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Original Article

Removal of H_2S in biogas from concentrated latex industry with iron(III)chelate in packed column

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Abstract

This work concerns hydrogen sulfide (H_2S) removal from biogas produced from wastewater of concentrated latex rubber industry (CLRI). H_2S content in the biogas of CLRI is significantly high (i.e., up to 0.77 mol/m^3 or 26,000 ppm) due to the use of H_2SO_4 during rubber coagulation process. Attempts to treat biogas with high H_2S have not been found in literature reviews. In this work, a chemical oxidation using an iron-chelated solution catalyzed by Fe(III)EDTA is selected for the treatment of such high H_2S concentrations. Experiments were performed using an industry-size packed column with diameter and packed height of 0.5 and 0.8 m, respectively. The biogas flow rate and H_2S concentration were in the range of 5.16×10^{-3} - 5.61×10^{-3} m^3/s and 0.35-0.77 mol/m^3, respectively. Experimental results indicated that Fe(III)EDTA solution was effective at removing H_2S from biogas with a maximum removal efficiency of 97%. Suitable operating conditions, including Fe(III)EDTA concentration, flow of Fe(III)EDTA and air flow rate were determined. In addition, no side-reaction of Fe(III) EDTA with methane was found. Thus, chemical oxidation using an iron-chelated solution catalyzed by Fe(III)EDTA is a promising technology for H_2S removal from biogas produced from CLRI or other industries. Finally, a mathematical model of the absorption and the reaction between H_2S and Fe(III)EDTA in a packed column is proposed and verified against the experimental data. The results confirm the potential use of the model to design packed column for H_2S removal from biogas using absorption coupled with oxidation by Fe(III)EDTA.

Keywords: H_2S, Fe(III)EDTA, biogas, concentrated latex, packed column

1. Introduction

Anaerobic wastewater treatment is generally advantageous for removing organic matter from wastewater without consuming a large amount of electrical energy. A by-product of the anaerobic treatment is biogas which can be used as a renewable energy. Due to the energy crisis, industries are seeking various kinds of alternative energies, including biogas. Biogas can be produced from wastewater of many industries such as beverage, animal farm, starch, palm oil and rubber industries. Concentrated rubber latex industry (CRLI) is a major industry in the southern part of Thailand. Wastewater from CRLI is being used to produce biogas which is currently used as an indirect heat source for rubber block drying. Problem arises since wastewater of CRLI contains high sulfate content, up to 1000 mg/L (Rerngnarong, 2007), due to the use of sulfuric acid, H_2SO_4, in skim rubber production. Consequently, biogas produced from wastewater of CRLI is high in hydrogen sulfide (H_2S) (0.35-0.77 mol/m^3), thus, it could not be used as a fuel directly. In order to use biogas more effectively and safely for an engine, removal of H_2S from the biogas is necessary and an effective H_2S removal system is required.

Numerous processes for H_2S removal from biogas have been developed. Among these processes are amine absorption, alkaline absorption, caustic absorption, and

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chemical oxidation. Iron is an excellent oxidizing agent for the conversion of H_2S to elemental sulfur. Iron, in its ferric state, is held in a solution by a chelating agent (i.e. ethylenediaminetetraacetic acid (EDTA), (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), or nitrilotriacetic acid (NTA)). The intent of the process is to oxidize hydrosulfide (HS^-) ions to elemental sulfur by reduction of ferric (Fe(III)) iron to ferrous (Fe(II)) iron, and subsequently, the ferrous ions are then oxidized back to ferric ions by oxygen in the air. In recent years, gas desulfurization processes based on iron chelate chemistry have received increasing attention from both industrial and academic research groups. Demmink and Beenackers (1998), using a new penetration model for mass transfer parallel to chemical reaction, described the oxidative absorption of H_2S by using ferric chelates of EDTA and HEDTA. Iliuta and Larachi (2003) presented a modeling framework for the design of a scrubbing packed bed column for a bifunctional redox process for treating H_2S containing effluents arising from the kraft mill processes. The framework consisted of an exhaustive absorption-reaction-transport model which integrated both the oxidation of H_2S in reactive ferric chelate solutions of EDTA and the regeneration of ferrous chelates resulting from oxidation of H_2S. The kinetic effect of electrolytes and dynamic of pH on the oxidation of H_2S with Fe(III)CDTA in anoxic condition were determined by Piché and Larachi (2006a) and Piché and Larachi (2006b). They proposed a reaction mechanism of H_2S oxidation on both effects. Demmink *et al*. (1998) reported that freshly precipitated sulfur particles acted as catalyst for H_2S absorption into aqueous solution of Fe-NTA and Demmink *et al.* (2002) described this phenomenon by developing a model based on Higbie's penetration theory. Horikawa *et al*. (2004) used Fe(III)EDTA to remove H_2S from synthetic biogas using a lab scale randomly packed column. The chelated iron process is applied to remove H_2S from gas streams in various industries, such as: natural gas processing, geothermal plants, refinery fuel gas, municipal odor control, landfill gas and municipal waste gasification.

Although much effort has been put into the development of H_2S removal process using wet-scrubber with iron-chelate oxidation as mention above, previous works, however, have been focused on H_2S removal from atmospheric emissions of sulfur or sulfate related industries such as natural gas and oil refining industry and pulp and paper industry. Only a few works were deal with H_2S removal from biogas and they were investigated using synthetic biogas or mixture of H_2S and balance gas such as N_2, CO_2 and air. It is noteworthy that iron-chelated route has never been explored with real biogas produced from wastewater of concentrated rubber latex industry where H_2S concentration is very high compared to H_2S content in atmospheric emissions of industries, or in biogas produced from others sectors such as animal farms and the palm oil industries.

Since concentration of H_2S in gas stream is known to play an important role on H_2S removal efficiencies (Piché *et al*., 2005), study of H_2S removal from biogas of concentrated rubber latex industry will provide useful information to operate and design wet-scrubbers employing iron-chelate process under high H_2S concentration.

The aim of this work was to remove H_2S from biogas of CRLI using industry-size packed column which can handle H_2S concentration up to 0.77 mol/m^3. Suitable operating conditions (i.e., Fe(III)EDTA concentration, flow of Fe(III)EDTA and air) for this case are determined to seek highest removal efficiency. A mathematical model describing absorptions and reactions between H_2S and Fe(III)EDTA in packed column under high H_2S concentration are also proposed.

2. Materials and Method

2.1 Chemicals

40% w/w Ferric chloride solution ($FeCl_3$) and EDTA·4Na powder of commercial grade were purchased from L.B. Science Ltd. Biogas was obtained from UASB (Up-flow Anaerobic Sludge Biodigester) of CRLI located in Songkhla province, Thailand.

2.2 Preparation of Fe(III)EDTA

A Fe(III)EDTA solution was prepared using the following recipe: 75 kg of EDTA·4Na powder was dissolved into 0.20 m^3 of water. 0.04 m^3 of 40% $FeCl_3$ solution was diluted to 0.20 m^3 with water. The EDTA solution was then gently rinsed into the diluted $FeCl_3$ with continuous stirring. 0.40 m^3 of Fe(III)EDTA solution was obtained with a concentration of 350 mol/m^3.

2.3 Apparatus

Figure 1 is a schematic diagram of the H_2S removal system which comprises of a packed column, a sedimentation tank, and a regeneration tank. The packed column is 2.2 m high, 0.5 m in diameter with 0.8 m packed section thickness. The packing material is composed of 5.0 cm Bio-Balls with a 190 m^2/m^3 surface area per volume. The top of column holds a demister head packed with 5.0 cm Bio-Balls for removing entrained droplets from the gas stream. The entire packed column sits on top of a vessel which serves as the sedimentation tank.

The scrubbing solution (Fe(III)EDTA solution) was pumped at a flow rate of 6.67×10^{-4} m^3/s from the regeneration tank and fed into the packed column at the top, counter-current to the biogas which was drawn from the UASB and fed to the packed column at the bottom with a flow rate of 5.16×10^{-3} - 5.61×10^{-3} m^3/s. H_2S in the biogas stream was absorbed into Fe(III)EDTA solution and transformed into a sulfur compound. The spent Fe(III)EDTA solution flowed out of the bottom of the packed column into the sedimentation tank where sulfur got settled and separated. The overflow of Fe(II)EDTA solution from the sedimentation tank was regenerated into Fe(III)EDTA using air bubbling in the

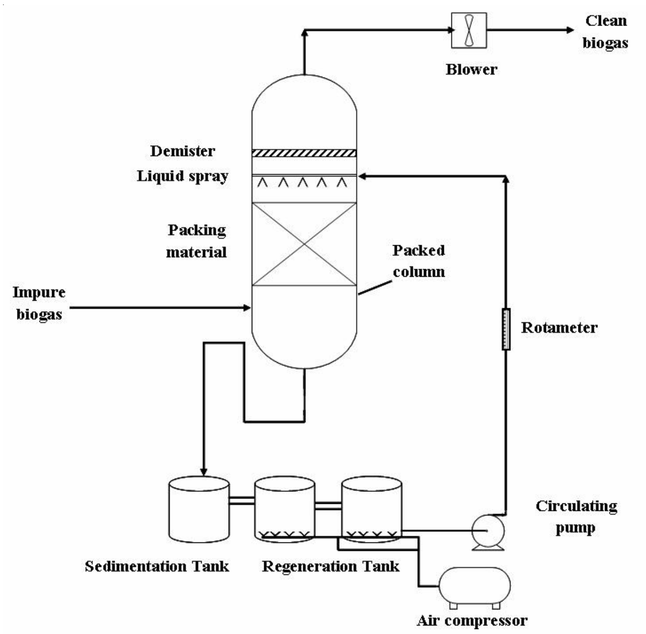

Figure 1. Schematic diagram of the gas scrubbing packed column for H_2S removal from biogas.

regeneration tank and recycled back to the packed column.

The concentration of H_2S in biogas produced by UASB from the CRLI varied from day to day depending on wastewater characteristics but remaining constant throughout each day. Thus, for each experiment, the inlet H_2S concentration was considered constant throughout the experimental time of 6 h. The initial H_2S concentration and the other experimental conditions, for each run are listed in Table 1.

2.4 Analysis

Samples of biogas at the inlet and the outlet of the packed column were taken during each experimental run using a gas sampling set which consists of an air sampling pump and a series of impingers containing a solution of Cadmium sulfate ($CdSO_4$). The biogas sample was drawn into the $CdSO_4$ solution which turned into Cadmium sulfide (CdS) upon contacting with H_2S. The concentration of H_2S was then measured from the amount of CdS formed by the iodometric method (EPA Method 11). CH_4 and CO_2 concentrations in the biogas were determined by gas chromatography using the ShinCarbon ST 100/120 micropacked column, expressed as a mass percentage.

The Fe(II)EDTA concentration, $C_{Fe(II)EDTA}$ in the inlet scrubbing liquid, as mol Fe(II)/m^3, was determined by Phenanthroline method. The amount of iron was determined from the absorbance at wavelength of 510 nm using HP 8453 UV-VIS Spectrophotometer. Fe(III) in the solution is reduced to Fe(II) state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3, (APHA, 1985). The total iron concentration, $C_{Fe\text{-}EDTA}$ is obtained and Fe(III)EDTA concentration, $C_{Fe(III)EDTA}$ can be determined by the following Equation:

$$C_{Fe(III)EDTA} = C_{Fe\text{-}EDTA} - C_{Fe(II)EDTA} \tag{1}$$

3. Results and Discussion

3.1 Iron analysis

Scrubbing liquid contains a number of species which can absorb UV light such as HS^-, S^{2-}, Fe(III)EDTA and Fe(II)EDTA. To analyze the iron concentration remaining in the scrubbing liquid by photometric measurement, the suitable wavelength must be determined. Figure 2 shows the UV band of Na_2S (represent HS^-, S^{2-} species), Fe(III)EDTA and Fe(II)-phenanthroline. It is clearly shown from Figure 2 that all species absorb UV light at difference wavelengths. The UV bands of Na_2S (represent HS^-, S^{2-} species) and Fe(III)EDTA were 210-260 nm, 230-400 nm, respectively, while that of Fe(II)-phenanthroline was found at 370-590 nm. Thus, $C_{Fe(II)EDTA}$ and $C_{Fe\text{-}EDTA}$ in scrubbing liquid was determined at the wavelength of 510 nm. The calibration curve for $C_{Fe(II)EDTA}$ and $C_{Fe\text{-}EDTA}$ measurements at 510 nm is shown in Figure 3.

3.2 H_2S Removal efficiency

The removal of H_2S from biogas using a packed column was carried out coinciding with the oxidation reaction using an iron chelate, Fe(III)EDTA, as an oxidative reagent. The H_2S removal efficiency (%) was determined from the H_2S inlet concentrations, $C_{H_2S}(g)_{in}$ and H_2S outlet concentrations, $C_{H_2S}(g)_{out}$ as given by Equation (2).

Table 1. Packed bed operating conditions.

Run . No	$G \times 10^3$ (m^3/s)	$C_{H_2S}(g)_{,in}$ mol/m^3	$C_{Fe(III)EDTA,in}$ (mol/m^3)	Fe-EDTA Volume (m^3)	Air flowrate (m^3/min)
1	5.61	2005	59.1	0.35	0.07
2	5.44	2408	268.6	0.35	0.07
3	5.52	1246	268.6	0.50	0.30
4	5.16	2485	268.6	0.50	0.30

$C_{Fe(III)EDTA,in}$: initial concentration of Fe(III)EDTA

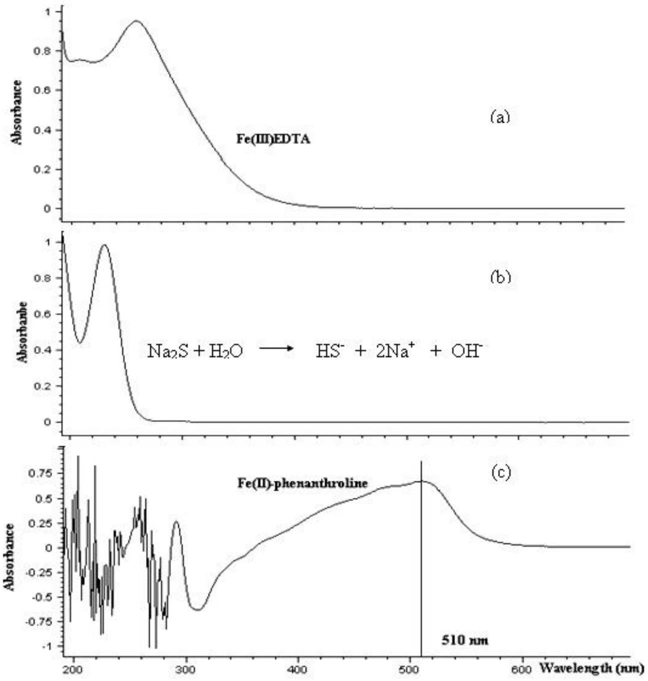

Figure 2. UV-VIS bands of (a) Fe(III)EDTA, (b) Na_2S and (c) Fe(II)-phenanthroline.

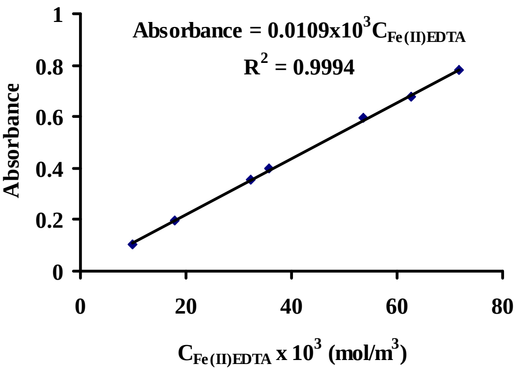

Figure 3. Standard curve for Fe determination by photometric method at 510 nm.

$$H_2S\ removal\ \ efficiency(\%) = \frac{C_{H_2S}(g)_{,in} - C_{H_2S}(g)_{,out}}{C_{H_2S}(g)_{,in}}\ x\ 100 \tag{2}$$

Figure 4 shows the H_2S removal efficiency (%) of four experiments for various operating conditions. For Run No.1, the H_2S removal efficiency for the first 20 minute was nearly 90%. Efficiency then continuously decreased with time. To improve the removal efficiency, the concentration of Fe(III)EDTA solution was increased to 268.8 mol/m^3 in Run No. 2. However, the H_2S concentration in the second run, 0.71 mol/m^3 was also higher than that presented in the first run, 0.57 mol/m^3. The H_2S removal efficiency of Run No. 2 is also shown in Figure 4. As compared to Run No.1, the removal efficiency of Run No.2 was slightly improved since it did not steadily decrease. The initial H_2S removal efficiency was also greater than 90%. As time increased, however, the H_2S removal efficiency decreased before it remained approximately constant at 75% for 3 h and further declined to 40% within 4 h. The main reason for the decreasing of the removal efficiency was the decreasing of Fe(III)EDTA concentration with time, as depicted in Figure 5. The decreasing in Fe(III)EDTA concentration indicated that the Fe(III)EDTA consumption rate was higher than the regeneration rate. Although the high ionic strength or conductivity of the solution caused the H_2S absorption rate to increase, the dissolved oxygen content also decreased (APHA, 1985). In order to maintain the H_2S removal efficiency of our system, the air flow rate was increased. The air flow rate of Run No.3 was increased to 0.30 m^3/min. As shown in Figure 4, H_2S removal efficiency was significantly improved. The H_2S removal efficiency can be held constant at approximately 97% throughout the experimental time of 6 h. The same results were obtained in Run No.4 although the H_2S inlet concentration was about two times higher than that of Run No.3. The results from Run No.3 and No.4 confirmed that air bubbling at a flow rate of 0.30 m^3/min is enough for Fe(III)EDTA regeneration, This is supported by the only slight decrease in Fe(III)EDTA concentration with time, as illustrated in Figure 5.

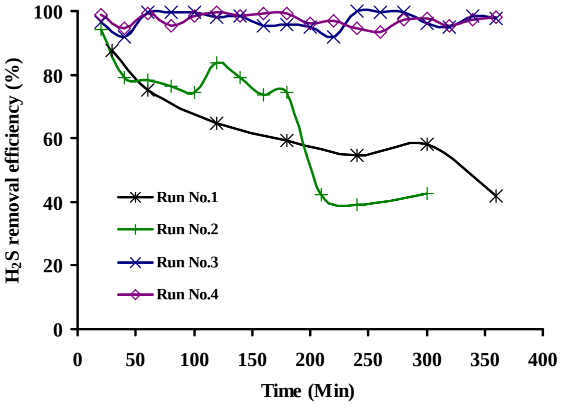

Figure 4. H_2S removal efficiency (%) with time in the oxidation reaction with Fe(III)EDTA at various conditions
(Run No. 1: G = 5.61 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 2005 mol/m^3, $C_{Fe(III)EDTA,in}$ = 59.1 mol/m^3, Volume of Fe-EDTA = 0.350 m^3 and Air flowrate = 0.07 m^3/min;
Run No. 2: G = 5.44 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 2408 mol/m^3, $C_{Fe(III)EDTA,in}$ = 268.6 mol/m^3, Volume of Fe-EDTA = 0.350 m^3 and Air flowrate = 0.07 m^3/min;
Run No. 3: G = 5.52 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 1246 mol/m^3, $C_{Fe(III)EDTA,in}$ = 268.6 mol/m^3, Volume of Fe-EDTA = 0.50 m^3 and Air flowrate = 0.30 m^3/min;
Run No. 4: G = 5.16 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 2485 mol/m^3, $C_{Fe(III)EDTA,in}$ = 268.6 mol/m^3, Volume of Fe-EDTA = 0.50 m^3 and Air flowrate = 0.30 m^3/min)

In addition, increasing the liquid temperature during the run, as shown in Figure 6, may cause a decrease in H_2S

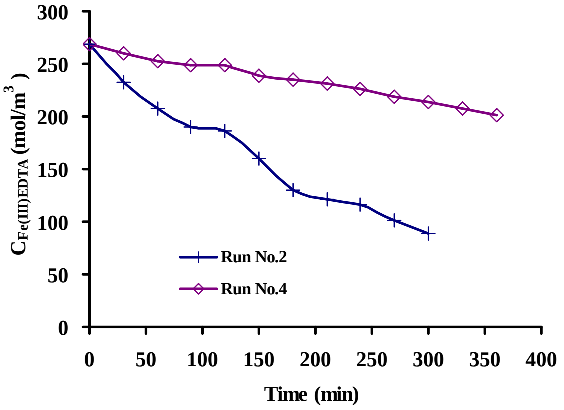

Figure 5. Change of Fe(III)EDTA concentration (mol/m^3) as function of reaction time for Run No. 2 and Run No. 4. (Run No. 2: G = 5.44 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 2408 mol/m^3, $C_{Fe(III)EDTA,in}$ = 268.6 mol/m^3, Volume of Fe-EDTA = 0.350 m^3 and Air flowrate = 0.07 m^3/min; Run No.4: G = 5.16 x10^{-3} m^3/s, $C_{H_2S}(g)_{,in}$ = 2485 mol/m^3, $C_{Fe(III)EDTA,in}$ = 268.6 mol/m^3, Volume of Fe-EDTA = 0.50 m^3 and Air flowrate = 0.30 m^3/min)

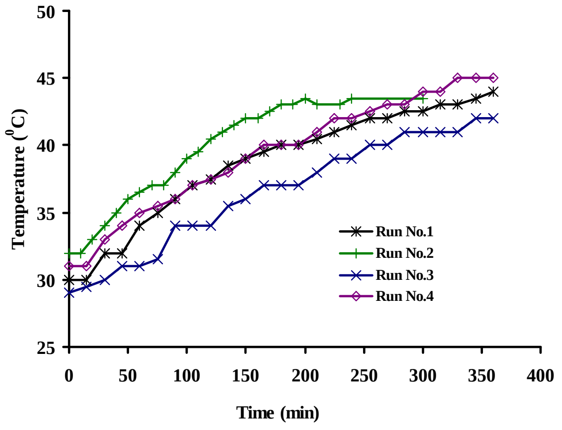

Figure 6. Temperature profile of the scrubbing liquid during the reaction period

removal efficiency. The increase in temperature not only decreases the H_2S absorption rate but also reduces oxygen solubility in Fe(III)EDTA solution, thus decreasing the regeneration rate of Fe(III)EDTA. During the experimental run, pH of the solution decreased from 7 to 6 which is suitable for H_2S absorption as described by Demmink and Beenackers (1998). A high pH enhances H_2S absorption rate but a higher OH^- concentration also enhances the CO_2 absorption (Couvert *et al.*, 2006). Thus the CO_2 absorption may affect the H_2S absorption at a pH higher than 7.

3.3 Compositions of inlet and outlet biogas.

The compositions of biogas at the inlet and the outlet of the system are shown in Table 2. It can be concluded that Fe(III)EDTA did not absorb or react with CH_4 or CO_2 as their inlet and outlet concentrations did not change. These results agree well with previous work by Horikawa *et al.* (2004).

Table 2. Mass percent of CH_4 and CO_2 in the biogas at the inlet and outlet

Sample	%CH_4	%CO_2
Inlet	77.14	17.69
Outlet	76.66	17.12

3.4 Absorption and reaction model for H_2S removal by oxidation with Fe(III)EDTA in packed column

In order to determine the height of the packed column when dealing with both absorption and reaction of H_2S with Fe(III)EDTA, the packed column is considered as a packed bed reactor where absorption and reaction are taking place in series. A number of mass transfer and reaction steps were involved. Details of the model development are described step by step as follows.

The rate of H_2S transfer from the bulk gas to the gas-liquid interface can be given by Equation (3) (Fogler, 1999).

$$-r_{H_2S} = k_G a_i [C_{H_2S}(\mathrm{g}) - C_{H_2Si}(\mathrm{g})] \tag{3}$$

where, $-r_{H_2S}$ is a mass transfer rate in mol/m^3·s, a_i is a gas-liquid interfacial area per volume of bed in m^2/m^3, $C_{H_2S}(\mathrm{g})$ is the concentration of H_2S in bulk gas phase (mol/m^3), $C_{H_2Si}(\mathrm{g})$ is the concentration of H_2S in the gas phase at the gas-liquid interface (mol/m^3), and k_G is a gas film mass transfer coefficient in m/s. k_G can be calculated by Equation (4) (Christie, 1993).

$$k_G = \frac{0.4548}{\varepsilon}\frac{G}{A}(Re_G)^{-0.4069}(Sc_G)^{-2/3} \tag{4}$$

where Re_G and Sc_G are the Reynolds number and the Schmidt number in the gas phase, respectively. These are defined in Equations (5) and (6).

$$Re_G = \frac{W_G d_P}{\mu_G} \tag{5}$$

$$Sc_G = \frac{\mu_G}{\rho_G D_{H_2S,G}} \tag{6}$$

where, W_G is the superficial mass gas velocity in kg/m^2·s, d_P is the nominal packing diameter (m), μ_G is the gas viscosity (Pa·s), ρ_G is the gas density (kg/m^3) and $D_{H_2S,G}$ is the diffusivity of H_2S in the gas (m^2/s). $D_{H_2S,G}$ can be estimated from the empirical equation of diffusivity for a binary gas mixture at low temperature as shown in Equation (7) (Bird *et al.*, 2002).

$$\frac{PD_{H_2S,G}}{(p_{C,H_2S}\,p_{C,CH_4})^{1/3}(T_{C,H_2S}T_{C,CH_4})^{5/12}(1/M_{H_2S}+1/M_{CH_4})^{1/2}} =$$

$$2.745x10^{-4}\left(\frac{T}{\sqrt{T_{C,H_2S}T_{C,CH_4}}}\right)^{1.823} x10^{-4} \qquad (7)$$

where P is pressure (atm), p_{C,H_2S} is the critical pressure (atm) of H_2S, p_{C,CH_4} is the critical pressure (atm) of CH_4, T_{C,H_2S} is the critical temperature (K) of H_2S, T_{C,CH_4} is the critical temperature (K) of CH_4, and M_{H_2S} and M_{CH_4} are the molecular weights of H_2S and CH_4, respectively.

C_{H_2Si}(g) is related to the concentration of H_2S in the liquid phase at the interface. C_{H_2Si} which is described by Equation (8) (Fogler, 1999).

$$C_{H_2Si} = C_{H_2Si}(\mathrm{g})/He \qquad (8)$$

Here, He is defined as H_{H_2S} $/RT$ where H_{H_2S} is the Henry's law constant in Pa m^3/mol, R is the gas constant (m^3 Pa/mol K) and T is the temperature (K).

The rate of absorption of H_2S at the liquid film is given by Equation (9).

$$-r_{H_2S} = k_L a_i E_{H_2S}[C_{H_2S_i} - C_{H_2S}] \qquad (9)$$

where, C_{H_2S} is the concentration of H_2S in bulk liquid phase (mol/m^3), E_{H_2S} is the liquid film enhancement factor which is defined in Equation (10) (Levenspiel, 1999).

$$E_{H_2S} = \frac{\text{rate of take up of } H_2S \text{ when reaction occurs}}{\text{rate of take up of } H_2S \text{ for straight mass transfer}} \qquad (10)$$

k_L is the liquid film mass transfer coefficient (m/s) which can be calculated from the liquid properties and the absorber characteristics as expressed by Equation (11) (Onda *et al.*, 1968).

$$k_L = 0.0051\left(\frac{\rho_L \nu_L}{a_i \mu_L}\right)^{2/3}\left(\frac{\mu_L}{\rho_L D_{AL}}\right)^{-1/2}\left(\frac{\rho_L}{\mu_L g}\right)^{-1/3}\left(a_T d_P\right)^{4/10} \qquad (11)$$

where, ν_L is the gas mass flux in kg/m^2·s, a_T is the specific surface area (m^2/m^3), μ_L is the liquid viscosity (Pa·s), ρ_L is the liquid density (kg/m^3), g is the gravitational acceleration (m/s^2) and $D_{H_2S,L}$ is the diffusivity of H_2S in liquid. $D_{H_2S,L}$ can be obtained from Wubs (1994).

The reaction of H_2S with Fe(III)EDTA took place in bulk liquid phase and was assumed to be the first order with respected to H_2S and Fe(III)EDTA as given by Equation (12) (Deberry, 1993).

$$-r_{H_2S} = k_r f_l C_{H_2S} C_{Fe(III)EDTA} \qquad (12)$$

where, k_r is the reaction rate constant (m^3/mol·s), $C_{Fe(III)EDTA}$ is the concentration of Fe(III)EDTA in bulk liquid (mol/m^3) and f_l is the ratio of volume of liquid to the reactor volume, which is 0.1.

Combining equation (3) to (12), the reaction rate of H_2S can be described as,

$$-r_{H_2S} = RC_{H_2S}(g)$$

where R is defined as (Levenspiel, 1999).

$$R = \left(\frac{1}{k_G a_i} + \frac{He}{k_L a_i E_{H_2S}} + \frac{He}{k_r C_{Fe(III)EDTA} f_l}\right)^{-1} \qquad (13)$$

The reaction rate is related to the height of the absorption tower, h, through the material balance of H_2S, as given by Equation (14) (Levenspiel, 1999).

$$h = \frac{G}{AR} ln\left(\frac{C_{H_2S}(g)_{,in}}{C_{H_2S}(g)_{,out}}\right) \qquad (14)$$

where G is the gas flow rate (m^3/s), A is the cross-sectional area of the tower (m^2), $C_{H_2S}(g)_{,in}$ is the concentration of H_2S in biogas at the tower inlet (mol/m^3), $C_{H_2S}(g)_{,out}$ is the concentration of H_2S in biogas at the tower outlet (mol/m^3).

The Hatta modulus, M_H (Hatta, 1932) is modified for this study and given by Equation (15).

$$M_H = \frac{\sqrt{k_r C_{Fe(III)EDTA} D_{H_2S,L}}}{k_L} \qquad (15)$$

From the experimental data, and other parameters at hand, we can calculate the M_H for each experimental run. The values of M_H, and the values of the other parameters required to calculate M_H, are listed in Tables 3 and 4.

The enhancement factor for an infinitely fast reaction, E_i, is defined for absorption and reaction by Levenspiel (1999) and is applied to this work with Equation (16).

$$E_i = 1 + \frac{D_{Fe(III)EDTA,L} C_{Fe(III)EDTA} H_{H_2S}}{b D_{H_2S,L} p_{H_2Si}} \qquad (16)$$

where $D_{Fe(III)EDTA,L}$ is the diffusion coefficient of Fe(III)EDTA in m^2/s, b is a stoichiometric coefficient for Fe(III)EDTA, and p_{H_2Si} is the inlet partial pressure of H_2S. The E_i values can be calculated for each experimental run. The obtained E_i values and values of other parameters for calculating E_i, are shown in Tables 3 and 4. Once E_i and M_H are known E_{H_2S} for each run is computed from Equation (17) (Levenspiel, 1999).

$$E_{H_2S} = M_H\left(1 - \frac{M_H - 1}{2E_i}\right) \qquad (17)$$

With the values of E_{H_2S} at hand, the values of R can be obtained according to Equation (13). The values of the other parameters including $k_G a_i, k_L a_i, k_r, f_l$ and other related parameters required for the determination of R, are listed in Table 3 and Table 4.

Finally, the height of absorption tower, h can be calculated from Equation (14) where the values of G, A, $C_{H_2S}(g)_{,in}$ and $C_{H_2S}(g)_{,out}$ were measured experimentally. The calculated

Table 3. The actual and the predicted packed height and other related parameters

Run No.	$k_L a_i$ x 10^3(s^{-1})	$k_g a_i$ (s^{-1})	M_H	E_i x10^{-3}	E_{H_2S}	R	$H_{predicted}$ (m)	h_{actual} (m)
1	3.19	0.265	27.43	1.8	27.22	0.08	1.26	0.8
2	3.28	0.261	56.95	6.5	56.70	0.126	0.78	0.8
3	3.28	0.263	56.95	13.0	56.82	0.126	0.78	0.8
4	3.28	0.253	56.95	5.9	56.68	0.124	0.75	0.8

Table 4. Parameter values for absorption and reaction modeling

Definition	Unit	Symbol	Value	Reference
Gas viscosity	Pa·s	μ_G	0.005	
Gas density	kg/m^3	ρ_G	1.15	
Liquid viscosity	Pa·s	μ_L	0.005	
Liquid density	kg/m^3	r_L	1210	
Critical pressures of H_2S	atm	p_{C,H_2S}	88.2	Bird *et al.*, 2002
Critical pressures of CH_4	atm	p_{C,CH_4}	45.8	Bird *et al.*, 2002
Critical temperatures of H_2S	K	T_{C,H_2S}	373.0	Bird *et al.*, 2002
Critical temperatures of CH_4,	K	T_{C,CH_4}	191.1	Bird *et al.*, 2002
Molecular weight of H_2S	g/gmol	M_{H_2S}	34	
Molecular weight of CH_4	g/gmol	M_{CH_4}	16	
Henry's law constant of H_2S in Fe(III)EDTA	Pa m^3/mol	H_{H_2S}	1.95x10^3	Deberry, 1993
Gas constant	m^3 Pa /mol K	R	8.314	
Temperature	K	T	303	
Nominal packing diameter	m	d_P	0.05	
Gas-liquid interfacial area	m^2/m^3	a_i	100	
Specific surface area	m^2/m^3	a_T	190	
Gravitational acceleration	m/s^2	g	9.8	
Diffusivity of H_2S in liquid	m^2/s	$D_{H_2S,L}$	1.44x10^{-9}	Wubs, 1994
Diffusion coefficient of Fe(III)EDTA	m^2/s	$D_{Fe(III)EDTA,L}$	0.54x10^{-9}	Wubs, 1994
Reaction rate constant	m^3/mol·s	k_r	9	Deberry, 1993
Stoichiometric coefficient of Fe(III)EDTA		b	2	Deberry, 1993

h, h_{cal} were then compared with the actual h, h_{actual} used in the experiment, as shown in Table 3, and it is shown that the calculated values agree well with the actual values - implying that the proposed model explains the absorption and reaction phenomena inside the packed column quite well. Thus, the potential use of the model for designing the packed column for H_2S removal from biogas using absorption coupled with oxidation by Fe(III)EDTA is confirmed.

3.5 Comparison with other literatures in terms of the overall height of a gas film transfer unit, H_{OG} and the overall number gas film transfer unit, N_{OG}

This experiment involves the absorption of H_2S gas from biogas by contacting it with an iron chelated catalyst through a packed column. The biogas used in the trials was approximately 1-3% H_2S, so it will be treated as a dilute mixture. The measure of the efficiency of the absorption process can be expressed in terms of the overall height of the gas film transfer unit, H_{OG} (m). The smaller H_{OG} is, the more efficient the absorption process will be. H_{OG} is a function of the overall number gas film transfer unit, N_{OG}. This quantity represents the degree of difficulty of the absorption process. A high N_{OG} value corresponds to a difficult separation.

The N_{OG} value can be calculated using a simplified method. The method assumes that the gas components are dilute and that components have 'unlimited' solubility in the liquid phase. Chemical reactions in the liquid phase reduce the equilibrium partial pressure of a solute over the solution, which greatly increases the driving force for mass transfer. The limiting case involves the assumption of an instantaneous, irreversible chemical reaction. This case corresponds

Table 5. Comparison of H_{OG} and N_{OG} values to other literatures.

Reference	Moosavi *et al.* (2005)	Horikawa *et al.* (2004)	Chen *et al.* (2001)	This study
System	H_2S-Air	Synthetic biogas	H_2S-Air	Biogas
Oxidant	NaOCl, H_2O_2	Fe(III)EDTA	NaOCl/NaOH	Fe(III)EDTA
Superficial H_2S mass velocity, W_{H_2S} (g /m^2·s)	0.017	0.041	0.088	0.690
N_{OG}, m	5.30	2.30	6.91	3.58
H_{OG}, m	0.13	0.16	0.31	0.22
H_{OG}/W_{H_2S}	7.65	3.90	3.52	0.32

to the maximum driving force, due to the reduction of the equilibrium partial pressure to zero (the reaction plane coincides with the interface). This is a reasonable assumption when iron chelate is used to oxidize the H_2S. For dilute systems, N_{OG} can be calculated using Equation 18 (Rafson and Harold, 1998).

$$N_{OG} = ln\left(\frac{C_{H_2S}(g)_{,in}}{C_{H_2S}(g)_{,out}}\right) \tag{18}$$

Precise values for the H_2S composition at these points are crucial. Small discrepancies in these values could lead to large errors. H_{OG} is then calculated from $N_{OG,}$ as expressed by Equation 19.

$$H_{OG} = h/ N_{OG} \tag{19}$$

The calculated H_{OG} and N_{OG} values of our system are compared with other values found from the literature, as shown in Table 5. The gas mass flow rate in our system is 10-40 times higher than those found in the literature. The gas mass flow rate also plays an important role in the separation process. We account for the superficial H_2S mass velocity, W_{H_2S}, by defining the ratio H_{OG}/W_{H_2S} which includes the effect of mass flow rate on separation efficiency. It can be seen that the H_{OG}/W_{H_2S} value of our system is lower than those previously reported, indicating that the system provides better efficiency for H_2S removal even at high H_2S concentrations.

4. Conclusions

Biogas produced from wastewater of concentrated latex industry contains a high level of H_2S. A low cost H_2S removal system is needed to treat the biogas before it can be utilized. A chemical oxidation using an iron-chelated solution catalyzed by Fe(III)EDTA in a packed column is proposed for H_2S removal from the biogas. The experimental results show that combination of absorption and oxidation by iron-chelated solution catalyzed by Fe(III)EDTA can remove H_2S from biogas with an efficiency up to 97% and the Fe(III)EDTA can be easily regenerated by bubbling air into the absorbing liquid. We conclude that chemical oxidation using an iron-chelated solution, catalyzed by Fe(III) EDTA is an economically promising technique to remove H_2S from biogas even at high H_2S concentrations. Additionally, a mathematical model of the absorption and the reaction between H_2S and Fe(III)EDTA in a packed column was proposed and verified against the experimental data. The results confirm the potential use of the model for the design of a packed column for H_2S removal from biogas using absorption coupled with oxidation by Fe(III)EDTA.

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