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Smart control for micro-aeration toward sulfide removal in sewer systems at low costs

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ABSTRACT

Sulfide control is a critical subject to guarantee the operational safety and process conditions in sewage treatment works. It can be related to the areas of biogas utilization, corrosion control, and odor management. This study introduces a simple low-cost approach to remove H_2S in wastewater headspace, and hence recover the elemental sulfur by micro-aeration. Lab-scale experiments were carried out to establish a simulation model to enhance aeration control, and predict the performance of a pilot-scale twin scrubber treating biogas generated from 1 m^3 anaerobic digester. The model successfully described the changing pH in the two systems. Experiment results from residual gases showed higher than 99% hydrogen sulfide removal. A real-time off-gas monitoring algorithm is developed to control the flow rates of gases going in the twin scrubber system for optimizing the sulfide removal and micro-aeration. The new process differs from other scrubber techniques with MDEA or biofilter media and may be particularly useful for decentralized sewer treatment units or nature water as it can be operated without the needs of harmful chemicals or process control of bioreactions.

Keywords: Micro-Aeration; Sulfide Removal; Twin Scrubbers; Gas Monitoring System

1. Introduction

Hong Kong's seawater toilet flushing system is a unique water management feature in the world [1]. However, it also creates various challenges in terms of wastewater treatment due to the high concentration of sulfate ions. Sulfate ions are reduced during anaerobic treatment which produces a high amount of H_2S gases and enhances the related risks in safety and operation. The preliminary tests showed that the H_2S concentration in the biogas generated from the anaerobic digester can be as high as 20,000 ppm, which is 67 times higher than that from the freshwater system. Therefore, there is an urge for treating H_2S in biogas before further treatment and release to ambient air in Hong Kong.

The main components of biogas include methane (CH_4), carbon dioxide (CO_2) and hydrogen sulfide (H_2S). H_2S and CO_2 can be removed by basic aqueous solutions as they are both acidic gases that have a high solubility in water. Protonation occurs as they dissolve in aqueous media, which is shown in Fig. 1 [2,3]. An increase in proton concentration causes a decline in the pH value of the solution. A solution with a high pH must be maintained in order to achieve optimum absorption efficiency. The operational costs are high as the absorbent must be replaced frequently. Therefore, a system without the need for absorbent replacement can be attractive to engineering applications.

The airflow meters were controlled as the scrubbing efficiency declined to approximately 90% in the absorbing tower and the residual O_2 content was above 18%. The refilling of absorbent can be prevented.

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There are some common industrial methods for the removal of H_2S from biogas. Claus process makes use of high temperature and high pressure to remove H_2S and SO_2 [4], forming sulfur while the LO-CAT process uses liquid to absorb H_2S and oxidize it to other substances and compounds by Fe-EDTA, an oxidizing agent [5,6]. Extreme conditions are required, and performances of catalysts used are not persistent in the long run.

The gas transfer is a technique adopted by passing through gas into a liquid. As substances in two different phases cannot directly dissolve and mixed at the same time, an equilibrium and rate equation exists in between the two phases. The outer layer of the gas bubble which is in contact with the liquid phase acts as a membrane that allows substances exchange between the gas bubble and the liquid. Table 1 shows the key mass transfer equations used in this study. The rate of mass transfer is greatly dependent on the present concentration of gas and its related species in the liquid phase. The proton balance simulation at dynamic conditions is also critical when simulating CO_2 and H_2S transfer from biogas and absorbents.

In this system, the gas monitoring system is adopted with selected gas sensors for determination of the number of gases getting into and emitted from the scrubber. A control algorithm was also developed to process the data obtained and calculate the optimal way to tackle the problem. This can help calculate the number of gases dissolved into the absorbent. H_2S contents are carefully monitored so as to control the amount emitted. Depending on the changes in gas concentrations, different diffusers and gas flow rate can be changed to achieve the required gas transfer coefficient and maximize the absorption efficiency of H_2S gas from biogas. The gas monitoring system can also help refrain from the attacks of sulfide species on metal electrodes in probes.

2. Materials and methods

2.1. Design of twin scrubber system

To attain a high H_2S removal efficiency from biogas, scrubbers have been used for scrubbing gases emitted from anaerobic digestors. It consists of a twin scrubber which was used for sulfide removal from biogas and sulfide oxidation, which is shown is Fig. 2. The twin-scrubber included an odorous gas-absorbing reactor filled with sodium hydroxide solution and a micro-aeration reactor. The design aimed to be applied in various conditions with a smart aeration strategy, while the aeration system was not limited to the twin-scrubber system. The mainstream gases were pumped through the first scrubber. The absorbent in the scrubbers varied depending on the gas required to be removed. Ultrafine bubble diffusers were used to produce bubbles with various sizes to control the gas transfer rate into the absorbent. The solution can be reused after converting sulfide to other sulfur species with higher oxidation states.

2.2. Algorithm development for a gas monitoring system in the absorption tower

The real-time gas monitoring system algorithm is illustrated in Fig. 3. The initial concentrations of CO_2 and H_2S were detected by their respective sensors. Table 1 has listed the required equations and parameters for the algorithm. After that, the saturation concentrations of respective species and partial pressure of gas were calculated, which can be used to find out the parameters in gas transfer equations. The mass transfer process was the next process, involving the calculation of the amount of CO_2 and H_2S entering into the solution and the change in pH-induced. The residual gas concentration was also monitored in the outlet gas pipe. This allowed the calculation of scrubbing efficiency in gas. By evaluating the scrubbing efficiency, gas composition and mass transfer coefficient, the need for flow rate change or change of diffusers in the system was considered. In the control algorithm, a small gas stream was collected with initial gas composition measured by an off-gas analyzer, which consisted of a gas collection hood, a vacuum pump sampler and several sensors constructed based on the conceptual principle from literature paper [7,8]. The gas monitor included different sensors to determine the important gases in the emitted gases, such as O_2, CO_2 and H_2S. The control strategies on the scrubbers were

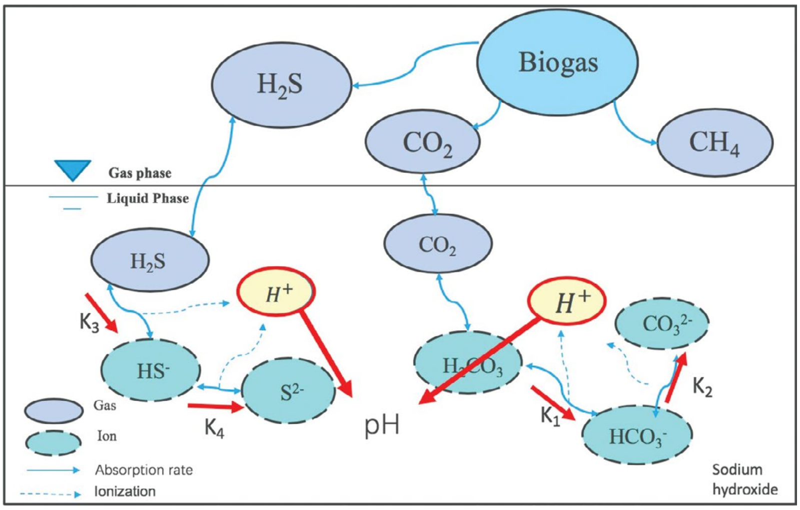


Fig. 1. Simulation concept of biogas contents.

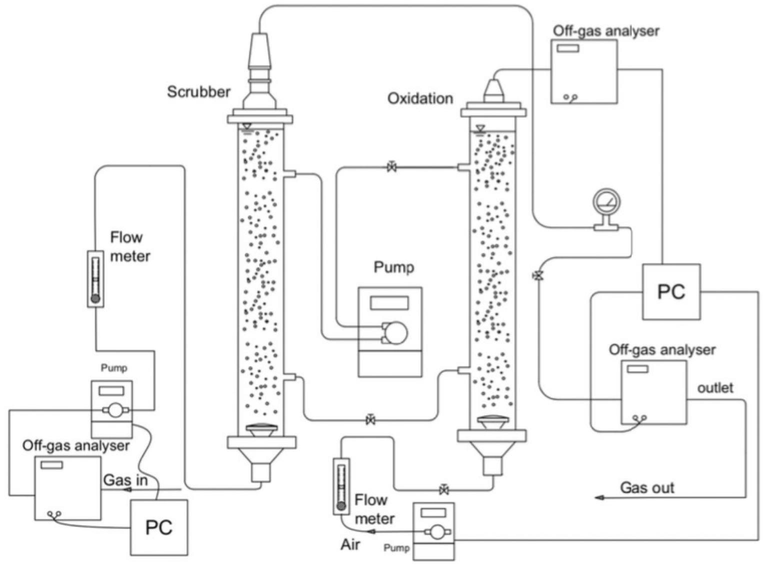


Fig. 2. Schematic diagram of the system.

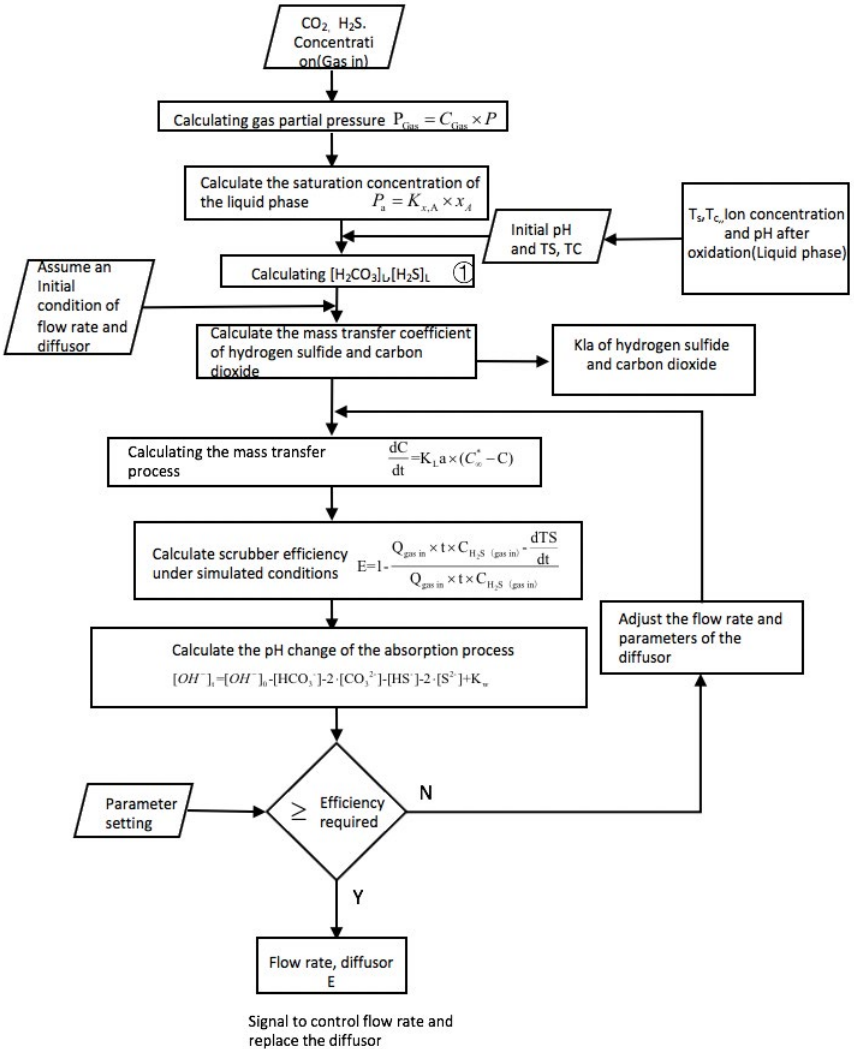


Fig. 3. Algorithm of the gas monitoring system.

Table 1
Mass transfer equations of CO_2 and H_2S in the aqueous phase

Symbol	Definition	Equation
T_{CO_2}	Total carbonate concentration in solution	$\frac{dT_{CO_2}}{dt} = K_L a_{O_2}\sqrt{\frac{D_{CO_2}}{D_{O_2}}}\times\left(\beta\cdot C_1 - T_{CO_2}\cdot R_1\right)$
T_{H_2S}	Total sulfide concentration in solution	$\frac{dT_{H_2S}}{dt} = K_L a_{O_2}\sqrt{\frac{D_{H_2S}}{D_{O_2}}}\times\left(\beta\cdot C_1 - T_{H_2S}\cdot R_4\right)$
C_1	Saturated concentration of species 1 in aqueous phase	$C_1 = \frac{P_{atm}\times C_g}{K_H}$
K_H	Henry's constant	$\left[OH^-\right]_t = \left[OH^-\right]_0 - T_{CO_2}\cdot R_2 - 2\cdot T_{CO_2}\cdot R_3 - T_{H_2S}\cdot R_5 - T_{H_2S}\cdot R_6$
c(H$^+$)	Concentration of hydrogen ions at different time t	$T_{CO_2} = \left[H_2CO_3\right]+\left[HCO_3^-\right]+\left[CO_3^{2-}\right]$
c(OH$^-$)	Concentration of hydroxide ions at different time t	$T_{H_2S} = \left[H_2S\right]+\left[HS^-\right]+\left[S^{2-}\right]$
β	Correction factor for the presence of dissolved solid in solution affecting	$R_1 = \frac{\left[H_2CO_3\right]}{T_{CO_2}} R_2 = \frac{\left[HCO_3^-\right]}{T_{CO_2}} R_3 = \frac{\left[CO_3^{2-}\right]}{T_{CO_2}}$
K_w	Dissociation constant of water	$R_4 = \frac{\left[H_2S\right]}{T_{H_2S}} R_5 = \frac{\left[HS^-\right]}{T_{H_2S}} R_6 = \frac{\left[S^{2-}\right]}{T_{H_2S}}$

adopted regarding the instantaneous results of gas compositions and their respective concentrations. Signals can be provided to the aeration instruments to achieve different targets like odor control and/or sulfur recovery.

2.3. Calibration of model

The model was calibrated based on the clean water test performed in a 4 L reactor. The calibrations were done by MatLab through the sensitivity analysis method. The line was fitted accordingly. The maximum error found was evaluated while the best fit line was evaluated.

3. Results and discussions

3.1. Removal performance in absorption tower and calibration of algorithm

The mean compositions of biogas generated by laboratory-scale anaerobic digestor used in this study were CH_4 (65.4%), CO_2 (29.3%), O_2 (0.4%), H_2S (3,217 ppm). The remaining gas included a trace amount of N_2 gas, NH_3, etc.

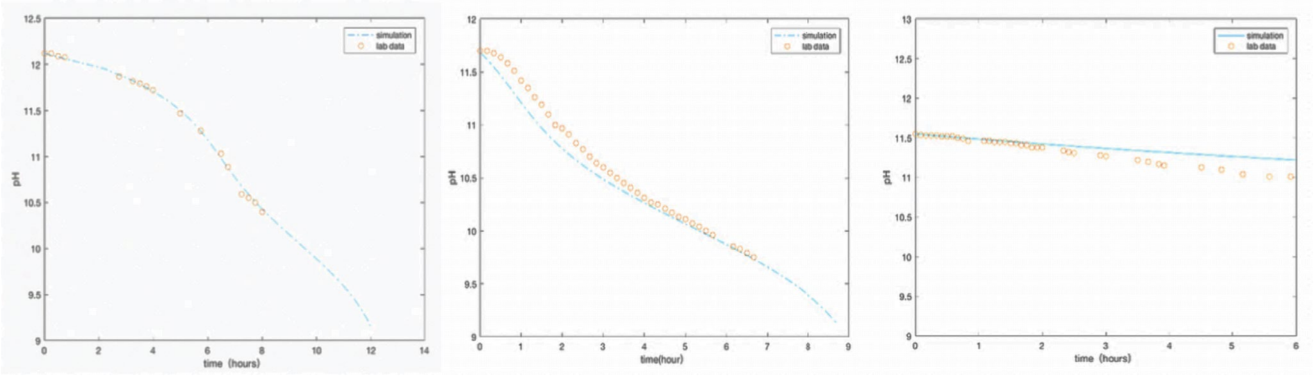
Biogas was cleansed by passing through the scrubber using the micro-aeration technique, producing very fine pore bubbles. Scrubbing solutions at pH 10, 11, and 12 were adopted and the residual H_2S concentrations are 20, 6, and 4 ppm respectively. The scrubbing efficiency in this scrubber achieved at least 99%. Nearly the whole portion of H_2S in biogas was removed. The scrubbing efficiency increased as the pH of the solution increased. CO_2 removal showed to have more than 99%.

The results were adopted to establish an algorithm for investigation on the amount of H_2S entered into the scrubbing solution. Different parameters were considered and inputted into the model, including changes in pH, bubble size and total sulfide concentration.

Air was implemented as the sampled gas to find out the gas transfer coefficients in different flow rate conditions. The gas transfer coefficient increased with the airflow rate, indicating that as more gas bubbles are injected into the system, the larger surface area was provided for gaseous exchange and O_2 could thus diffuse into the solution. The gas transfer coefficients of CO_2 and H_2S could be evaluated using the diffusion coefficients of the respective gases. The gas transfer coefficient was crucial for optimizing the removal efficiency of H_2S from biogas.

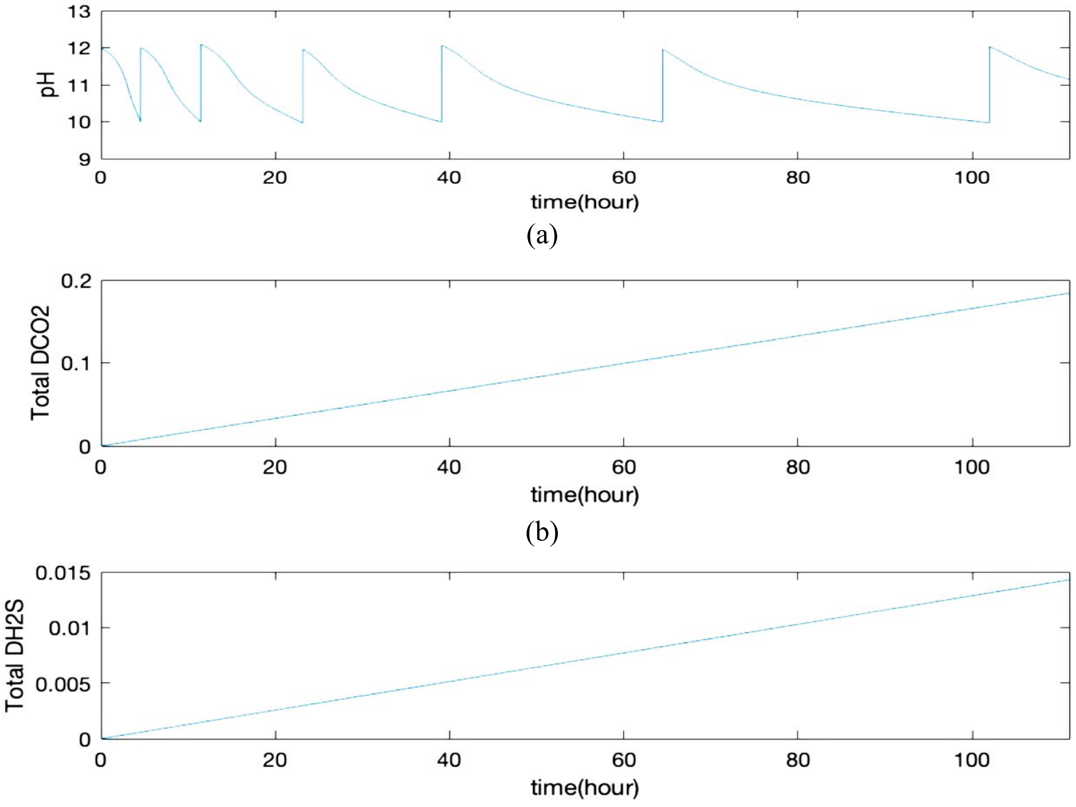
Fig. 4 shows the results obtained from the simulation showing the change in pH along with the continuous operation of the scrubber. Actual results were also adopted to confirm the accuracy of the simulation models. The conditions used were solutions with total dissolved carbonate (TDC) concentration of 0, 0.02, and 0.18 M respectively. Sensitivity analyses have been done so that the maximum errors found were less than 2.7%.

The model was also used to predict the changes in pH total carbonate and total sulfide concentrations in a continuous operation, which is shown in Fig. 5. Equations related to mass transfer of chemical species were used in this model.



(a) (b) (c)

Fig. 4. Simulation results for conditions under continuous operation in scrubber (a) TDC = 0 M, (b) TDC = 0.02 M, and (c) TDC = 0.18 M.



(a)

(b)

(c)

Fig. 5. Simulation results on changes in (a) pH, (b) total carbonate, and (c) total sulfide over time in continuous operation.

The model could predict the change in pH of the solution along with the total carbonate species and total sulfide species. The information obtained was the main part of the algorithm.

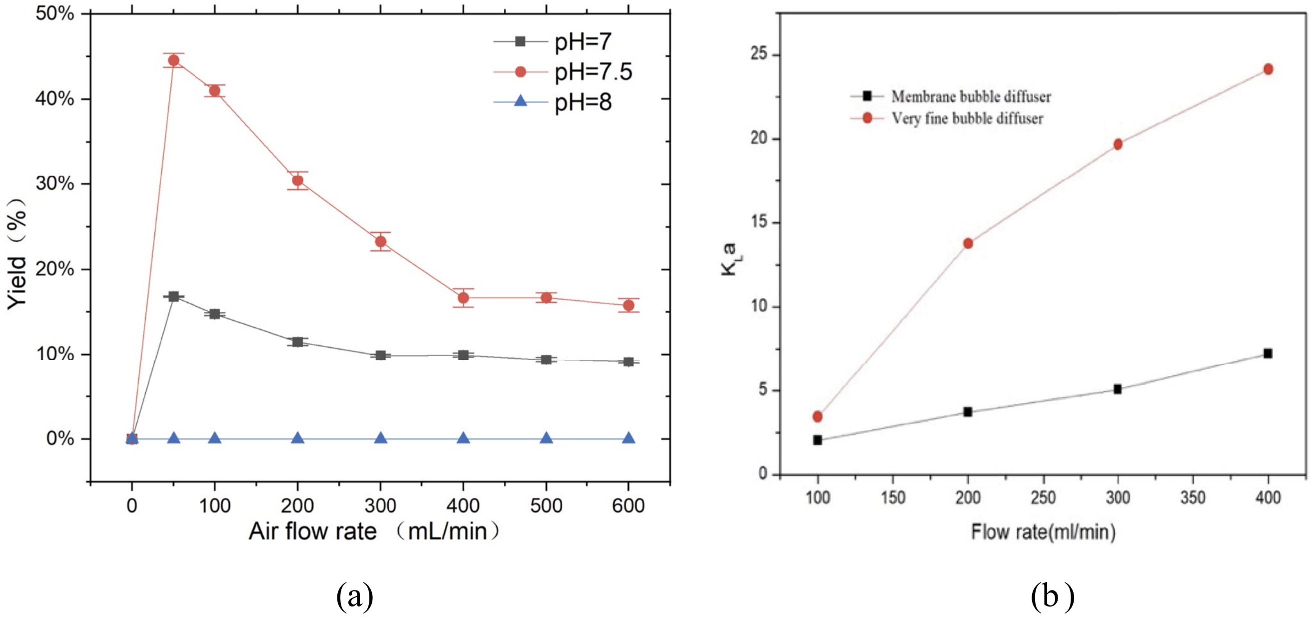
3.2. Effect of airflow rate and initial pH on elemental sulfur recovery

In order to remove sulfide dissolved in the scrubbing solution, oxidation is applied to convert sulfide to species with higher oxidation states like sulfate ion (SO_4^{2-}) and sulfite ion (SO_3^{2-}). Elemental sulfur is one of the desired products as sulfur is solid when formed, which is insoluble in the absorbent. However, the target of producing elemental sulfur relies on sophisticated control on micro-aeration that must be adopted.

The reaction of sulfide to sulfur is a partial oxidation process. A well-controlled environment can maximize the yield of sulfur. Therefore, aeration is adopted for controlling the reaction condition. The gas transfer coefficient (K_La) in different airflow rates can help control the rate of dissolved oxygen concentration in the aqueous phase for oxidation.

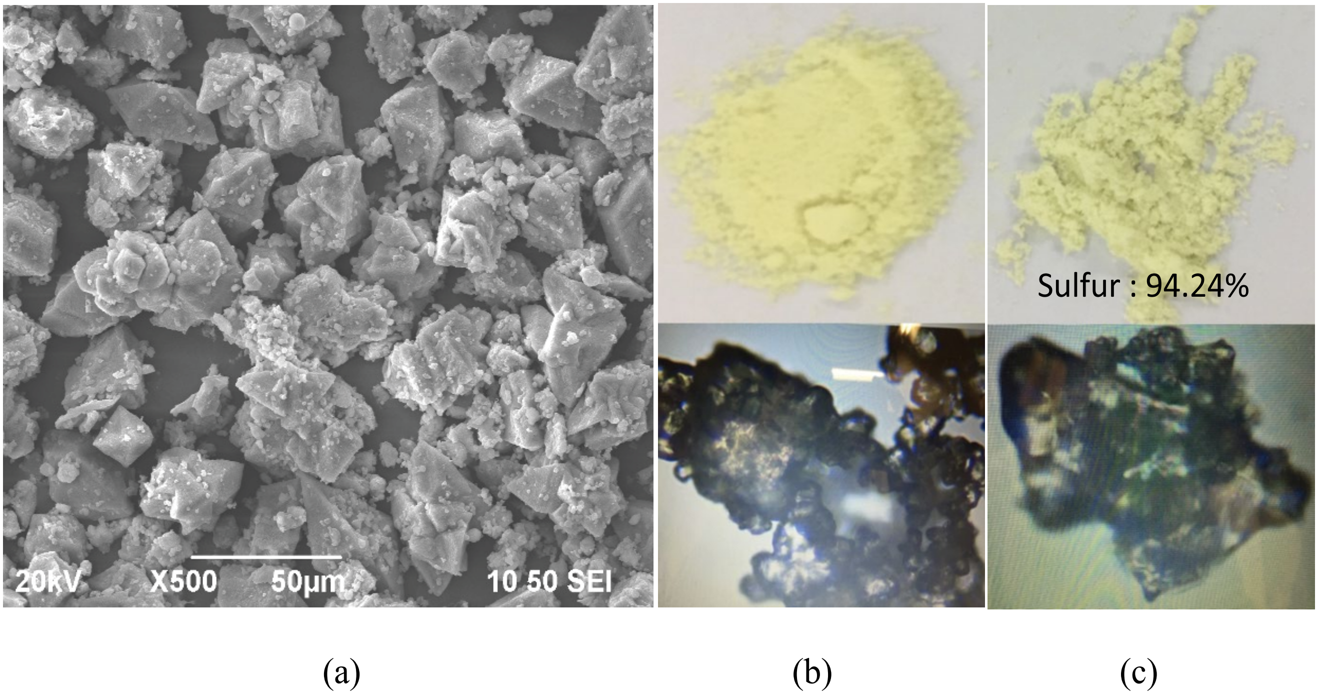
The recovery of elemental sulfur was conducted in the oxidation chamber. Diffusers were placed at the bottom of the chamber to allow gas bubbles to enter into the solution. Normal air was used as the oxidizing agent. The oxidizing chamber was operated for 24 h for the removal process. The solution inside the chamber was filtered, the residue was collected and dried in the oven. The solid was then weighed to evaluate the yield and the sample was used to confirm the chemical composition by the elemental analyzer.

Fig. 6b shows the amount of sulfur formed in different airflow rates. The sulfur yield showed an inverse relationship with K_La as shown in Figs. 6a and b. The membrane bubble diffuser produced coarse bubbles which showed lower K_La value than those produced in very fine bubble diffuser.



(a) (b)

Fig. 6. (a) Changes in gas transfer coefficient and (b) sulfur yield in different air flow rate and different initial pH values.



(a) (b) (c)

Fig. 7. (a) Sample under a scanning electron microscope, (b) comparison of commercial sulfur, and (c) sample under a microscope.

Different airflow rates could maintain different dissolved oxygen levels in the solution, of which the amount of sulfur formed was affected. Moreover, H_2S was also stripped out through the exchange in gases during the aeration process. A larger air flow rate led to a larger surface area to volume ratio of gas bubbles in the solution at a particular time, providing more area for H_2S to be removed from the solution, which also affected the amount of sulfur formed.

Moreover, changes in different initial pH were also investigated. According to the pE-pH diagram of sulfur, the window for redox reactions of sulfur-containing ions to form sulfur is very small and dependent on pH as well. From Fig. 6b, the yield of sulfur is the highest with an initial pH of 7.5 of the reaction. As the flow rate decreases, the amount of elemental sulfur formed increases. However, the absence of elemental sulfur was observed when starting the reaction at pH 8. The formation of elemental sulfur by oxidation reaction was not favored as the solution reached a pH higher than 8. Although a higher pH can help maintain more sulfide species in aqueous solution for aqueous oxidation reactions. However, the balance between the pH value in the solution and the number of sulfide species must be balanced in order to obtain an optimal yield of elemental sulfur.

The solid formed has a mean sulfur content of 94.24%. This showed that the solid formed was mainly elemental sulfur. The solid was also being analyzed under the microscope and scanning electron microscope, which is shown in Figs. 7a–c.

4. Conclusion

The twin scrubber system successfully removed H_2S presented in biogas generated in the anaerobic digestor along with the establishment of the absorption algorithm with several simulation models for calculation and prediction of changes in absorbent and removal rate, which helped optimize the removal efficiency of H_2S in biogas for other usages. The removal efficiency of H_2S from biogas reaches over 99% and recovered valuable elemental sulfur at high purity. Aeration was adopted in this process and very fine pore bubble diffusers were used to introduce a large surface area to volume ratio for gas to enter into the absorbent. This algorithm can be vastly applied in various situations like odor control systems, wastewater treatment systems, centrifugal gas transfer units and even establishing a scrubbing unit in tall buildings for treating the gases generated by residents. Oxidation was also performed in the oxidation chamber for partial oxidation of sulfide species to elemental sulfur for aqueous phase sulfide removal, which had attained the highest yield of 44.8%. Elemental analyses showed that the mean sulfur content in the solid obtained is 94.24% with a trace amount of impurities.

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