

Biological oxidation of ferrous iron in an air-lift bioreactor

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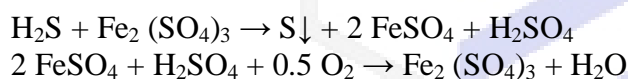
Abstract

Biological oxidation of ferrous iron is an important potential in industrial processes such as H₂S removal in natural gas, leaching operation or treatment of acid mine drainage water. Owing to the fact that bio-oxidation process has high efficiency and economical benefits, it is evident that we should expand our knowledge in this case. The purpose of this paper was to treat Fe²⁺ ions with the usage of Thiobacillus ferrooxidans in laboratory, and after finding appropriate results, we designed an air-lift bioreactor and expanded our work to that vessel in continuous mode.

Key words: Bio-oxidation, Thiobacillus ferrooxidans, Hydrogen sulfide, Biological desulphurization, Ferrous iron.

1- Introduction

H₂S is extremely an unpleasant component in natural gas. Removal of this compound is really mentioned since it is highly corrosive, hazardous to human health, environment and has a bad smell. Although chemical processes of H₂S removal are performed regularly, biological methods have attracted the attention of lots of big oil companies recently. A variety of biochemical processes using different bacterial species are operated, but the one that we utilized was Thiobacillus ferrooxidans. The process of desulphurization operates in two stages. In the first stage, H₂S oxidized to elemental sulphur by a chemical oxidation process using ferric sulphate solution as an oxidant. This reaction is very fast. In the second stage, the reduced oxidant (ferrous sulphate) is biologically oxidized for recycling in the first stage of the process.



2- Material and methods

2.1. Microorganism and growth condition

The strain used was T. ferrooxidans (PTCC-1647) obtained from the microbial collection of Iran Scientific and Industrial Research Institute. The composition of the media used for the cultivation of T. ferrooxidans was 0.4 g l⁻¹ of K₂HPO₄; 0.4 g l⁻¹ MgSO₄.7H₂O; 0.4 g l⁻¹ (NH₄)₂SO₄; 33.3 g l⁻¹ FeSO₄.7H₂O; and 1000.0 ml 0.1 N H₂SO₄. The pH was adjusted to 1.5±0.1. The media was inoculated with 20% (vol/vol) of inoculum and the T. ferrooxidans cultures were shaken at 130 rpm on an orbital shaker at room temperature. Subcultures were carried out every week.

2.2. Immobilization procedure

Activated carbon granules were used as bacterial support. In order to prepare the granules, the following operations were performed:

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- 200 grams of activated carbon granules was washed with water.
- Granules were washed with the media solution.

Afterwards the biomass support was added to an air-lift reactor containing 700 ml media and 700 ml of *T. ferrooxidans* culture. The air flow was 500 ml/min, and room temperature was applied. After each 3-4 days (when the complete oxidation of ferrous iron happened) the solution was drained out and fresh media was added. This procedure was repeated a further 2 times.

2.3. Bioreactor

The biological oxidation of ferrous iron was studied in an air-lift bioreactor. The reactor was based on a glass column surrounded with a jacket. The total operation volume of the bioreactor was about 2 liters. The air injected in to the internal tube causes the recirculation of liquid media which expands the bed of the particles. The draft tube diameter was 3 cm_s, and its height was 40 cm_s. The fresh media and nutrient salts solution were provided by peristaltic pumps. Activated carbon with a mean diameter of 1.5 mm and BET 1200 cm³gr⁻¹ was used as biofilm support media. Figure 1 shows the bioreactor scheme.

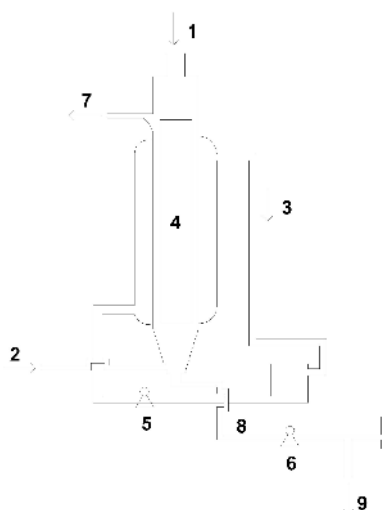


Fig 1. The bioreactor scheme.

1: fresh feed, 2: air inlet, 3: water circulation, 4: support, 5 and 6: Peristaltic pumps, 7: air outlet, 8: product, 9: sampling.

2.4. Experimental procedure

After immobilization of the cells, support particles were placed in the bioreactor and the reactor was filled with fresh media. The reactor operated as a batch reactor till more than 95% of Fe²⁺ was oxidized to Fe³⁺. Then the reactor mode was changed to a continuous operation. Steady-state conditions were achieved when less than 5% changes occurred in the iron oxidation rate. Different flow rates of feed were applied and Fe³⁺ concentration, Fe total concentration and iron oxidation rate were determined in each operation.

2.4. Analysis

Measurements were made of the pH, a spectrometric technique was used to analyze the ferric and total iron and the biomass concentration was measured in a Thoma chamber under light microscopy. The concentration of ferric and ferrous iron was analyzed by colorimetric using sulfosalysilic acid as the indicator.

3- Result and discussion

All experiments were conducted under following condition:

Substrate dilution rate, $0.1-1 \text{ hr}^{-1}$; ferrous iron concentration, $2-8 \text{ grlit}^{-1}$; pH, 1.5 ± 0.1 ; room temperature; air flow rate, 500 mlmin^{-1} .

3.1. pH optimization

In order to find the best pH for the growth of microorganism and use it as the optimum pH in all the tests, an experiment in which five 500 ml flasks were filled with 100 ml of media with 20 % (vol/vol) inoculums was run. Then the pH of those flasks was adjusted according to the table 1.

Table 1. The properties of different flasks used in pH optimization test.

Flask No.	1	2	3	4	5
pH	1	1.2	1.4	1.6	1.8

The results are shown in figure 2 and 3. As you can see the best cell growth and ferric production were found in pH=1.6. Consequently pH=1.6 was chosen as the optimum pH and was used in all the following tests.

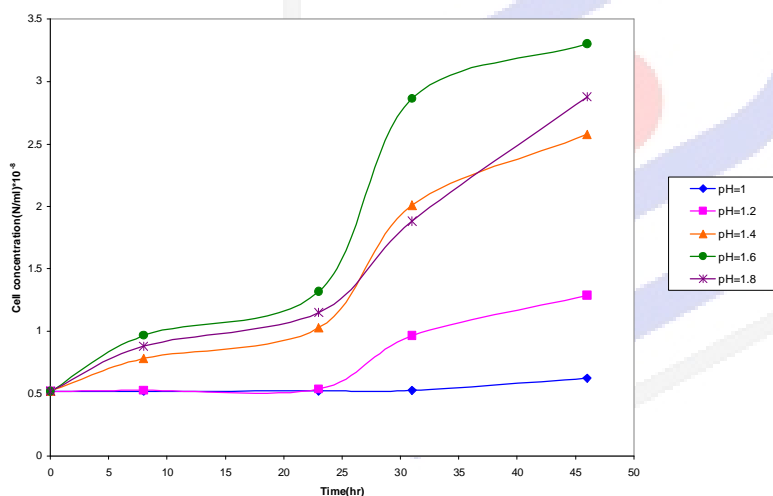


Fig.2. The comparison between cell concentration in different pHs.

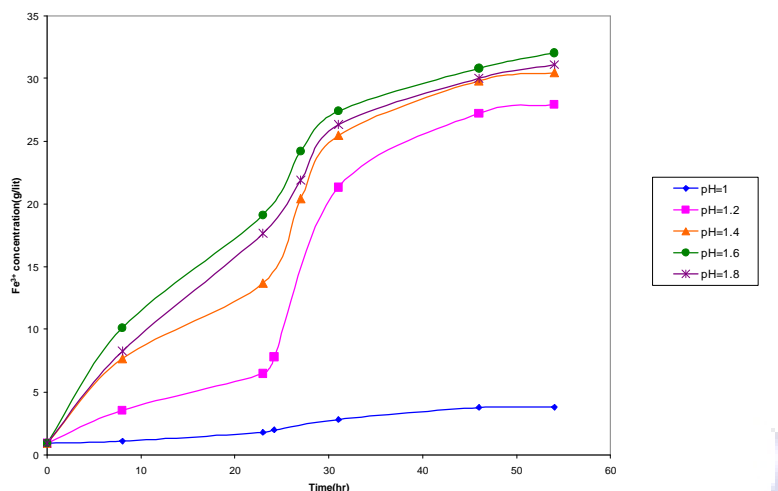


Fig.3. The comparison between Fe³⁺ concentration in different pHs.

3.2. The operation of bioreactor

In continuous system three tests were run with different initial ferrous sulfate concentration. The experiments with 6.66g/lit⁻¹ initial ferrous sulfate concentration were done in 3 dilution rates: 0.06, 0.21 and 0.4 hr⁻¹.

In D=0.06 hr⁻¹ (feed flow rate=2 mlmin⁻¹) and D=0.21 hr⁻¹ (feed flow rate=7 mlmin⁻¹) 95% of fe²⁺ converted to fe³⁺ but in D=0.4 hr⁻¹ (feed flow rate=13 mlmin⁻¹) and more the system was not able to complete the production of fe³⁺. The results are shown in figure 4 and 5.

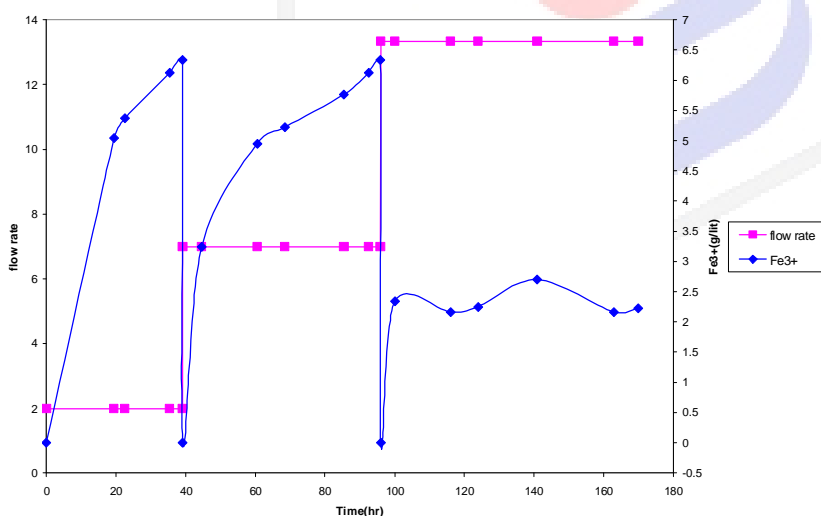


Fig.4. The comparison between Fe³⁺ concentration in different flow rates in continuous system. Initial ferrous sulfate concentration: 6.66g/lit⁻¹.

In figure 4 the comparison of Fe^{3+} production in different feed flow rates is obvious. While the flow rate increases, the residence time reduces and longer period is needed to convert 95% of Fe^{2+} to Fe^{3+} .

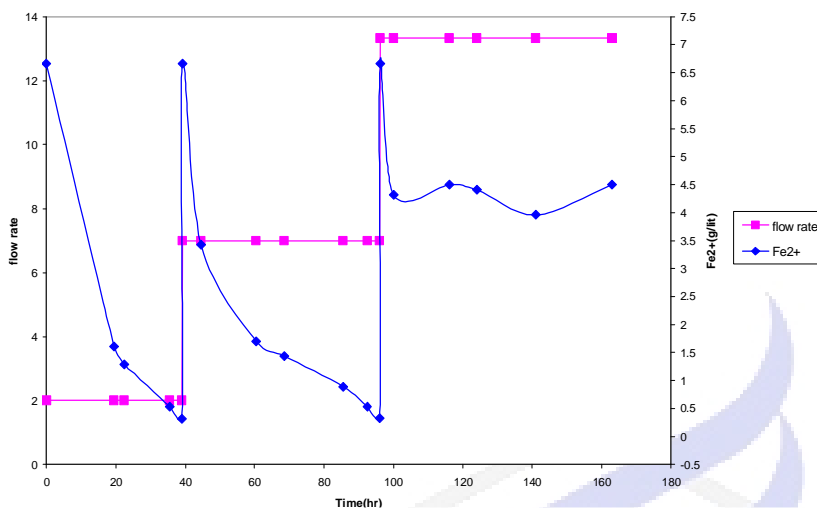


Fig.5. The comparison between Fe^{2+} concentration in different flow rates in continuous system. Initial ferrous sulfate concentration: 6.66 glit^{-1} .

The variation of Fe^{2+} concentration is shown in figure 5. In each flow rate, when the Fe^{3+} concentration reached 95% of initial Fe^{2+} concentration, the bioreactor was drained and the reactor was filled with fresh media. Then the flow rate was raised and the test was continued till the oxidation of ferrous became complete.

In $D=0.4 \text{ hr}^{-1}$ the bio-oxidation was not complete and the maximum Fe^{3+} concentration was 2.702 glit^{-1} .

The oxidation rate was calculated according to the Fe^{2+} concentration and the period length. Figure 6 shows the results. The maximum oxidation rate was $0.1625 \text{ glit}^{-1} \text{ hr}^{-1}$.

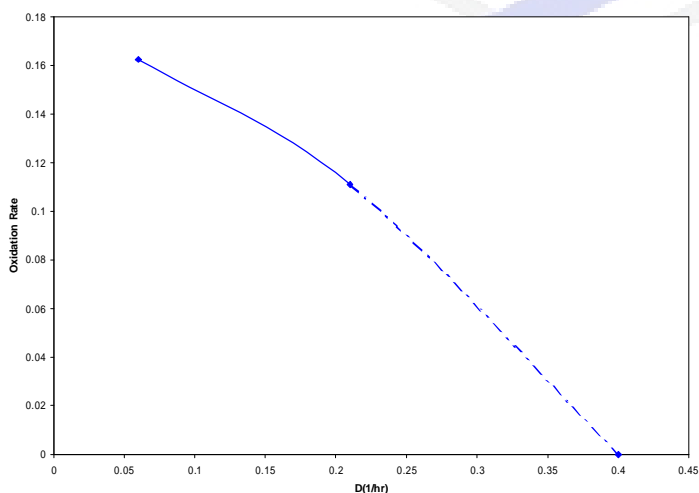


Fig.6. Oxidation rate in different dilution rates in continuous system. Initial ferrous sulfate concentration: 6.66 glit^{-1} .

The second series of tests in continuous system were conducted with 11.1 glit⁻¹ of initial ferrous sulfate concentration. The variations of fe³⁺ and fe²⁺ concentration are shown in figure 7 and figure 8.

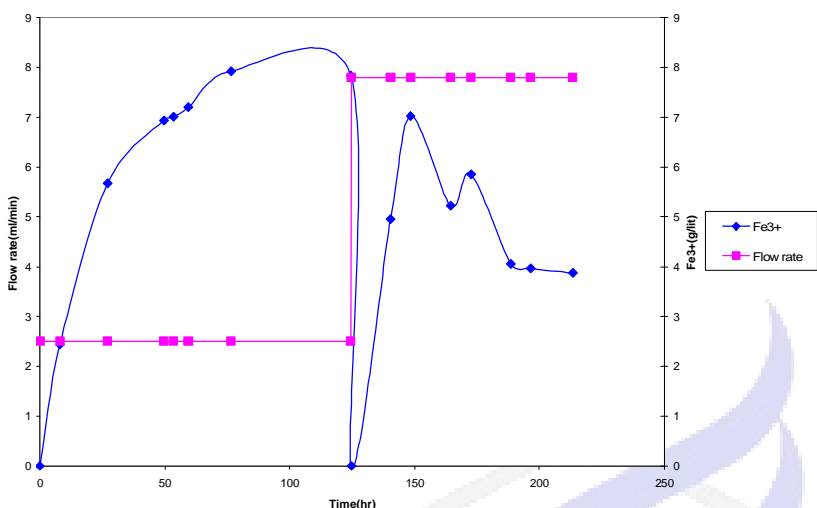


Fig.7. The comparison between Fe³⁺ concentration in different flow rates in continuous system. Initial ferrous sulfate concentration: 11.1 glit⁻¹.

As it is clear, in none of these experiments the bio-oxidation of ferrous ion was completed. Although we chose low dilution rates for this series; $D=0.075, 0.234 \text{ hr}^{-1}$ (feed flow rate = 2.5, 8 mlmin⁻¹), 95% of fe²⁺ bio-oxidation was not gained.

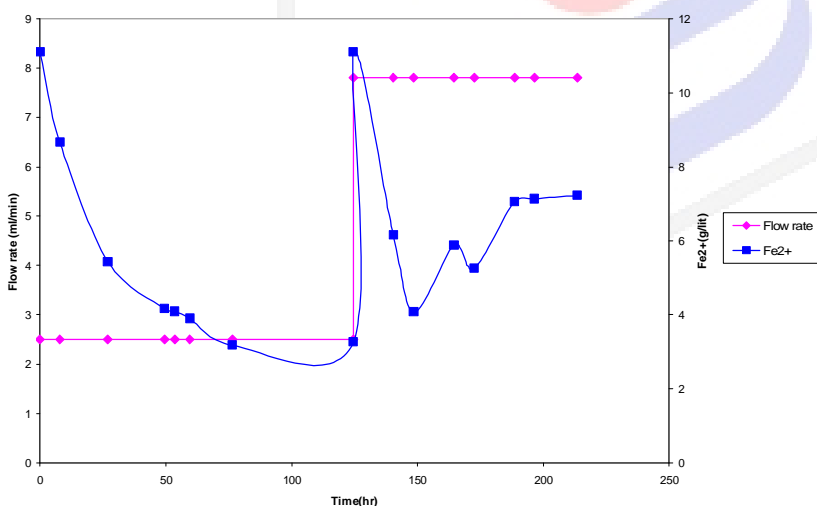


Fig.8. The comparison between Fe²⁺ concentration in different flow rates in continuous system. Initial ferrous sulfate concentration: 11.1 glit⁻¹.

In $D=0.075 \text{ hr}^{-1}$ (feed flow rate= 2.5 mlmin^{-1}) the maximum Fe^{3+} concentration was 7.92 glit^{-1} and finally $3.26 \text{ glit}^{-1} \text{ Fe}^{2+}$ was remained in the system. In $D=0.234 \text{ hr}^{-1}$ (feed flow rate= 8 mlmin^{-1}) the maximum Fe^{3+} concentration was 7.027 glit^{-1} and $7.227 \text{ glit}^{-1} \text{ Fe}^{2+}$ was remained in the system. Since the bio-oxidation was not complete, the oxidation rate could not be calculated.

4- Results

In this research the biological oxidation of ferrous ion with the usage of *Thiobacillus ferrooxidans* was studied. At first, pH was optimized and $\text{pH}=1.6$ was chosen as the best one. Then the bio-oxidation of Fe^{2+} in continuous system was studied. Two series of experiments were conducted; one in initial ferrous sulfate concentration of 6.66 glit^{-1} and the other in 11.1 glit^{-1} of ferrous sulfate concentration. The maximum oxidation rate was found in initial ferrous sulfate concentration of 6.66 glit^{-1} and dilution rate equal with 0.06 hr^{-1} , which was $0.1625 \text{ glit}^{-1} \text{ hr}^{-1}$. In all dilution rates in initial ferrous sulfate concentration of 11.1 glit^{-1} and in $D=0.4 \text{ hr}^{-1}$ and more, in initial ferrous sulfate concentration of 6.66 glit^{-1} system was not able to complete the bio-oxidation.

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