulfate from rainfall become the source of electron acceptors for the conversion of sulfate to sulfide in wastewater. Sulfide, in turn, is converted to H₂S and later to sulfuric acid which leads to concrete corrosion. Flowrate directly relates to the amount of wastewater entering the plant. Hence understanding flow rate pattern will help to analyze H₂S generation. Flow rate and H₂S concentrations were recorded every two-hours for four days in a wastewater treatment plant. Wastewater samples of 50ml were collected at each sampling event coinciding the recording intervals. Samples were analyzed for sulphate and sulfide concentrations using HACH® kits. Total sulfur was calculated from the collected data. The correlations were analyzed using Minitab®. It was found out that average flow rate was negatively related to average H₂S concentration. H₂S concentration is higher during night when the flow rate is lower, which is a result of greater resident time. Flowrate changes in a cyclic manner throughout the day. During night, sulfate and total sulfur concentrations are higher, H₂S concentration is maximum during this time. It is contrariwise during the day. Sulfate and total sulfide follow a pattern that is similar to that of flowrate. Analyzing these parameters is a critical step in successfully modelling H₂S generation.

Keywords: Hydrogen sulfide, Concrete corrosion, Pattern, Odor control, Toxicity.

1 INTRODUCTION

Hydrogen sulfide (H₂S) is a colorless, toxic gas, which is a source of nuisance, lethal odor (Wu et al. 2013). It is associated with the generation of corrosive sulfuric acid in wastewater treatment applications (USEPA 1991). H₂S is formed during anaerobic degradation of organic substrates (Davis et al. 1998). When dissolved oxygen and nitrates in wastewater get depleted, the sewage becomes septic (Boon and Vincent 2003). Sulfur reducing bacteria (SRB) utilizes sulfate from wastewater and convert them to either bisulfite or H₂S. Since wastewater is generally acidic, H₂S formation is favored (Talaiekhozani et al. 2016). H₂S has low solubility in water, and hence quickly gets converted to gas phase (Cwalina 2008). This H₂S gas is adsorbed on the slime layer at the wet surface of concrete tank. Here H₂S is oxidized to sulfuric acid (H₂SO₄) by sulfur oxidizing bacteria (SOB) (De Belie et al. 2004). H₂SO₄ reacts with concrete forming gypsum and
ettringite. These further accelerate the deterioration of concrete (Yongsiri et al. 2004a). Corrosion of concrete is affected by multiple material and environmental factors. The rate of sulfide formation is relatively independent of the sulfate concentration when there is a surplus amount of sulfate in wastewater (Coatings 1967). If sulfate is limited, sulfide production will be proportional to sulfate concentration. However, sulfate concentrations more than 5-15 gS/m3 would not be a sulfide formation limiting factor (Hvitved-Jacobsen et al. 1998; Jensen et al. 2011). The mass transfer restriction at the air-water interface is principally regulated by concentration gradients inside the water film. As a result, the process is predominantly influenced by the hydrodynamics of the wastewater flow. As a consequence of the greater advection velocities, H2S emitted at a point of high turbulence will reach further downstream (Nielsen et al. 2012). This will cause corrosion to a larger area of the downstream pipe, but at a lower H2S surface loading. Higher turbulence can rapidly transport H2S(aq) to the interface and thus accelerate the transfer of H2S(aq) to the gas phase (Liss and Slater 1974). Increased turbulence can result in a larger interfacial area, which increases the chances of H2S(aq) molecules being transferred. The relative transfer rate distribution is affected as turbulence modifies the interfacial thickness, rather than the dissociation of hydrogen sulfide (Yongsiri et al. 2004b). Sulfur-containing compounds contribute to H2S generation by acting as electron acceptors (Boon and Vincent 2003), making them an essential contributor in H2S production in wastewater systems. It is essential to study the influence of these parameters on H2S generation to evaluate and control corrosion of concrete.

2 MATERIALS AND METHODS

2.1 Description of Study Area

The data was collected from sewage collection unit before the screening unit at Al Saad Wastewater treatment plant. Sewage coming from neighboring areas and collection tankers are treated in the plant. The height of wastewater in the tank varied while the width of the tank was six meters. The air flow was observed to be zero at the headspace of the tank. The average pH, dissolved oxygen (DO), and temperature of the wastewater was measured to be 7.07, 0.47 ppm, and 32.5°C, respectively. The average chemical oxygen demand (COD) of wastewater measured was 279.2 ppm.

2.2 Experimental Procedures

The sampling events were conducted twice, once on the 8th, 9th, and 10th of October 2020 and again on the 16th, 17th, and 18th of June 2021 at comparable climatic conditions. A data collection unit consisting of Acrulog® H2S analyzer was installed at the headworks of the collecting unit. The H2S analyzer records H2S gas concentration every ten seconds. Acrustat software was used to retrieve the data in CSV format. It was then converted to excel worksheet for analysis. The variations in flowrate values and wastewater temperature were collected from SCADA unit of the wastewater treatment plant. The data was collected every two-hours for 48 hours. The sampling started from 12:00 noon and ended at 12:00 noon, completing 48 hours.

2.3 Laboratory Analysis

50 ml of wastewater samples were collected during each sampling event. The time of collection was coincided with the H2S gas emission recordings. Fluoropolymer containers were used for sample collection and the samples were refrigerated after collection. The pH of wastewater was measured using EXTECH® pH probe and DO was measured using EXTECH® DO probe. COD,
sulfate, sulfide was analyzed using HACH kit (LCK514, LCK353, 2244500) and measured using HACH DR 3900 spectrophotometer. Total sulfur was calculated using the values of H₂S concentration, sulfide, and sulfate.

2.4 Parameter Analysis

The data collected from wastewater treatment plant and laboratory was analyzed using Minitab™. The data was entered to Excel worksheet and extracted to Minitab™. Correlation and patterns were identified using graphs. Scatterplot graphs were used for this purpose. Various correlations relating H₂S concentration and parameters were explored with respect to time. Distinguished patterns were manually identified.

3 RESULTS AND DESCRIPTION

3.1 Flowrate Pattern

Wastewater flowrate causes turbulence in the wastewater stream and increases or reduces re-aeration with high or low flow respectively. It also determines the amount of sulfate entering the system (Nielsen and Hvitved-Jacobsen 1988). It was observed that the flowrate changes cyclically throughout the day (Figure 1). This pattern also is repeating in the second sampling event. The first sampling event has a longer cyclic pattern. The range of flowrate is broader than the second sampling event. However, in terms of H₂S concentration, the range is broader in the second sample. Both the cycles have 8:00 PM on one end and 8:00 AM on the other, depicting the beginning and end of the cycle. The highest point of the first and second cycles are at 2:00 AM where the H₂S concentrations are 252 ppm and 236 ppm respectively. The lowest point is different for both samples. Flowrate during the daytime of the first sample is higher, resulting in an elevated cycle.

![Figure 1. Scatterplot of average H2S concentration and average flowrate (D1 and N1 are day and night for the first sample. D2 and N2 are day and night for the second sample respectively).](image-url)
3.2 Sulfate Pattern

When there is an increase in sulfate concentration, \( \text{H}_2\text{S} \) emission also increases, as sulfate is considered as the substrate in \( \text{H}_2\text{S} \) generation (Hvitved-Jacobsen 2001). It was observed that the variation in sulfate concentration with \( \text{H}_2\text{S} \) has a cyclic pattern as depicted in Figure 2. The scatter plot with regression lines showing sulfate in mg/L on the x-axis against \( \text{H}_2\text{S} \) concentrations in ppm in increments of 25 on the y-axis. The sulfate concentration is lower during the day (D1, D2) and higher during the night (N1, N2) for both sampling events. This pattern is noticed in the first second sampling event. The second sampling event has a longer cyclic pattern as the range of sulfate concentration is broader than in the first sampling event. Even in terms of \( \text{H}_2\text{S} \) concentration, the range is broader in the second sample. Both the cycles have 6:00 PM on one end and 10:00 AM on the other, depicting the beginning and end of a cycle. The lowest point of the first and second cycles are at 6:00 PM where the \( \text{H}_2\text{S} \) concentrations are 77 ppm and 15 ppm respectively. The highest point is different for both samples.

![Figure 2. Scatterplot of average H2S concentration and average sulfate (D1 and N1 are day and night for the first sample. D2 and N2 are day and night for the second sample respectively).](image)

3.3 Total Sulfur Pattern

Total sulfide is the sum of all sulfur-containing compounds present in both air and water combined. It was assumed that \( \text{H}_2\text{S} \) from headspace and sulfide and sulfate from wastewater represent the majority of sulfur-containing compounds at a particular time. It was observed that variation in total sulfur concentration in wastewater has a cyclic pattern as illustrated in Figure 3. The scatter plot shows total sulfur concentration in mg/L on the x-axis against time in hours in increments of 50 on the y-axis. The total sulfur concentration is lower during the day (D1, D2) and higher during the night (N1, N2) for both sampling events. This pattern also is observed in the first and second sampling event. The first sampling event has a longer cyclic pattern. The range of total sulfur is broader in the first sampling event. Resulting in a slightly erect cyclic pattern for the second sampling event. The highest point of the first and second cycles are at 6:00 AM where the total sulfur concentrations are 215 mg/L and 306 mg/L respectively. The lowest point is different for both samples. This cyclic pattern is very similar to the pattern of flowrate and sulfate.
4. CONCLUSION

H$_2$S is a toxic gas that is naturally formed from sulfur decomposition. The fluctuations of wastewater parameters throughout the sampling events are discussed. In this study, three parameters were studied, which includes flowrate, sulfate, and total sulfur. Flowrate increases during the day and reduces during night. It is negatively correlated with H$_2$S concentration. Sulfate and total sulfur concentrations fluctuates with H$_2$S concentration. It was observed that these parameters have a cyclic pattern with H$_2$S concentration measured in the headspace. These patterns can be used to predict the H$_2$S concentration at a particular point of time in a day. Prediction of H$_2$S emission can help in reducing the cost associated with H$_2$S management at a wastewater treatment plant.

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