

## The Sulfide Oxidation in an Electrolytic Sulfide Oxidizing Bioreactor using Graphite Anode

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**Summary:** The goal of the present research was the direct conversion of sulfide (an important contaminant in various industrial wastewaters) to sulfate, whose discharge limits are much less stringent than those for sulfide. The electrolysis of sodium sulfide was investigated under different conditions such as: pH, current density and working area *etc.* along with cyclic voltammetry. By the use of a graphite anode, we achieved near-quantitative electrochemical conversion of sulfide ions to sulfate with current efficiency of 88%. Kinetically, the reaction is first order in current density. The experimental results revealed that the sulfide removal rate of more than 88% could be achieved under the conditions T=30 °C, pH = 7, current density of 1mA/cm<sup>2</sup> at anode area of 225 cm<sup>2</sup>. The process can be practically coupled with bioreactor for an effective sulfide removal.

### Introduction

Hydrogen sulfide (H<sub>2</sub>S) is toxic to human in addition to imparting severe effects on ecosystems even at very low concentrations [1]. Being the most reduced form of sulfur, sulfide possesses a high oxygen demand of 2 mol O<sub>2</sub>/mol S<sup>2-</sup> causing depletion of oxygen upon discharge of sour wastewater [2]. Various toxicological effects of sulfide upon human health have been described elsewhere [3-5]. Biogenic production of H<sub>2</sub>S in oil and gas reservoirs causes contamination of oil products with sulfur compounds [6]. The activity of sulfidogenic bacteria produces sulfides in the water from secondary oil production [7]. Toxic and corrosive nature of sulfides demands their removal from the produced fluids to prevent emission of sulfur oxides during combustion of fossil fuels [8].

A variety of physicochemical methods such as chemical oxidation and catalytic conversion [1] have been used to oxidize sulfide to either elemental sulfur or sulfate, thus achieving sulfide removal from wastewater. Biochemical method focused on the desulfuration of wastewaters where simultaneous removal of sulfur and nitrogen was accomplished [1]. Electrochemical processes offer several advantages over the aforementioned methods, including good energy efficiency, environmental compatibility, versatility and cost effectiveness [10]. Sulfide (H<sub>2</sub>S, HS<sup>-</sup>, S<sup>2-</sup>) is an electrochemically active component that can react at anodic electrode and directly donate

electrons to the electrode. Depending on the experimental conditions elemental sulfur, polysulfides, sulfate, dithionate or thiosulfate may be produced during sulfide oxidation. Elemental sulfur has been found to be the main electrochemical product [11-13].

To date, most of the studies were performed in alkaline media by electrolysis at high anode potentials through catalytic conversion in a single chamber reactor. The electrochemical oxidation of pyrite (FeS<sub>2</sub>) the most common sulfide mineral was also reported [14]. Zaman and Chakma [15] and Kameyama *et. al.* [16] extracted two valuable products hydrogen and sulfur from gaseous hydrogen sulfide using electrochemical oxidation.

All previous researchers used the single electrolysis compartment; however, none has considered the combined electrolysis system in combination with the bioreactor that can be used to prevent the harmful effects of sulfide on the microbial communities. The specific aim of the present study was to combine anaerobic bioreactor with the electrolysis system. In this work we focus on the conversion of sulfide to sulfate, using synthetic solutions of sulfide in water. Moreover, the reactor performance was investigated in the presence of varying sulfide concentrations that could supply some new ideas for its practical application at full-scale anaerobic treatment of sulfate-containing wastewater.

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## Results and Discussion

The potential of an electrolytic process coupled with a bioreactor was also investigated. We presented the results of various aspects of sulfide oxidation using electrolytic process only.

### Sulfide Concentration

Cyclic voltametry (CV) was used for the general characterization of the electrochemical behavior of sulfide on the graphite electrode. Fig. 1 showed the effect of potential sweep rate and various sulfide concentrations in the effluent. Three CV curves in the range of -2.0 to 1.0 V/SCE were recorded for different concentrations of Na<sub>2</sub>S at a sweep rate of 10 mV/s as shown in Fig. 1. The CV peaks were recorded around zero potential that corresponded to the sulfide oxidation at the sweeping potential range of -2.0 to 1.0 V/SCE. The results were not similar to one obtained by Yi Qing-feng [17]. This was because of different pH of Na<sub>2</sub>S solution. Yi Qing-feng used alkaline environment while sulfide oxidation was investigated at neutral pH in the present study. Fig.1 showed that anodic peaks and cathodic peaks were separated with larger potentials values and that cathodic peaks were also obvious. Therefore, the anodic process transferring electrons kept balance.

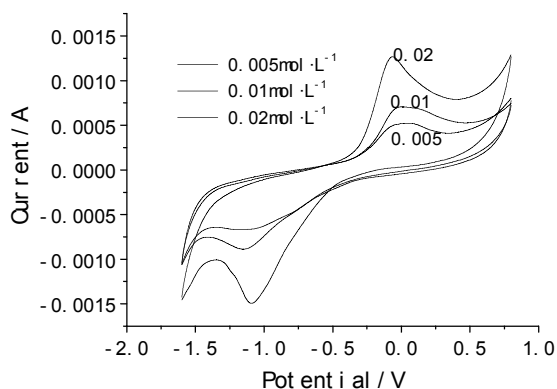


Fig. 1: Cyclic voltammogram of different sulfide concentrations; the operational conditions were Na<sub>2</sub>S Molar concentration = 0.02 mol/L, pH = 7,  $v = 10$  mV/s, 30 °C and Anode area of 12 cm<sup>2</sup>.

The dependence of the currents peaks for both anode and cathode on the sulfide concentration in solution, respectively, were shown in Fig. 2, which were approximately linear indicating that the sulfide

oxidation was reversible reaction at pH = 7.

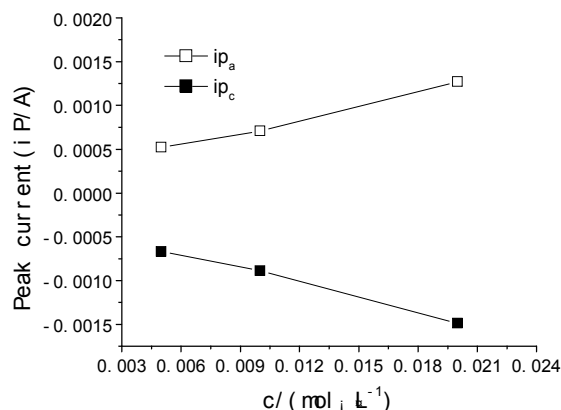


Fig. 2: Relationship between  $i_{pa}$  and  $i_{pc}$ , other conditions were same as given in Fig. 1.

### Effect of pH on Sulfide Removal

The pH is an important factor which decides the ionic behavior of the sulfide in the solution. Fig. 3 showed that obvious differences were present in anodic peaks at different pH at similar conditions as shown in Fig. 2.

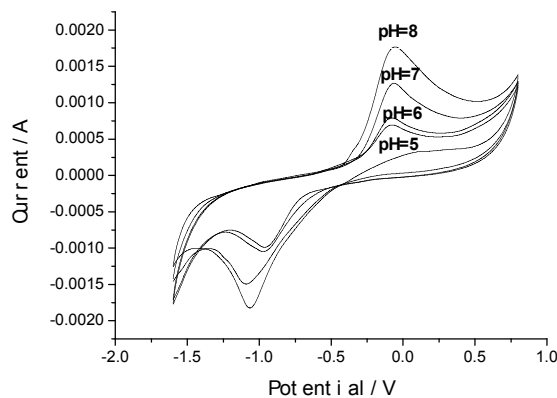


Fig. 3: Cyclic voltammogram at different pH values with Na<sub>2</sub>S molar concentration of 0.02 mol/L;  $v = 10$  mV/s and anodic area of 12 cm<sup>2</sup> at 30 °C.

In this case, the peaks were also observed around zero potential. With the increasing pH values, anodic peak current also increased thus a linear relationship existed between anodic peak and pH values. Fig. 4 showed the relationship between sulfide removal rate and the reaction time. It was evident that the sulfide removal rate increased with the passage of time at every pH. As the pH increased from 5 to 7, the

sulfide removal rate also increased; the sulfide removal percentage was almost equal both for pH = 8 and the pH = 7. However, the highest sulfide removal rate was observed at pH 8. It is an established fact that most of the microorganisms survive best at neutral pH. Thus, there was a possibility to couple this process with bioreactor.

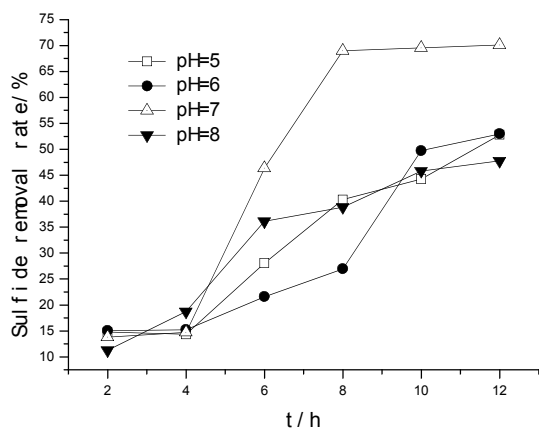


Fig. 4: Removal rate of sulfide at different pH, Na<sub>2</sub>S Molar concentration = 0.02 mol/ L.

*Current Density*

The effect of various current densities (1, 0.9 and 0.8 mA/cm<sup>2</sup>) on the sulfide removal rates at pH 7 are shown in Fig. 5. It was evident that, the sulfide removal rate increased with the increasing current density at pH = 7. Three stages could be identified in the curve (Fig. 5). The first phase was noted for 0-4 h where the curve was flat; the second steep slope was observed for 4-8 h when the sulfide decrease was faster. The sulfide removal had a good linear relationship with increasing current density during second stage as shown in Table-1; thus kinetically the reaction was first order with respect to applied current density (Fig. 6). The last stage was noted for 8-26 h where the sulfide removal rate increased slowly which could reach above 80%.

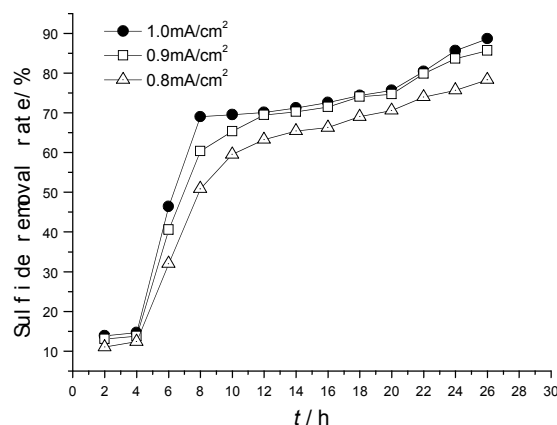


Fig. 5: Sulfide removal rate under different current densities.

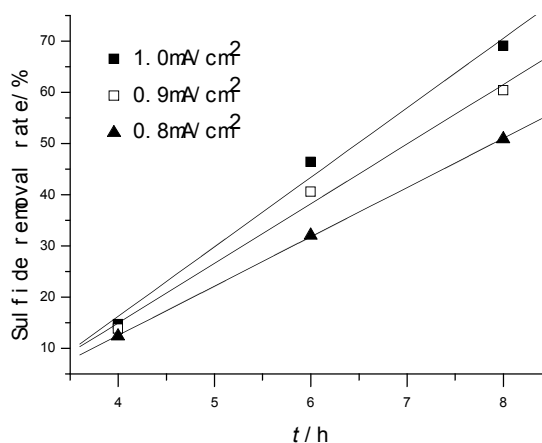


Fig. 6: Curve of linear fit from 4 h to 8 h at pH = 7.

*Effect of Anode Area*

While keeping conditions as pH = 7, Na<sub>2</sub>S Molar concentration = 0.02 mol/L, current density = 1mA/cm<sup>2</sup>, the relationship between sulfide removal rate and anode area (225, 175, 125, 75, 25cm<sup>2</sup>) was investigated (Fig. 7). The sulfate concentration was measured after every two hours. It was noted that sulfate can be a product of the sulfide oxidation. Fig. 8 shows the concentration of sulfate and its transformation rate under different anode area of the

Table-1: Parameters of linear fit for various current densities to remove sulfide from wastewater.

Current density mA/cm <sup>2</sup>	Linear Regression Equation Y = A + B * X	Correlation Coefficient R	Standard Deviation SD	Data Numbers N	probability P
1	Y = -38.07 + 13.57 * X	0.995	3.67	3	0.06
0.9	Y = -31.63 + 11.64 * X	0.996	2.84	3	0.054
0.8	Y = -26.01 + 9.625 * X	0.999	0.32	3	0.007

X= independent variable, Y= dependent variable, while A and B=model parameters

experiment. It was evident that with the increase of the anode area, the sulfide removal rate and the production of the sulfate also increased and the sulfide removal rate could reach up to 80%, even more when the anode area was 225 cm<sup>2</sup>. The sulfide transformation could reach up to 50%. However, some sulfur content was also expected to be deposited on the anode.

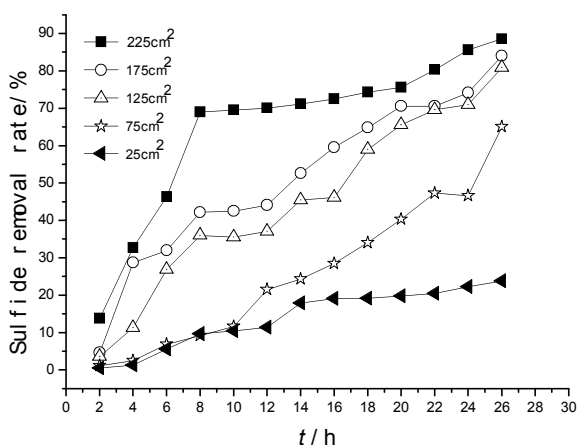


Fig. 7: Sulfide removal rate at different anode area.

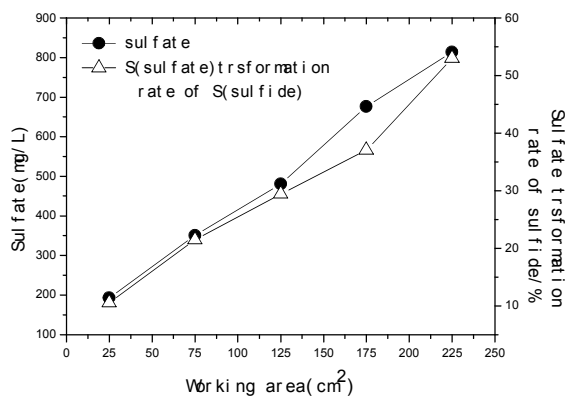


Fig.8: Concentration of sulfate produced employing variable anode area.

Ateya and Al-Kharafi [18] studied the electrochemical oxidation of sulfide to sulfur, which deposited on the surface of their graphite anodes. In subsequent work, Ateya *et al.*, [19] achieved oxidation of sulfide in a synthetic geothermal brine that contained 3.5% by mass of NaCl. X-ray photoelectron spectroscopy revealed that elemental sulfur was deposited on the surface of the carbon felt anode, causing passivation. Although the large surface area of the anode was claimed to alleviate this problem, it would presumably lead to failure of the method in long-term operation. The authors argued

that further oxidation of elemental sulfur to sulfur oxyanions must be much slower than the oxidation of sulfide to the element under these conditions, because they observed no other species sorbed to the graphite felt. However, it is not clear whether the material balance for sulfur was investigated. The reaction rate increased at higher temperatures and at higher concentrations of sulfide, although the likely first-order dependence was not demonstrated.

Miller and Chen [20] found that the oxidation of sulfide at a Ti/Ta<sub>2</sub>O<sub>5</sub>-IrO<sub>2</sub> anode gave galvanic voltammograms whose potential showed large periodic excursions over a wide range of applied currents. Similar behaviour has been observed at platinum anodes [21]. The oscillations were explained in terms of deposits of elemental sulfur, which repeatedly formed on the anode surface and either flaked off [20] or was dissolved as polysulfide by the action of excess sulfide ion [22]. In the work of Ateya *et al.*, [19], no sulfur was deposited on a titanium anode; with a stainless steel anode, pitting of the electrode occurred [23]. The latter observation is consistent with the report that sulfide can be removed from wastewaters by electrocoagulation at iron or aluminum sacrificial anodes [24], in the former case with the formation of FeS [25]. At aluminum, much of the anion removal occurred through chemisorption at pH values at which the precipitate of M(OH)<sub>3</sub> was positively charged.

A major question to address is whether the objective of treating a solution polluted by sulfide is to recover sulfur and/or hydrogen from H<sub>2</sub>S, or to convert toxic sulfide to a benign form such as sulfate. Mitigating the first approach, elemental sulfur is available at low cost and high purity from the Claus process in the sweetening of natural gas. Regarding the complete oxidation of sulfide to sulfate, Allison *et al.* [26] noted that the success of this conversion with conventional oxidizing agents requires that elemental sulfur does not precipitate from the solution. They achieved this condition by using surface active agents to prolong contact between the sulfide ion and the oxidant. This is consistent with the conclusion of Ateya *et al.* [23] that in the electrolysis of sulfide at graphite anodes, the deposited sulfur was stable with respect to further oxidation on kinetic rather than thermodynamic grounds.

The present study showed that sulfate was the major product of sulfide oxidation which is far less toxic than sulfide. The chemical sulfide oxidation can be coupled with biological wastewater treatment

which has not been applied earlier. Further evaluation of chemically coupled sulfide oxidation with biological wastewater treatment is under investigation in our laboratory.

## Experimental

### *Electrolytic Sulfide Oxidizing Bioreactor*

The electrolytic sulfide-oxidizing reactor was an up flow reactor with biomass retention. One laboratory scale reactor made of perspex with working volume of 2.8 L capacity was used in this study. The height of the reactor was 0.7 m. The reactor was operated in upflow mode to which the electrolysis system was connected to the side of the reactor as shown in Fig. 9. The electrolytic system consisted of a columnar tank consisting of a cathodic and anodic chambers separated by cation-exchange membrane. The cross sectional area of the electrolytic chamber was  $0.06 \times 0.06$  m with a height of 0.15 m. We used the graphite as anode of the electrolysis and iron as the cathode. The anode and cathode solution were sulfide solution and sodium chloride, respectively. The synthetic influent was pumped through a peristaltic pump from the 5-L influent vessel to the reactor. The flow rate could vary between 0.6 and 12.5 L per day, which gave the possibility operating at HRTs between 2.0 and 0.1 days. A recycling pump was used in order to mix the influent (substrate) and sludge (biocatalyst) well and hence to decrease possible substrate inhibition. The ratio of recycling flow to the influent flow was set about 2.5–3.0. The temperature of the reactor can be controlled between 20 and 70 °C using a thermostat, although the normal operational temperature was 30 °C.

### *Experiment Set-Up*

Inoculum was taken from the anaerobic methanogenic reactor in Dengta Wastewater Treatment Plant located in Hang Zhou city, China. Its total solids (TS) and volatile solids (VS) were measured as 154.10 and 50.89 g/L, respectively, providing VS/TS ratio of 0.322. Before sulfide (0.02 mol/L) addition, the synthetic influent was flushed with nitrogen gas for 15 minutes to get rid of the dissolved oxygen. Different sulfide concentrations were used as per requirement for the present investigation.

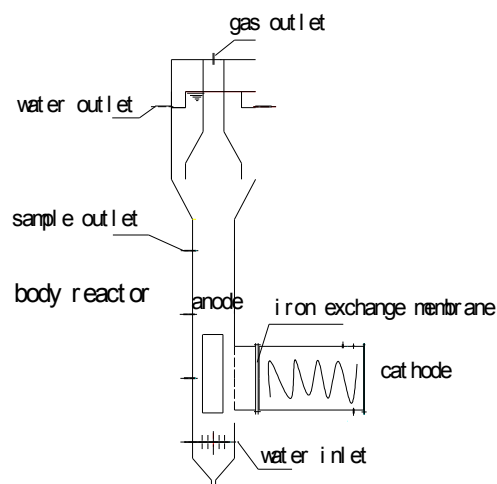


Fig. 9: The schematic presentation of the electrolytic sulfide oxidizing bioreactor; the influent was pumped into reactor at the bottom. The recycling stream was first introduced into electrolytic apparatus attached to the side of the bioreactor and finally back into reactor.

### *Analytical Procedures*

Voltammetric curve was obtained by workstation CHI660A, pH was measured by meter (PHS—3B) which was also used to measure sulfide. Anode and cathode are both graphite. Cathode solution was 0.1 mol/L NaCl, anode solution was  $\text{Na}_2\text{S}$  and 0.1 mol/L NaCl to increase the conduct ability of the system. The temperature in the reactor was maintained at  $30 \pm 1$  °C by heater. Before the cyclic voltammetry experiment, the graphite was polished by sand paper, washed by deionized water, and then dried in the air.

## Conclusions

We considered the possibility of developing electrochemical oxidation of sulfide to sulfate to be coupled with biological wastewater treatment as a technology. Following key characteristics were concluded from this study.

- 1) CV peaks occurring around zero potential corresponded to the sulfide oxidation under conditions of  $T = 30$  °C and  $\text{pH} = 7$ .

- 2) The sulfide removal rate of more than 88% was observed under the conditions  $T=30^{\circ}\text{C}$ ,  $\text{pH}=7$ , current density of  $1\text{mA}/\text{cm}^2$  and anode area of  $225\text{cm}^2$ .
- 3) At different current densities for 4-8 h, the sulfide removal rate had a good linear relationship with the reaction time. The reaction was first order in current density.
- 4) All this information suggested that the process could be effectively coupled with biological wastewater treatment.

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