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The Removal of H_2S in Biogas from Concentrated Latex Industry with Iron(III)chelate in Packed Column

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Abstract

This work concernes biogas cleaning process in order to remove hydrogen sulfide (H_2S) from biogas. The H_2S was removed by means of chemical absorption using an iron-chelated solution catalyzed by Fe(III)EDTA, which converts H_2S into elemental sulfur (S). The experiments were performed using pilot packed column coupling with oxidizing scrubbing solution which provided both absorption and oxidation to remove H_2S from biogas. The experimental results indicated that the Fe(III)EDTA solution provided high ability to remove H_2S from biogas. The initial removal efficiency was greater than 90%. In order to maintain the removal efficiency, the efficient regeneration system for Fe(III)EDTA is required. In addition, no side reaction of Fe(III)EDTA with methane was found. Thus the removal of H_2S from biogas using Fe(III)EDTA solution with enough oxygen feed rate for Fe(III)EDTA regeneration is highly possible.

Keywords: H_2S, Fe(III)EDTA, Biogas, Packed column

1. Introduction

Biogas consists mainly of methane (CH_4) and carbon dioxide (CO_2), with a small amounts of water vapor, a trace amounts of hydrogen sulfide (H_2S), and the trace amounts of other impurities. Biogas is combust more cleanly than coal and produces more energy with less emission of carbon dioxide. The harvesting of biogas is an important role of waste management because the methane gas is a greenhouse gas with a greater global warming potential than carbon dioxide. However, H_2S is typically the most problematic contaminant because it is toxic and corrosive to most equipment. Additionally, combustion of H_2S leads to sulfur dioxide emissions, which have harmful environmental effects. Removing H_2S from biogas is recommended to protect downstream equipment, increase safety, and enable possible utilization of the biogas in more efficient technologies such as microturbines and fuel cells.

For these goals, numerous methodologies have been developed, and more than half a dozen have been demonstrated commercially. Among these methods are amine absorption, alkaline salt absorption, dry oxidation, liquid phase oxidation and demonstrated scavengers for gas purification and adsorption, and caustic absorption and chemical oxidation for end-of-pipe odor control [1]. Many commercial processes are available for the removal of H_2S from gaseous streams. Most of the processes use gas–liquid contactors in which the H_2S is absorbed into a complexing reagent to give either another dissolved sulfide containing components or elemental sulfur as a precipitate, [2]. In this process, iron, in its ferric state, is held in solution by chelating agents (i.e. ethylenediaminetetraacetate, EDTA). The intent of the process is to oxidize hydrosulfide (HS^-) ions to elemental sulfur by the reduction of the ferric (Fe(III)) iron to ferrous (Fe(II)) iron, and the subsequent reoxidation of the ferrous ions to ferric ions by contact with air. The chemistry of all chelated iron processes is given by Eq.1 to Eq. 6 [3] with (l) and (g) representing the liquid and vapor states, respectively.

$$H_2S(g) + H_2O(l) \rightarrow H_2S(l) \quad (1)$$

$$H_2S(l) \rightarrow H^+ + HS^- \quad (2)$$

$$HS^- + 2Fe^{3+}L \rightarrow S + 2Fe^{2+}L + H^+ \quad (3)$$

$$0.5\ O_2(air) + H_2O(l) \rightarrow 0.5\ O_2(l) + H_2O(l) \quad (4)$$

$$2Fe^{2+}L + 0.5\ O_2(l) + H_2O(l) \rightarrow 2Fe^{3+}L + 2OH^- \quad (5)$$

Overall Reaction

$$H_2S(g) + 0.5\ O_2(g) \xrightarrow{Fe} S + H_2O \quad (6)$$

From Eq. 1 to Eq. 6, it is interesting to note that the chelating agents (L) do not appear in the process chemistry, and in the overall chemical reaction, the iron cancels out. However, the chelated iron is required since it serves as two purposes in the process chemistry. First, it serves as an electron donor and acceptor, or in other words, a reagent. Secondly, it serves as a catalyst in accelerating the overall reaction. Because of this dual purpose, the iron is often called a "catalytic reagent". The chelating agent(s) do not take part at all in the process chemistry. The sole purpose of the chelating agents is to solubilize iron in water, thus it is possible to have an iron solution, [3].

The study determined the removal efficiency of H_2S removed from biogas in packed column which is the simplest and most commonly used approaches for gas scrubbing. The H_2S from biogas is absorbed into and reacted with the scrubbing liquor thus reduced H_2S concentration in biogas.

2. Materials and Method

2.1 Chemical

40 %w/w Ferric chloride solution ($FeCl_3$) and EDTA 4Na powder with commercial grade were purchased from L.B.Science LTD,Part. The H_2S containing biogas stream obtained from UASB (Up-flow Anaerobic Sludge Biodigester) of Chalong Latex Industry Co., Ltd. located in Songkhla province, Thailand.

2.2 Preparation of Fe(III)EDTA

A Fe(III)EDTA solution was prepared using the following recipe.

A 75 kg of EDTA 4 Na powder was dissolved into 200 L of water. A 40 L of 40% $FeCl_3$ solution was diluted to 200 L with water. The EDTA solution was then gentle rinse into the diluted $FeCL_3$ with continuous stirring. The 400 L of Fe(III)EDTA solution was obtained.

2.3 Apparatus

Figure 1. is a schematic of the packed column gas scrubbing system. The packed column is 2.2 m height, 0.5 m diameter, and 0.8 m bed section. The packing material is 5.0 cm Bio-Ball with 190 m^2/m^3 surface area per volume. The top of column hold a demister head packed with 5.0 cm Bio-Ball for removing entrained droplets from the gas stream. The entire packed column sits on top of a vessel which serves as the scrubbing solution reservoir.

The scrubbing solution (Fe(III)EDTA solution) was pumped from the storage tank and fed to the top of the packed column. The Fe(III)EDTA solution was then sprayed down on the packed bed, countercurrent to the gas flow. H_2S in the gas stream is absorbed into Fe(III)EDTA solution and transformed into sulfur, according eq. (1) to eq. (5). The spent Fe(III)EDTA solution was flow out from packed column into the sedimentation tank where sulfur is settled. The over flow of Fe(II)EDTA solution from sedimentation tank is regenerated into Fe(III)EDTA in a bubbling air tank and recycled back to the packed column.

The biogas containing H_2S is drawn from UASB that 100 m far from the packed column by the 2 hp blower.

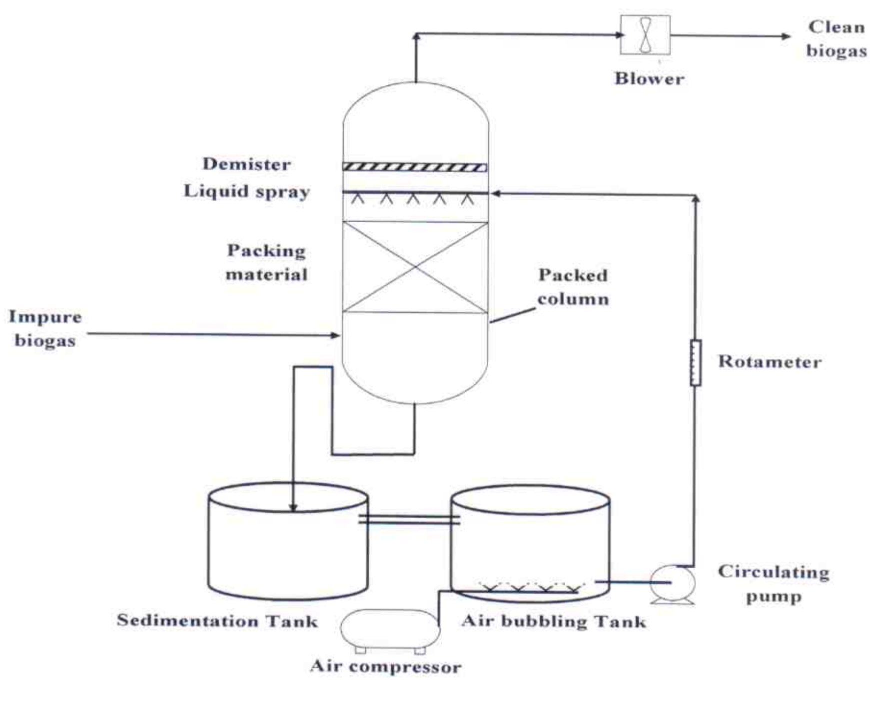

Figure 1. Schematic of the packed column gas scrubbing

2.4 Analysis

Samples of the inlet and outlet (or treated) biogas were taken during experimental tests. Biogas sample was collected in a series of impingers containing cadmium sulfate ($CdSO_4$) which turns to cadmium sulfide (CdS) as contacted with H_2S. The concentration of H_2S was then measured from amount of CdS formed by iodometric method [4].

CH_4 and CO_2 in biogas were determined by gas chromatography using ShinCarbon ST 100/120 micropacked column, expressed as a mass percentage.

Phenanthroline method was selected to determine Fe(II)EDTA concentration as mg Fe(II)/L.. The amount of iron in the samples was determined from the absorbance at 510 nm. Fe(III) in solution is reduced to the Fe(II) state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3, [4]

$$Fe(III) = Fe(total) - Fe(II) \quad (7)$$

3. Results and Discussion

The H_2S removal from biogas using packed column was carry out coincide with the oxidation reaction using iron chelate, Fe(III)EDTA, as an oxidative reagent. The H_2S removal efficiency was determined from H_2S inlet and outlet concentrations as given by Eq.8.

$$\%\,H_2S\ Removal = \frac{H_2S\ inlet - H_2S\ outlet}{H_2S\ inlet} \ x\ 100 \quad (8)$$

For photometric measurement, there are many species present in the sampling solution such as HS^-, S^{2-} Fe(III)EDTA and Fe(II)EDTA. The formation Fe(II) phenanthroline was analyzed also.. The Fe(II)chelate spectroscopic absorbance is small when compared to FE(III)chelate, [6]. The UV band of Na_2S, Fe(III)EDTA and Fe(II)phenanthroline are 210-260 nm, 230-400 nm and 370-590 nm respectively (Figure 2.). So, quantitative processing of Fe(II) and Fe(total) was achieved using the calibration curve at 510 nm wavelength (Figure3).

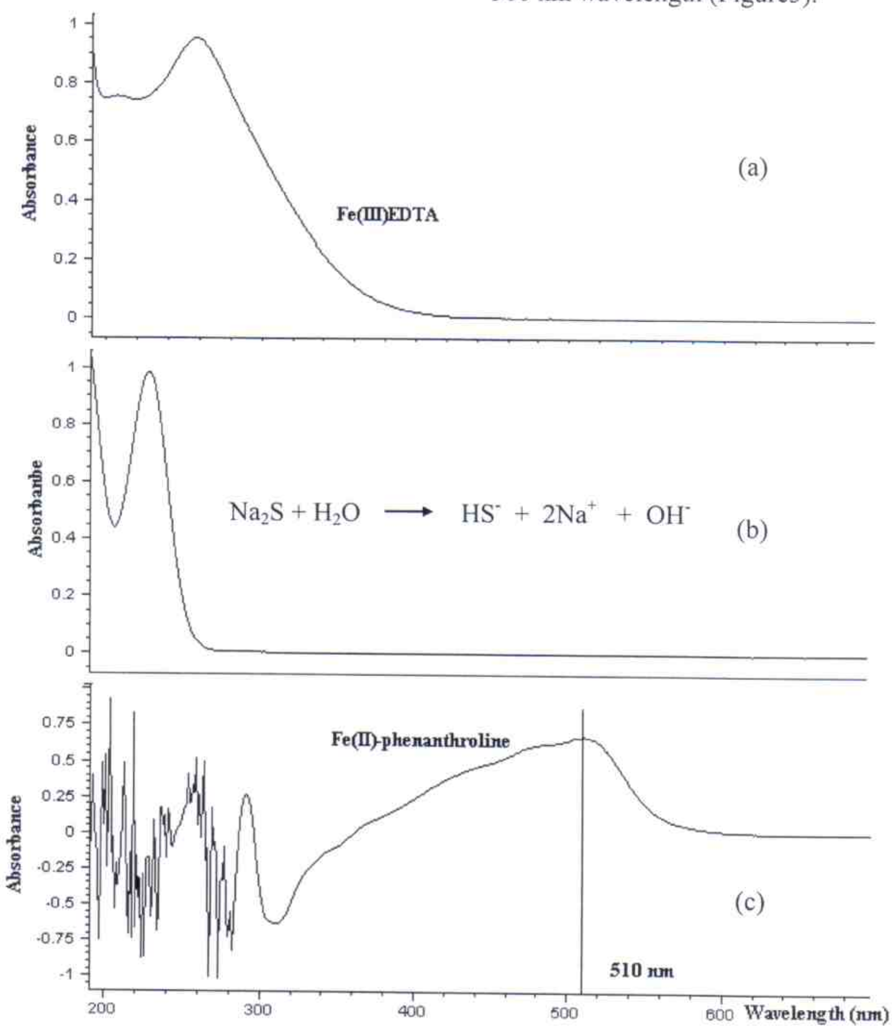

Figure 2. UV-VIS bands of (a) Fe(III)EDTA, (b) Na_2S and (c) Fe(II)-phenanthroline .

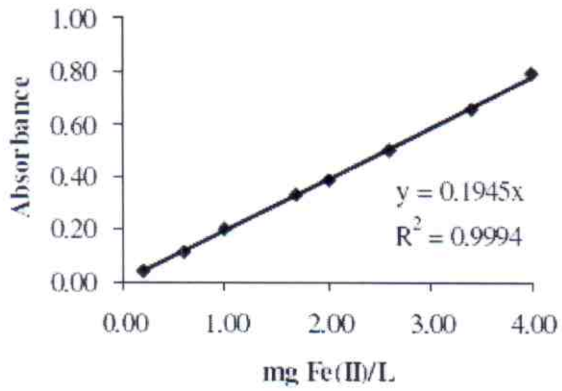

Figure 3. Standard curve for determine Fe

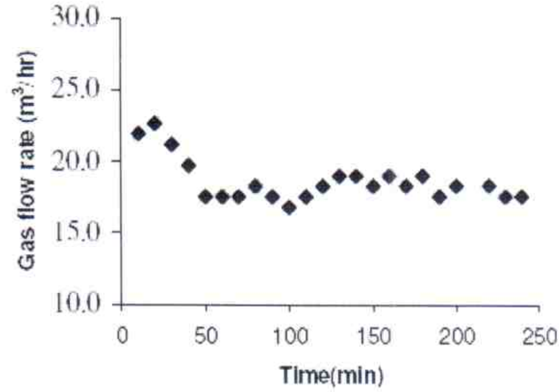

Figure 4. Biogas volumetric flow rate

The volumetric flow rate of biogas used in this study is fluctuated depending on biogas generation rate as shows in Fig. 4 resulting in the fluctuation of inlet H_2S concentration in the range of 19,000 to 29,000 mg/m^3 as depicted in Fig. 5.

The initial concentration of Fe(III)EDTA in the system was 15 g Fe(III)/L. A 350 L of Fe(III)EDTA solution was used in system with a gas flow rate of 2.4 m^3/hr. The experimental results indicated that this concentration of Fe(III)EDTA had ability to remove H_2S from biogas. The initial removal efficiency was greater than 90%. The removal efficiency was then decline before remain approximately at 75% for 3 hr and further decline to 40% within 4 hr. The main reason for the decreasing of the removal efficiency was the decreasing of Fe(III)EDTA concentration with time as plotted in Fig. 7. Although the high ionic strength or conductivity of solution caused increasing of H_2S absorption rate but the dissolved oxygen is decreasing [5]. The decreasing in Fe(III)EDTA concentration indicted that the Fe(III)EDTA consumption rate is higher than the regeneration rate.

In addition the increasing of a liquid temperature during the run as expressed in Fig. 8 may cause the decreasing of H_2S removal efficiency. The increasing in temperature not only decreases the H_2S absorption rate but also reduces the oxygen solubility in Fe(III)EDTA solution thus prevent the regeneration of Fe(III)EDTA . During the experimental run, a pH of solution was decreased from 7 to 6 which is suitable for H_2S absorption. Demmink and Beenackers [6] reported that the maximum H_2S removal using Fe(III)EDTA occur at pH 7 and at pH<6 most ferric EDTA is present in its hydrated form, $Fe^{3+}EDTA^{4-}$, which appears to have a relatively low reactivity to H_2S. At pH > 6, most ferric EDTA is present either as reactive hydroxylated species or as a *i*-oxo dimer, whose reactivity now appears to be high, [7]. Although high pH enhance H_2S absorption rate but the higher OH^- concentration , the more important the CO_2 absorption, the hydroxide ions enhancing the CO_2 mass transfer from the gas phase to liquid phase, [8]. Thus the CO_2 absorption may affect the H_2S absorption at pH higher than 7

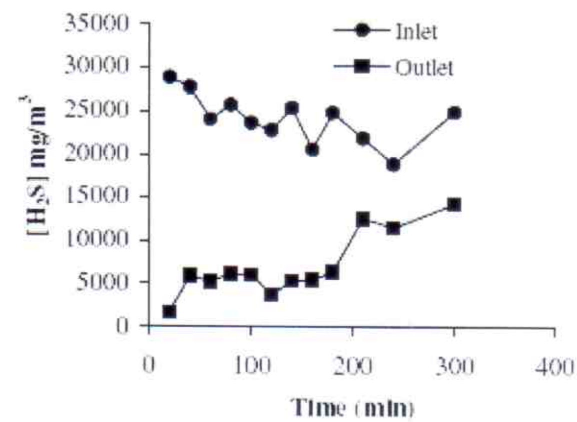

Figure 5. Inlet and outlet H_2S concentrations (mg/m^3)

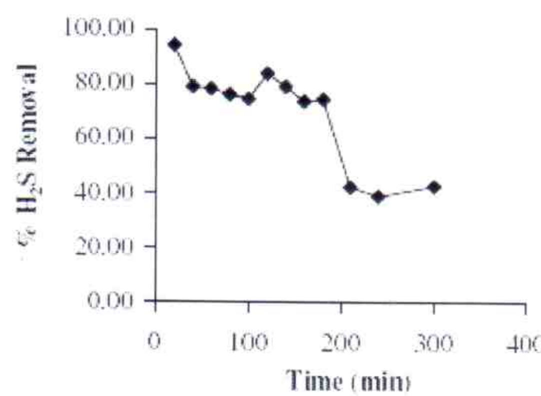

Figure 6. % H_2S Removal by oxidation reaction with Fe(III)EDTA

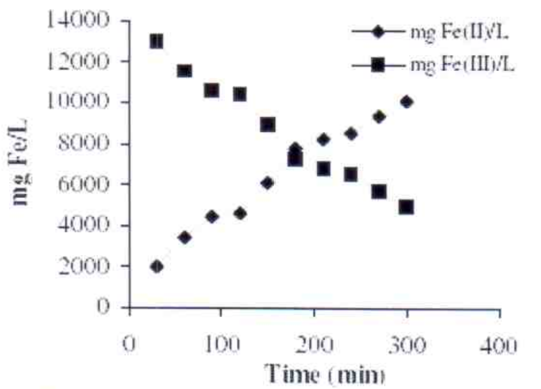

Figure 7. Fe(III)EDTA and Fe(II)EDTA concentration (mg/L) during run

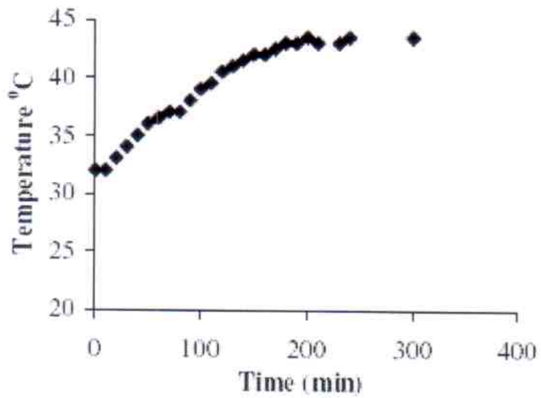

Figure 8. Temperature (^{0}C) during run

The compositions of the biogas at the inlet and the outlet of the system are shown in Table 1. It can be seen that no absorbing or reaction of CH_4 and CO_2 with Fe(III)EDTA solution were found as indicated by the inlet and outlet concentration are the same. This results agree well with previous work by Horikawa1*et al.* [9].

Table 1. Mass percent composition of inlet and outlet biogas.

Sample	% CH_4	% CO_2
Inlet	77.14	17.69
Outlet	76.66	17.12

4. Conclusions

This work concerned the H_2S removal from biogas by scrubbing and reacting with Fe(III)EDTA solution in packed bed column. The experimental results indicated that the Fe(III)EDTA solution provided ability to remove H_2S from biogas. The initial removal efficiency was greater than 90%. In order to maintain the removal efficiency, the efficient regeneration system for Fe(III)EDTA is required. In addition, no side reaction of Fe(III)EDTA with methane was found. Thus the removal of H_2S from biogas using Fe(III)EDTA solution with enough oxygen feed rate for Fe(III)EDTA regeneration is highly possible.

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