



Removal of H₂S and COD Using UV, Ferrate and UV/Ferrate from Municipal Wastewater

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ABSTRACT

Background: The aim of this study is to compare UV, ferrate (VI) and UV/ferrate (VI) methods for removal of hydrogen sulfide and chemical oxygen demand (COD) from municipal wastewater under a continuous condition.

Methods: The experiment was divided into three parts: 1) pollutants removal by using ferrate (VI) alone; 2) pollutants removal using UV alone; 3) pollutants removal using a combination of UV/ferrate (VI). The electrolysis process was utilized to generate ferrate (VI).

Results: The results showed that UV had the highest pollutants removal, so that 89% and 85% of hydrogen sulfide and COD were removed from the wastewater, respectively. UV/ferrate (VI) ranked as the next most efficient method. This method removed 65% and 73% of hydrogen sulfide and COD, respectively from the wastewater.

Conclusion: Using ferrate (VI) alone had the lowest pollutant removal efficiency, with 41% and 48% of hydrogen sulfide and COD removal from wastewater, respectively. UV has a higher ability to remove hydrogen sulfide and COD from wastewater, compared with UV/ferrate (VI) and ferrate (VI) alone.

1. Introduction

Nowadays, water scarcity is a global problem. It has been reported that 1.2 billion people worldwide have no access to sanitary potable water (1, 2). Collection and treatment of wastewater is a suitable way to prepare water needed for agriculture and industry. Municipal wastewater contains several different organic compounds. Chemical oxygen demand (COD) is an indicator to show the amount of organic compounds in wastewater. Organic compounds can be utilized as carbon and energy sources for a wide range of microorganisms. Since aerobic microorganisms need oxygen during utilizing

organic compounds, dissolved oxygen in water contaminated with wastewater is rapidly reduced. In the absence of oxygen, anaerobic microorganisms are activated and the production of malodorous compounds such as hydrogen sulfide will start. Hydrogen sulfide production in wastewater collection and treatment systems leads to serious corrosion of these facilities and emission of malodors (3). This gas is produced under anaerobic conditions by sulfur-reducing bacteria (SRBs). Hydrogen sulfide is a dangerous gas for human health in concentrations of more

than 500 ppm. Therefore, controlling hydrogen sulfide production is extremely important (4).

Hydrogen sulfide is extremely corrosive to concrete pipes. Hydrogen sulfide is converted to sulfuric acid in the presence of aerobic bacteria such as *Thiobacillus thiooxidans*.

The produced sulfuric acid reacts with concrete. This reaction produces plaster (CaSO₄).

The plaster increases continually over time, instigating deterioration in the concrete. In addition to sulfuric acid production, a chemical compound named ettringite with the chemical formulation of Ca₆A₁₂(SO₄)₃(OH)₁₂.26H₂O is produced, which causes cracks and holes in concrete (3). This deterioration in the quality of the concrete increases the depth of sulfuric acid penetration. These conditions cause weakness in wastewater collection pipes, culminating in pipe destruction after a few years (5). This information shows that controlling hydrogen sulfide is not only vital to human health, but also essential for increasing the longevity of wastewater collection pipes.

The simplest method to remove hydrogen sulfide and COD from raw wastewater is aeration.

Hydrogen sulfide is oxidized to elemental sulfur (S) in the presence of oxygen (3). Elemental sulfur is not accessible for microorganisms due to its poor water solubility. Also, a part of wastewater COD is removed by a wide number of indigenous microorganisms presented in raw wastewater when enough oxygen is provided. Although both hydrogen sulfide and COD are removed by aeration, supplying enough amount of oxygen in wastewater collection pipes is not easy. Therefore, other methods to control hydrogen sulfide and COD in wastewater collection pipes such as using oxidants have been developed. Malodor and corrosion of hydrogen sulfide can be controlled by adding oxidants such as hydrogen peroxide, chlorine or potassium permanganate to wastewater (2).

Chlorine is one of the cheapest and strongest oxidants. Using chlorine to remove hydrogen sulfide from untreated wastewater generates

several carcinogenic compounds, including trihalomethanes. Therefore, there is a serious limitation for chlorine application and its derivatives such as sodium and potassium hypochlorite in raw wastewater. Ozone and chlorine dioxide are other strong oxidants that do not produce any by-products. However, both ozone and chlorine dioxide are extremely expensive (4). Ultraviolet (UV) is also used to disinfect and eliminate pollutants from wastewater. Different UV systems, including UV/O₃, UV/H₂O₂ and UV/ferric(III), have been developed to remove pesticides and other recalcitrant water pollutants (6). Recent studies have shown that the microorganisms can be reactivated after the disinfection of water by UV radiation (6, 7).

Therefore, more investigation is needed to use UV alone for wastewater treatment and disinfection. Biological processes are other effective methods to remove both H₂S and COD from wastewater.

Since water pollution is increasing worldwide and standards for releasing wastewater into the environment are upgraded annually, new compounds are needed to meet the new standards' demands. Compounds for chemical treatment of wastewater ideally must have following criteria: 1) must disinfect water; 2) must degrade organic and inorganic pollutants in water; 3) must not produce any harmful by-products and 4) must have the ability to remove heavy metals and particles from water (4). A novel method for disinfection and water pollutants oxidation uses ferrate (VI) (1).

Ferrate (VI) is a strong oxidant with high oxidation potential of 2.2eV under acidic conditions. In addition, ferrate (VI) converts to a strong coagulant, ferric (III), over time (8).

Therefore, ferrate (VI) can be widely used in various stages of water and wastewater treatment, such as disinfection, coagulation or pollutant oxidation (9, 10).

It is estimated that the cost of electrical energy for ferrate (VI) production by electrochemical method is \$144 for each gram of ferrate (VI).

Furthermore, \$8.7 and \$0.36 are needed for the removal of 1 g of hydrogen sulfide and COD, respectively using ferrate (VI) (11). Ferrate (VI) is able to remove a major part of hydrogen sulfide from wastewater and simultaneously kill SRBs, thereby preventing hydrogen sulfide production in further parts of the wastewater collection system (12, 13). Production of ferrate (VI) through electrolysis is simple, therefore, this method can be practically used for the control of odor emission and corrosion in wastewater collection systems.

Although many studies have been conducted on using ferrate (VI) for the removal of different pollutants from water in a batch system, there are no studies concerning its continuous use.

Therefore, the aim of this study is to evaluate three different methods to use ferrate (VI), UV and UV/ferrate (VI) for the removal of hydrogen sulfide and chemical oxygen demand of municipal wastewater.

2. Materials and Methods

2.1. The pilot study

Since in actual conditions, wastewater flow in sewer pipes or wastewater treatment plants is permanent and ongoing, the removal of hydrogen sulfide and COD from wastewater in a continuous condition was investigated in this study. First, a pilot study was prepared, as displayed in Figure 1.

Ferrate (VI) was produced in electrolysis tank containing 500 ml of 14 molar NaOH solution using two iron electrodes. The electrode was attached to an electrical supply system with the voltage of 9 V and the amperage of 6 ampere. The hydraulic retention time in electrolysis tank was equal to 30 min (14). Wastewater and ferrate (VI) solution flows were introduced into the oxidation tank at flow rates of 18 ml/min and 10 ml/min.

Eskandari (2016) reported that the optimum hydraulic retention time for the removal of hydrogen sulfide and COD is around 33 min (11).

Consequently, hydraulic retention time of the oxidation tank was adjusted on 33 min. The oxidation tank was equipped with a mixer that stirred the contents of the oxidation tank throughout the experiments. The oxidation tank was outfitted with a UV lamp at 8W power to investigate its effect on hydrogen sulfide and COD removal from wastewater in continuous conditions. The distance between the UV lamp and the surface of the wastewater entering into the oxidation tank was 15 mm.

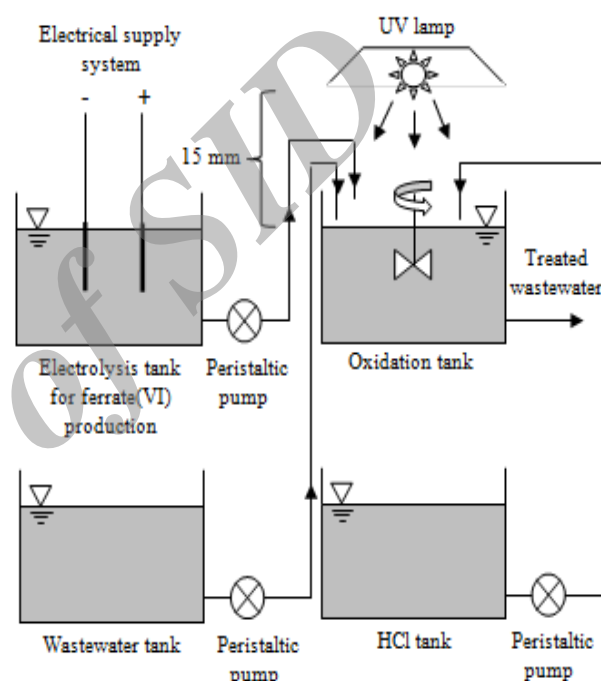


Fig.1: Schematic view of pilot scale oxidation tank used in this study.

2.2. Used wastewater

In this study, 40 L of raw wastewater was collected from the biological wastewater treatment plant of the city of Fooladshahr, in Isfahan Province, Iran. The wastewater COD, phosphorous, nitrogen and hydrogen sulfide concentration were 260, 4, 40 and 6.8 mg/l, respectively. The collected wastewater was relocated into a cool box with a temperature of 4°C, and then transferred to the research laboratory of Jami Institute of Technology, which has a campus in Fooladshahr. Concentration of hydrogen sulfide and COD in the wastewater was

immediately measured after filtration of wastewater in the laboratory.

2.3. Evaluation of hydrogen sulfide and COD removal

Figure 1 shows that the collected wastewater and ferrate (VI) solution with flow rates of 18 ml/min and 10 ml/min were simultaneously pumped into the oxidation tank via two peristaltic pumps. The pH of the oxidation tank was adjusted in 2 by adding a suitable amount of HCl. The content of the oxidation tank was continuously stirred by a rotary mixer to disperse ferrate (VI) throughout the tank. The mixture of wastewater and ferrate (VI) solution remained in the tank for 33 min before exiting the tank. The concentration of hydrogen sulfide and COD in the effluent of the oxidation tank was measured every 10 min. The experiment was continuous until steady state was achieved. In this study, steady state was recognized when the difference in the concentration of hydrogen sulfide and COD of the oxidation tank effluent in three consecutive tests was less than 5%. The experiment was repeated again without ferrate (VI) to show the role of evaporation in hydrogen sulfide and COD removal.

2.4. Analytical methods

In this study, hydrogen sulfide was measured by iodometric titration (15). In iodometric titration method sulfide was reacted with iodine in acidic condition. Then, the amount of remaining iodine was measured by titration with sodium thiosulfate in the presence of starch as an indicator. The end of the titration was indicated by changing solution color from blue to light-straw color. A blank is treated exactly the same as the samples. Next, Equation 1 was used for calculation of hydrogen sulfide.

$$H_2S \left(\frac{mg}{l} \right) = \frac{(A \times B) - (C \times D) \times 16000}{mL \text{ sample}} \quad (1)$$

Where A is used iodine in mL, B is normality of iodine solution, C is used sodium thiosulfate in mL, and D is normality of sodium thiosulfate.

COD was measured by standard methods for water and wastewater examination (10). The pH was also measured by a digital pH meter of AZ, made in China.

3. Results and Discussion

3.1. Ferrate (VI)

Figure 2 presents the results of the experiments for the removal of hydrogen sulfide and COD by ferrate (VI). During the experiments, the efficiency of the hydrogen sulfide and COD removal increased to 41% and 48%, respectively.

The removal efficiency of both compounds stabilized after approximately 110 min. Concentration of generated ferrate (VI) in the electrolysis tank was measured by iodometric methods (14) to as much as 0.16 mg/l. The flow ratio of ferrate (VI) to the wastewater was 0.55.

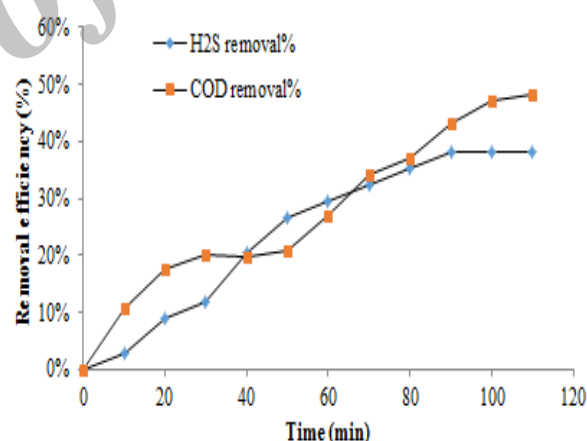


Fig.2: Hydrogen sulfide and COD removal by ferrate (VI) over time.

Application of ferrate (VI) can remove only 48% and 41% of hydrogen sulfide and COD from the wastewater, respectively. Eskandari (2016) reported that ferrate (VI) degrades over time, so that after 100 min nearly 86% of ferrate (VI) is removed from the solution. Equation 2 predicts the amount of ferrate (VI) degradation over time (11).

$$FC = -0.0019 t + 0.2269 \quad (2)$$

Where FC is concentration of ferrate (VI) in mg/L and t is time in min. Eskandari (2016) showed that high hydraulic retention time cannot help to improve ferrate (VI) removal in a batch system (14). The hydraulic retention time in this study was 33 min. Based on Equation 3, within 33 min only about 19% of ferrate (VI) was degraded and 79% of it remained for oxidation of hydrogen sulfide and COD. Since ferrate (VI) is a corrosive chemical, it can react with concrete which leads to concrete pipes destruction. Therefore, the effect of ferrate (VI) on concrete pipes must be investigated. Nowadays, concrete pipes are being replaced by polyethylene pipes. Therefore, in the near future, ferrate (VI) can be used for corrosion prevention and odor control without the fear of reaction between ferrate (VI) and obsolete concrete pipes.

Manoli et al., (2016) reported that ferrate (VI) can be activated by adding a few acids such as hydrochloric acid, nitric acid or acetic acid. They reported that activated ferrate (VI) increases the removal of caffeine, acesulfame potassium and atenolol within seconds to minutes (16), while without adding acid to the solution (un-activated Ferrate (VI)), the removal of the above mentioned chemicals occurred in minutes to hours under similar pH conditions. In the present study hydrogen sulfide and COD were removed from the wastewater by ferrate (VI) after adding HCl and reducing pH value to fewer than 2. Unlike the results of Manoli et al., (2016) and Feng et al., (2016) hydrogen sulfide and COD need longer removal time compared to caffeine, acesulfame potassium and atenolol (16, 17). An imaginable reason for the removal increase of organics may be the raised formation of reactive intermediate species including Fe (V) and Fe (IV), in the Ferrate (VI)-contaminant acid mixed solution.

3.2. UV

By the application of UV radiation alone, nearly 88% of COD and 85% of hydrogen sulfide were removed from wastewater in the continuous system shown in Figure 3. The hydraulic residence time of the oxidation tank, where the removal reactions occur, is 33 min. This continuous system

reaches steady-state after 100 min. Thus, all measurements on this continuous system were made at 110 min after the startup.

UV damages the microorganisms' DNA and kills them, which is the primary reason why UV is used as a disinfectant in water- treatment systems. UV alone was able to remove 89% and 85% of COD and hydrogen sulfide, respectively. Although several methods such as biological methods have been utilized for the removal of both hydrogen sulfide and COD (3, 18, 19), the use of UV is much simpler. UV light is powerful electromagnetic radiation with a wavelength of 10-380 nm. Although the wavelength of UV radiation is shorter than that of visible light, it is longer than X-ray radiation. UV is part of sunlight and also can be produced by mercury-vapor or tanning lamps. UV radiation triggers chemical reactions, and causes many substances to glow or emit fluorescence. Consequently, the biological effects of UV are greater than its simple heating effects, and many practical applications of UV radiation derive from its interactions with organic molecules (14).

Unlike ferrate (VI), UV has no negative effect on concrete pipes. Therefore, it can be applied to control hydrogen sulfide production in concrete wastewater collection pipes. UV can not only remove hydrogen sulfide from wastewater (12), but it can also prevent hydrogen sulfide production by killing the SRBs in wastewater. However, the limit of UV penetration in wastewater is a challenge to the practical uses of UV. Zupanc et al., (2013) reported that UV alone is not so efficient to remove the most pharmaceuticals (20), whereas combination of biological, hydrodynamic cavitation and UV processes removes 98% of these compounds. By contrast, our results show that UV radiation alone is an effective process to remove hydrogen sulfide and COD from the wastewater. It might be due to complication of pharmaceuticals molecules compared with hydrogen sulfide and other organic contaminants of municipal wastewater.

3.3. UV/Ferrate (VI)

The results of UV/ferrate (VI) application to remove hydrogen sulfide and COD demonstrate that pollutant removal was improved by using this combination, compared with using ferrate (VI) alone (Figure 4).

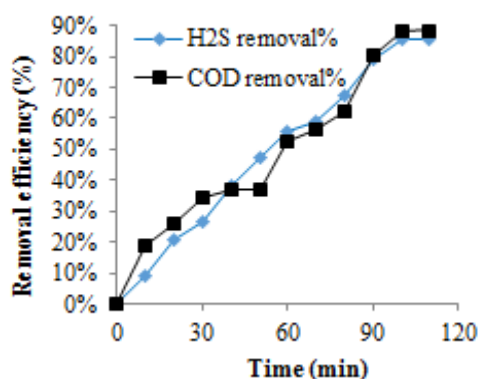


Fig.3: Hydrogen sulfide and COD removal by UV radiation.

It should be noted that the removal of both hydrogen sulfide and COD was lower with this combined treatment, compared with using UV alone.

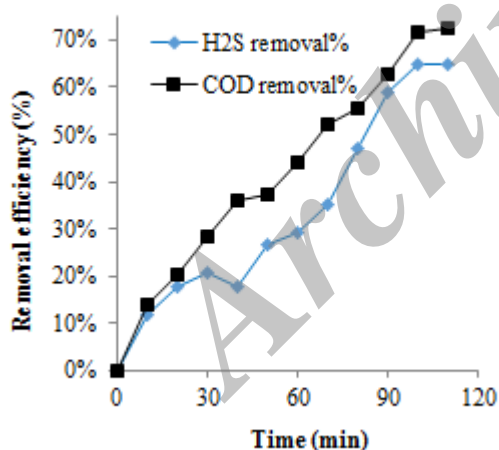


Fig.4: Hydrogen sulfide and COD removal by combination of ferrate (VI) and UV radiation.

A comparison of the three methods containing UV/ferrate (VI), UV and ferrate (VI) is shown in Figure 5. Also, the rate of COD and H₂S removal is shown in Table 1. This Figure shows that the combination of UV and ferrate (VI) increases the hydrogen sulfide and COD removal from the

wastewater compared with ferrate (VI) application. However, this removal efficiency is not as much as UV application alone. Although the interaction between UV and ferrate (VI) is not well known, UV radiation may accelerate degradation of ferrate (VI) to ferric (III).

Therefore, the efficacy of hydrogen sulfide and COD removal is reduced compared with UV application alone. Further studies are required to determine exactly the mechanism of interaction between UV and ferrate (VI). UV/ferrate (VI) can not only remove hydrogen sulfide from wastewater (12), but it can also prevent hydrogen sulfide production through killing SRBs in wastewater.

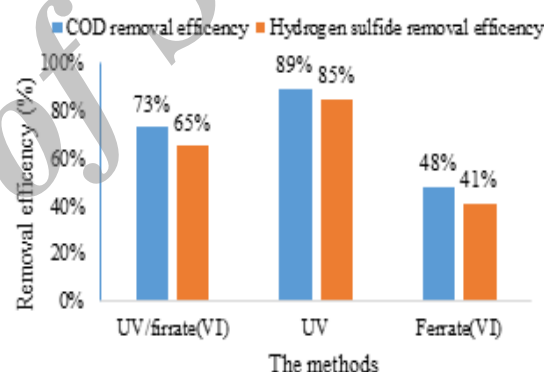
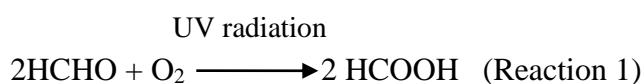
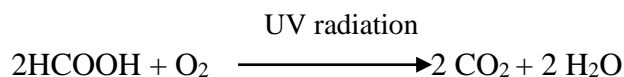


Fig.5: Comparison of hydrogen sulfide and COD removal by UV/ferrate (VI), UV and ferrate (VI) method.

Formaldehyde is an unstable substance that can be converted to formic acid under proper conditions. UV radiation can increase formaldehyde oxidation to formic acid in the presence of dissolved oxygen in water (Reaction 1). It also can increase the rate of formic acid oxidation process to carbon dioxide and water (Reaction 2) (21). This theory is confirmed by reduction of COD, because COD reduction shows that formaldehyde is converted to an inorganic substance.





(Reaction 2)

Table 1: The rate of COD and H₂S removal by the three methods including ferrate (VI), ferrate (VI)/UV and UV.

	The rate of pollutant removal (in M L ⁻¹ min ⁻¹)	
	COD	H ₂ S
Ferrate (VI)	0.14	0.0008
Ferrate (VI)/UV	0.21	0.0011
UV	0.26	0.0016

4. Conclusion

In this study UV, ferrate (VI) and UV/ferrate (VI) methods for removal of hydrogen sulfide and chemical oxygen demand from municipal wastewater were investigated. Each of these three methods was able to remove both hydrogen sulfide and chemical oxygen demand.

However, under the same conditions, the most effective method for both pollutants was the UV method, which can remove 89% and 85% of hydrogen sulfide and chemical oxygen demand, respectively. In addition, it was observed that using UV/ferrate (VI) has higher efficacy than ferrate (VI) alone. UV and UV/ferrate (VI) are effective methods for reducing adverse effects of hydrogen sulfide, such as corrosion of wastewater collection and treatment systems and malodorous emissions.

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Ethical issue

The authors are aware of, and comply with, best practices in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Author contribution

It is certified that all the authors have the same contribution in the experiments and manuscript writing.

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