

間欠接触酸化法による硫化物の生物学的除去

Biological Removal of Sulfide by the Intermittent Contact Oxidation Process

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1. Research Background and Objectives

Sulfide can be generated in sewage, anaerobic digesters, and some industries in the form of S^{2-} , HS^- and $H_2S(aq)$ by sulfate-reducing bacteria as a result of anaerobic reactions, and then form hydrogen sulfide gas when the turbulence in the pipe increases [1].

Hydrogen sulfide gas is associated with several problems, including biogenic corrosion of concrete and metal, release of obnoxious odors as well as toxicity to human and microorganisms [2]. Conventional methods to treat sulfide are heavy metal addition and sulfide oxidation by bubbling water with air. However, for heavy metal addition, the chemicals are expensive and generated sludge need to be handled, and for oxidation by bubbling, it will cause much more hydrogen sulfide gas emission, thus worse corrosion occur.

Intermittent contact oxidation process (ICOP) maybe a promising biological technology to remove sulfide from wastewater by installing porous media like sponge inside a sewer pipe. In the ICOP, reduced chemical species including sulfide would be entrapped in sponge, then oxidized when the sponge is exposed to air. As water is not bubbled to supply oxygen, emission of H_2S gas is significantly less. In this

study, the ICOP was investigated as an alternative method to treat sulfide-containing wastewater in sewer and wastewater treatment plant. Specifically, to 1) evaluate the sulfide removal rate by ICOP and to 2) determine the sulfide transformation process.

2. Methodology

2.1 Reactor Setup

A lab-scale reactor incorporating the ICOP was fabricated. The schematic is as shown in Figure 1. This reactor consisted of a rectangular channel made of 0.5 cm thick transparent polyvinylchloride plastic plates with a dimension of 48.5 cm (length) \times 7 cm (width) \times 6 cm (depth), a piece of sponge (BCD-2, pore cell density 6 cell/cm, Achilles Corporation Tokyo, Japan) made of polyurethane with a dimension of 43.5 cm \times 7 cm \times 1 cm for microorganism habitat and carrier, and a recirculation tank (working volume 1 L) for synthetic feed supply. The slope of this reactor was around 2%. The reactor temperature was maintained at 25 °C during the study.

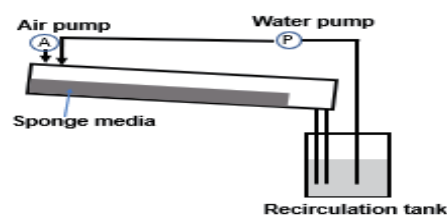


Fig.1 The schematic of airtight reactor setup

2.2 Reactor Operation

The reactor was inoculated with activated sludge. After that, seven months of operation was devoted mainly for acquiring skills and acclimatization of microorganisms. Then main experiments were conducted from Runs 1 to 3 with different feed sulfide concentrations of 40, 80, and 120mgS L⁻¹, respectively, during the next three months. Throughout the operation, every day, 1L of synthetic feed containing different concentrations of sulfide was prepared and filled in the recirculation tank. Then, the synthetic feed was recirculated intermittently to the channel at a rate of 200mL min⁻¹ for 5min every 20min repeatedly. An air pump was operated for 5 minutes every 1 hour to refresh the oxygen inside the reactor. The monitoring data from 3 days' operation in Runs 1 to 3 and in control experiment are reported here.

2.3 Analytical methods

During the experiment, samples were all collected from the recirculation tank. The following parameters were analyzed: sulfide concentration, sulfate concentration, intermediate sulfur products concentration and turbidity. The sulfide concentration was determined by the methylene blue method [5], and sulfate concentration was measured by ion chromatography. Intermediate sulfur products were oxidized into sulfate by oxidizing agent, and its concentration was obtained by the difference of sulfate concentration with and without oxidation [6].

2.4 Control experiment without sponge

To figure out the chemical oxidation contribution during the ICOP, a control

experiment was undertaken without sponge media after reactor and pipes were thoroughly cleaned. This experiment was conducted for one day after Run 3 was finished. In this experiment, synthetic feed with 120mgS L⁻¹ was recirculated intermittently through the channel for 5min every 20min repeatedly.

3. Results

3.1 Sulfide removal rate

Changes in sulfide concentration with different sulfide supply in Runs 1 to 3 are shown in Figure 2. It was found that, for Runs 1 to 3, sulfide concentration was fully reduced in initial 200, 440 and 620min after the synthetic wastewater was introduced, respectively. Further, all the sulfide removal showed a consistent trend of initially faster and later slower. From the sulfide reduction during the initial 80 minutes, the initial removal rates per area of sponge were calculated to be 16.2, 20.1 and 29.7gS m⁻² d⁻¹, respectively.

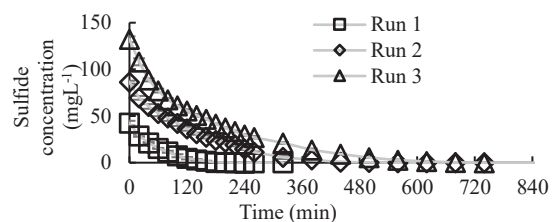


Fig.2 Changes in sulfide concentration in Runs 1 to 3. The error bar represents the standard deviation, n = 3.

3.2 Sulfide transformation to sulfate

Variation of sulfate concentration in Run 1 to Run 3 are illustrated in Figure 3.

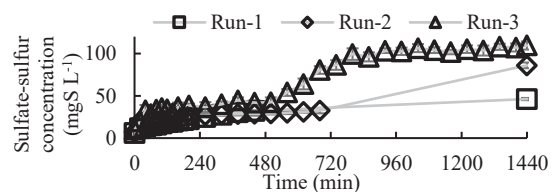


Fig.3 Changes in sulfide concentration in Runs 1 to 3. The error bar represents the standard deviation, n = 3.

For Run 1 and Run 2, sulfate concentration was observed to gradually increase during the initial 440 and 680min, respectively, and the final sulfate-sulfur concentration at 1440min was close to the added sulfide concentration. In Run 3, sulfate concentration increased rapidly twice in the initial 30min and between 500 to 800min, and the final sulfate-sulfur concentration was less than the added sulfide concentration. It reveals that some part of the removed sulfide was transformed into sulfate.

3.3 Sulfide transformation to intermediate sulfur products

As shown in Figure 4, in all Runs 1 to 3, the concentration of intermediate sulfur products gradually increased and then reached its maximum at 200,440 and 620 minutes when sulfide was almost completely removed, respectively. It indicates that some part of the removed sulfide was converted into intermediate sulfur products.

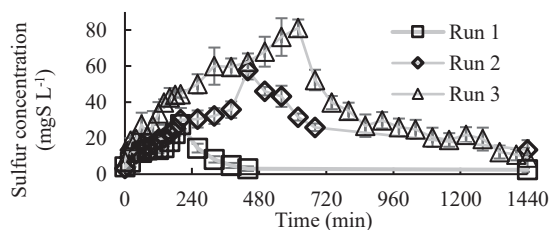


Fig.4 Changes in intermediate sulfur product concentration in Runs 1 to 3. The error bar represents the standard deviation, $n = 3$.

3.4 Control experiment without sponge

The results are shown in Figure 5. It was found that sulfide concentration gradually dropped throughout the monitoring. Initial sulfide removal rate per area of sponge during the initial 80 minutes was $10.72 \text{ gS m}^{-2} \text{ d}^{-1}$, which was about one third of the removal rate in Run 3 (120 mgS L^{-1} and with sponge) of 29.7 gS m^{-2}

d^{-1} , indicating sulfide removal was partly induced by chemical oxidation. Moreover, compared with microbial sulfide removal in Run 3, both intermediate sulfur products and sulfate did not increase significantly.

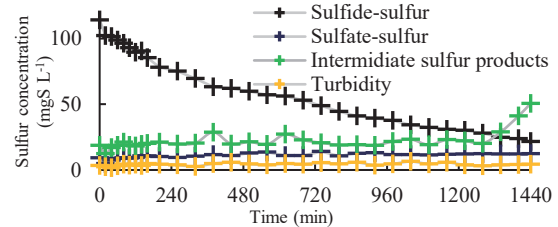


Fig.5 Sulfide removal without sponge for one day.

4. Discussion

4.1 Sulfide removal rate

As was mentioned in section 3.1, sulfide removal was faster initially and then slower. It may be attributed to oxygen competition between sulfide and accumulated intermediate sulfur products. The factors that affect the sulfide removal rate during the ICOP may include initial sulfide concentration, microbial activity, and oxygen availability to microorganisms. Moreover, whether the removal rate in initial 80 minutes can be sustained for one day is unknown, thus flow-through experiment is necessary to achieve continuous high sulfide load supply. Besides, when considering generalizing this removal pattern for real application, experiment under different conditions such as different temperature and oxygen concentration should be conducted.

Note that in my study, the meaning of sulfide removal only refers to the disappearance of sulfide, and it need not involve the full oxidation to form sulfate. However, if sulfide remaining in water as intermediated products, it

can consume oxygen in latter treatment process.

4.2 Sulfide transformation process

To grasp the sulfur conversion from sulfide to sulfate from a whole picture during the ICOP, sulfur mass balance in Run 3 is presented in Figure 4. And several implications were obtained from it:

1. During the ICOP, some part of the removed sulfide was converted into intermediate products and then finally to sulfate.
2. From the results of Runs 1 to 3, the disappearing sulfide was suspected to be captured in the sponge. However, the results from control experiment also showed the disappearing sulfide. It indicates that sulfide was converted to other soluble sulfur species, which cannot be detected by the protocols used in this study.

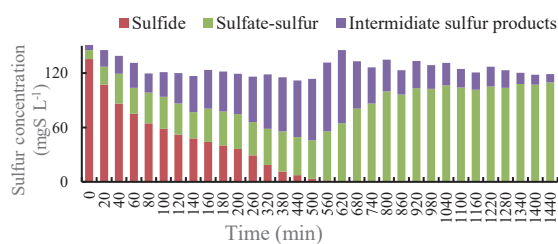


Fig.6 Sulfur mass balance for Run 3 (The leftmost bar at 0 minute is for freshly prepared synthetic wastewater)

5. Conclusions and limitations

In this research, sulfide removal rate and sulfide transformation were explored during the ICOP. Following results were obtained:

1. The maximum sulfide removal rate was $29.7\text{gS m}^{-2} \text{d}^{-1}$, which was observe during initial 80min with initial sulfide

concentration of 120mgS L^{-1} .

2. Removed sulfide was finally converted to sulfate via intermediate products.
3. While chemical reaction contributed to some extent, microbial activity played significant role in the removal and oxidation of sulfide.

The result suggests that ICOP application has the potential to treat sulfide-containing wastewater. However, to further understand the sulfide removal mechanism, sulfide removal in the sponge media and the real composition of intermediate sulfur products should be investigated. Besides, more exploration is needed for practical application of ICOP for the removal of sulfide.

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