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Effective sulfur and energy recovery from hydrogen sulfide through incorporating an air-cathode fuel cell into chelated-iron process

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HIGHLIGHTS

- Effective sulfur and energy recoveries from H_2S in a novel chelated-iron process.
- Air-cathode fuel cell was employed for the catalyst regeneration.
- The problem of chelate degradation was well controlled.
- This process maintained stable efficiency in the recycling operation.
- Results in treating a H_2S-containing biogas confirmed the feasibility of process.

ARTICLE INFO

ABSTRACT

The chelated-iron process is among the most promising techniques for the hydrogen sulfide (H_2S) removal due to its double advantage of waste minimization and resource recovery. However, this technology has encountered the problem of chelate degradation which made it difficult to ensure reliable and economical operation. This work aims to develop a novel fuel-cell-assisted chelated-iron process which employs an air-cathode fuel cell for the catalyst regeneration. By using such a process, sulfur and electricity were effectively recovered from H_2S and the problem of chelate degradation was well controlled. Experiment on a synthetic sulfide solution showed the fuel-cell-assisted chelated-iron process could maintain high sulfur recovery efficiencies generally above 90.0%. The EDTA was preferable to NTA as the chelating agent for electricity generation, given the Coulombic efficiencies (CEs) of $17.8 \pm 0.5\%$ to $75.1 \pm 0.5\%$ for the EDTA-chelated process versus $9.6 \pm 0.8\%$ to $51.1 \pm 2.7\%$ for the NTA-chelated process in the pH range of 4.0–10.0. The Fe (III)/S^{2-} ratio exhibited notable influence on the electricity generation, with the CEs improved by more than 25% as the Fe (III)/S^{2-} molar ratio increased from 2.5:1 to 3.5:1. Application of this novel process in treating a H_2S-containing biogas stream achieved 99% of H_2S removal efficiency, 78% of sulfur recovery efficiency, and 78.6% of energy recovery efficiency, suggesting the fuel-cell-assisted chelated-iron process was effective to remove the H_2S from gas streams with favorable sulfur and energy recovery efficiencies.

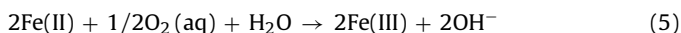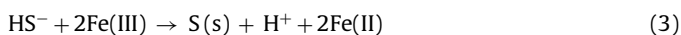© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen sulfide (H_2S) is produced by many industrial activities such as petroleum refining, pulp manufacturing, natural gas production, and aerobic and anaerobic wastewater treatments. Since the H_2S is toxic, corrosive and foul-smelling, a large amount of effort has been undertaken to remove H_2S from various gaseous streams [1–3]. The chelated-iron approach is among the most promising techniques for the H_2S removal due to its double advantage of waste minimization and resource recovery [4]. In a typical chelated-iron process, iron is presented in the ferric (Fe(III)) state which

is held in solution by chelating agents such as EDTA and NTA [5]. The H_2S is firstly absorbed into the chelated-Fe(III) solution and converted into elemental sulfur which is then separated by filtration or sedimentation. Meanwhile, chelated-Fe(III) is reduced to the chelated-ferrous (Fe(II)) state. Next, the chelated-Fe(II) is oxidized through contacting with oxygen (O_2) containing gas (such as air) to regenerate chelated-Fe(III). The chemistry involved in the chelated-iron process is summarized as follows with (g), (aq) and (s) representing the gaseous, aqueous and solid states, respectively:
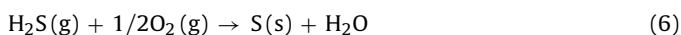
$$H_2S(g) \rightarrow H_2S(aq) \tag{1}$$

$$H_2S(aq) \rightarrow HS^- + H^+ \tag{2}$$

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$$HS^- + 2Fe(III) \rightarrow S(s) + H^+ + 2Fe(II) \tag{3}$$

$$1/2O_2(g) \rightarrow 1/2O_2(aq) \tag{4}$$

$$2Fe(II) + 1/2O_2(aq) + H_2O \rightarrow 2Fe(III) + 2OH^- \tag{5}$$

The overall process is depicted by the following net reaction:

$$H_2S(g) + 1/2O_2(g) \rightarrow S(s) + H_2O \tag{6}$$

It is clear the chelated-iron is recycled in the whole process, which is therefore regarded as a pseudo-catalyst in the reaction of H_2S with O_2 [6]. Since the chelated-iron process is able to selectively remove H_2S from gas streams under mild operation condition and the produced elemental sulfur is very easily recovered, it has been extensively applied in the purification of various industrial gases.

So far, the greatest challenge in the chelated-iron process is related to the step of catalyst regeneration, which is critical to determine the efficiency of whole process. Catalyst regeneration is typically accomplished through the direct oxidation of chelated-Fe(II) by O_2, while the chelating agents are easily degraded in the presence of O_2 thus inducing considerable loss of chelating agents and generation of undesired products [5]. In addition, the catalyst regeneration is comprised of mass transfer of O_2 into chelated-Fe(II) solution and subsequent oxidation of Fe(II) by aqueous O_2. However, due to the low solubility of O_2 in water, very few O_2 is available in solution for the Fe(II) oxidation. As a result, the overall catalyst regeneration rate is dramatically limited by the slow gas–liquid mass transfer kinetics of O_2 [7].

The recently developed air-cathode fuel cell technology may provide an alternative approach for the catalyst regeneration in chelated-iron process, so that the problems related to chelate degradation and slow Fe(III) regeneration rate are anticipated to be alleviated. In a typical air-cathode fuel cell, the Fe(II) is spontaneously oxidized to the Fe(III) at the anode and at the cathode O_2 is reduced to water with electricity simultaneously generated [8,9]. The cell reaction is described as follows:

$$\text{Anode:} \quad Fe(II) \rightarrow Fe(III) + e^- \tag{7}$$

$$\text{Cathode:} \quad 1/4O_2(g) + H^+ + e^- \rightarrow 1/2H_2O \tag{8}$$
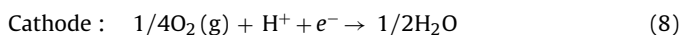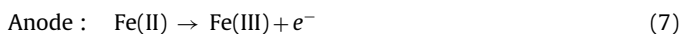
Obviously in the fuel cell the oxidation rate of Fe(II) is no longer restricted by the slow gas–liquid mass transfer kinetics of O_2. Moreover, since the oxidation of Fe(II) and reduction of O_2 are performed at separated electrodes, the problem of chelate degradation might be avoided as well. The electricity generation is an additional advantage of the fuel cell, given the up to nearly 100% of energy recovery efficiency from the electro-oxidation of Fe(II) reported by Cheng et al. [8,9].

In our previous study, we have achieved simultaneous sulfur and electricity recovery from sulfide in wastewater by incorporating the air-cathode fuel cell technology into the low-pH iron redox sulfur recovery process. However, such a process has encountered the drawback of iron precipitation due to the absence of chelating agents [10]. The chelating agents, such as EDTA and NTA, have been suggested to prevent iron species from precipitating while at the same time to maintain fluent reaction in conventional chelated-iron process [7,11]. Therefore, more effective sulfide removal is expected if the air-cathode fuel cell can be successfully applied in the chelated-iron process.

The objective of this work was thus to develop a novel fuel-cell-assisted chelated-iron process for effective H_2S removal from gas streams. The air-cathode fuel cell was employed to regenerate the iron catalyst in chelated-iron process, so that sulfur and electricity were simultaneously recovered from H_2S. Experiments were performed on a synthetic sulfide solution as well as H_2S-containing biogas, and feasibility of this fuel-cell-assisted chelated-iron process was comprehensively evaluated in terms of sulfur recovery, electricity generation and operational stability of system. Our results demonstrated that sulfur and energy could be effectively recovered from H_2S in the process, and that the iron catalyst regenerated by the fuel cell could be recycled for reuse.

2. Materials and methods

2.1. Chemicals

The sulfide stock solution was prepared by dissolving $Na_2S \cdot 9H_2O$ into distilled water which had been deoxygenated, and then concentration of sulfide was iodometrically determined [12]. The chelated-Fe(III) solution was prepared by dissolving pre-determined amounts of $FeCl_3 \cdot 6H_2O$ and chelating agent in 0.2 M of NaCl solution which contained 50 mM of $NaHCO_3$ as solution buffer. The sodium salts of nitrilotriacetic acid (NTA) and ethylene diamine tetraacetic acid (EDTA) were supplied as chelating agents. The molar ratio of Fe(III) to sulfide was 2.5:1 to 3.5:1 and molar ratio of chelating agent to Fe(III) was 1.5:1 to 3.0:1 according to the experimental design.

2.2. Operation of the fuel-cell-assisted chelated-iron process for sulfide removal

The efficiency and stability of the fuel-cell-assisted chelated-iron process were evaluated on a synthetic sulfide solution. The experiment on sulfide oxidation was carried out in a 250 mL air-tight glass reactor filled with 150 mL of chelated-Fe(III) solution. Prior to experiment, the reactor was firstly purged with a mixture of carbon dioxide (CO_2) and nitrogen (N_2) for 20 min to remove O_2, and then solution pH was adjusted by NaOH titration and CO_2 sparging [13]. Concentration of dissolved oxygen in the reactor was determined to be lower than 0.1 mg L^{-1} with a LeiCi JPB-607A oxygen analyzer (Shanghai INESA & Scientific Instrument CO. LTD). The reaction was started by adding the sulfide stocks into the reactor at a final concentration of 1.36 mM. After 12 h of reaction, the produced sulfur particles were collected by filtration and then washed with deionized water. The recovered sulfur was weighted after drying overnight at 50 °C. Next, the solution was moved into the anodic chamber of an air-cathode fuel cell under a N_2 atmosphere for the catalyst regeneration. The 175 mL glass-made single-chamber fuel cell reactor was applied in the experiment, with a 2 cm × 2.5 cm carbon paper (non wet-proofed, 090S, Toray Co., Japan) as anode and a 2 cm × 2 cm Pt-coated carbon paper as cathode [14]. The fuel cell was started by connecting the two electrodes with a 1 kΩ resistor. Voltage across the 1 kΩ resistor was recorded at 10 min intervals using a data acquisition system (USB2801, ATD Co., China) until it dropped below 1 mV. Experiments were conducted in duplicate at ambient temperature of 25 °C.

In the recycling experiment, the chelated-Fe(III) solution recovered from the fuel cell was firstly titrated by HCl to pH 5.0. Then solution pH was adjusted to a desired value by NaOH titration under continuous CO_2 sparging. After that, the chelated-Fe(III) solution was recycled back for the H_2S oxidation.

2.3. Treatment of H_2S in gaseous effluent from an anaerobic bioreactor

The fuel-cell-assisted chelated-iron process was applied to remove the H_2S from gaseous effluent of a 5 L upflow anaerobic sludge blanket (UASB) bioreactor. The UASB bioreactor was used to treat soybean-protein wastewater and generated 4.5 L of biogas per day, which contained ca. 2.4% of H_2S, 0.6% of O_2, 3.8% of N_2, 20.3% of CO_2, 65.1% of methane (CH_4) and 7.8% of hydrogen (H_2). The chemical absorption of H_2S was performed in a 250 mL glass adsorption