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CFD model of a packed-bed reactor with sulfide oxidizing bacteria

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Abstract. This research is aimed to develop a computational fluid dynamic model for determining the hydrogen sulfide (H_2S) reduction in a packed-bed reactor with sulfide oxidizing bacteria (SOB). The kinetic models involving the reduction reaction of hydrogen sulfide and the growth rate of bacteria were utilized. The Monod's equation was used to predict the hydrogen sulfide removal rate under suitable specific parameters such as the maximum specific growth rate (μ_{max}) of 0.035 h^{-1}, the half saturation constant of H_2S in water (K_s) of 0.15 mg-S/L, the yield coefficient of the SOB strain by the H_2S oxidation ($Y_{x/s}$) of 0.093 mg-dry weight/L and the mass transfer coefficient for H_2S in water (K_La_s) of 0.72 min^{-1}. The simulation results were compared with the results from the experiment on the packed-bed reactor with diameter of 8 cm and filled with the packed-bed medium of 80 cm in height after operating for 4 hours. The comparison results on the H_2S removal rate confirmed the model accuracy to be within ±5% of the experimental results. The determined reactor has the potential to remove H_2S concentration by 97%. The proposed model can be further utilized in design and performance prediction of packed-bed reactors for removal of contaminated hydrogen sulfide in biogas.

1. Introduction

Nowadays biogas production converts waste or remnant from livestock or industrial plants such as dung, waste water or waste matter from industrial plant through fermentation process to producing biogas capable of being used as a renewable energy [1]. Biogas is a product from the process of organic degradation by anaerobic bacteria. The biogas generation process consists of four subsequent chemical and biochemical reactions [2], -i.e. Hydrolysis reaction, Acidogenesis reaction, Acetogenesis reaction and Methanogenesis reaction. Hydrolysis reaction decomposes organic molecule such as carbohydrates, proteins and fats into glucose, amino acids and fatty acids, respectively. Acidogenesis converts those generated small organic molecules to volatile organic acids with help from bacteria. During the Acetogenesis process, bacteria in the acetic group digests volatile organic acids and releases acetic acid. Lastly, anaerobic bacteria in the methanogenic producing bacteria group will complete the Methanogenesis process by converting acetic acid to methane gas and other contaminated gases in biogas. Normally, the component of biogas consists of 40% - 75% methane, 25% - 40% carbon dioxide, 0.1% - 0.5% ammonia, 0.5% - 2.5% nitrogen, 1% - 3% hydrogen and 0.1% - 0.5% hydrogen sulfide [3] – [5].

Cautiously, hydrogen sulfide has rotten-egg-like odor and is highly hazardous, corrosive and harmful to human nervous system. Hydrogen sulfide has demonstrated the corrosive effects on

combustion chamber and engine parts when used as fuel for internal combustion engines [6] – [7]. Therefore, hydrogen sulfide must be diminished to improve the cleanliness of biogas fuel. Currently, there exists three common techniques for hydrogen sulfide reduction, -i.e. solid adsorbent technique, gas-in-liquid adsorption technique and biological filtration technique by sulfide oxidizing bacteria (SOB). In solid adsorbent technique [8] – [10], zeolite medias can be packed together to form a packed bed that obstructs the flow of biogas. While biogas is trying to permeate the packed bed, zeolite media will act as the adsorbent and reduce the hydrogen sulfide concentration in biogas. This technique is highly effective to guarantee the cleanliness quality of biogas, in the contrary is quite impractical due to the necessary to periodically replace the zeolite media and the cost of zeolite media itself. In the gas-in-liquid adsorption technique, gas can normally be soluble in liquid solution to some extent. Practically, a solvent of Potassium Permanganate (KMnO4) in water is the common solution that is used for absorbing hydrogen sulfide from biogas that flows through an absorption tower [11]. After the hydrogen sulfide adsorption process, the regenerative process can be conducted to recycle the Potassium Permanganate (KMnO4) for repeatedly supply to the absorption tower. Due to feasibility and noncomplexed process structure, the biological filtration technique is the most popular technique among the three-available hydrogen sulfide reduction methods commonly utilized for reduction of hydrogen sulfide in biogas. Sulfide Oxidizing Bacteria (SOB) is raised and expanded in number under controllable condition inside the packed bed reactor of a wetted scrubber tower [12] – [13]. Sulfide Oxidizing Bacteria (SOB) is capable of digesting hydrogen sulfide to create soluble sulfate ion. There are only small precautions over external impurities that may cause the damage to bacteria [14], such as chromium, ammonia and potassium, only at high concentration.

To achieve the high purity and cleanliness of biogas, the design of biofiltration reactor is very crucial to biogas business. Normally the biofiltration reactor is design based on lump chemical models with an unrealistic assumption of having homogenous reaction throughout the reactor. In fact, the nonuniformity of flow may cause the non-homogenous reaction inside the reactor, which may affect the overall performance of hydrogen sulfide reduction of the reactor. Recently, Computational Fluid Dynamics method (CFD) and finite element method have been applied in design of the chemical reaction that involves gas reduction [15] – [17].

In this work, the commercial finite element package, COMSOL MULTIPHYSICs version 3.5a (research package) was used to determine the hydrogen sulfide reduction behavior inside a packed bed reactor with 8 cm in diameter and 80 cm in length. The chemical kinetic models relating to hydrogen sulfide digestion of bacteria and gas-in-liquid adsorption behavior such as Monod model were added to the commercial program beside the already equipped diffusion, convection and fluid flow. The accuracy was verified by comparing with the previous experimental results on the biofiltration reactor with similar geometry from literature [18].

2. Computational domain and governing equations

The focus of this work was to develop a computational model for evaluating and predicting the hydrogen sulfide removal efficiency of a bioscrubber. Biogas contaminated with hydrogen sulfide was directed to enter the bottom part of the reactor in order to create the counter-flow condition against the sprayed absorbent liquid as shown in Figure 1. The circular reactor with the diameter of 80 cm and height of 100 cm as in Figure 2 contained an 80-cm-in-height packed bed with porosity of 0.55. The packed bed habituated sulfide oxidizing bacteria (SOB) that digest the soluble hydrogen sulfide in the absorbent liquid. The performance of the bioscrubber was evaluated by determining the hydrogen sulfide removal efficiency, which is defined by

$$\%RE = \frac{C_{Gin} - C_{Gout}}{C_{Gin}} x100 \quad (1)$$

For the sake of simplicity, these following assumptions were applied;

- the biogas entered the bio-wetted scrubber reactor with uniform flow distribution,

- the biogas entered the bio-wetted scrubber reactor with homogenous concentration of hydrogen sulfide, and
- the biogas diffused through the packed bed with isothermal flow condition at the constant reaction temperature of 35°C.

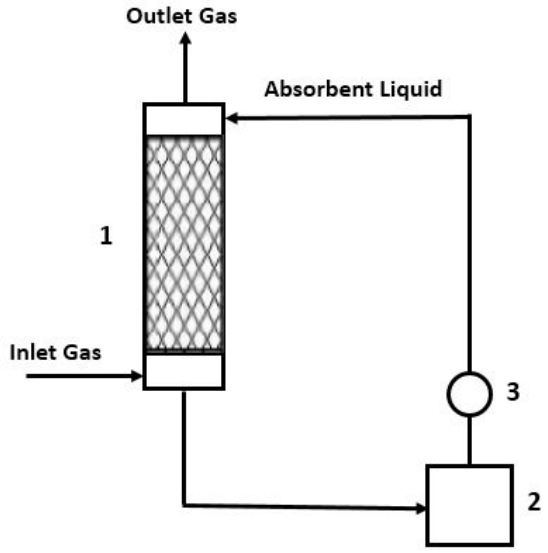

Figure. 1. Schematic diagram of the bioscrubber in this experiment: 1. Packed bed reactor; 2. Recirculation tank; 3. Pump.

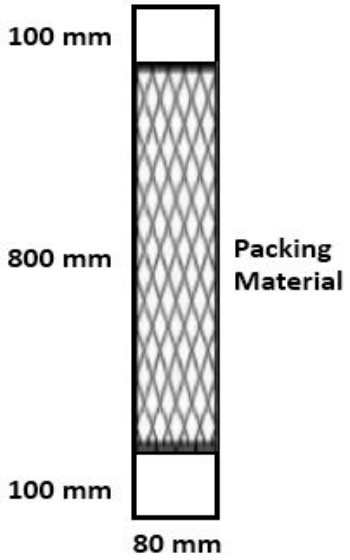

Figure. 2. Dimension of bioscrubber

To computationally illustrate the concentration change of hydrogen sulfide throughout the reactor, a commercial CFD program, Comsol Multiphysics Version 3.5a was used to determine momentum transfer, mass convection and diffusion through porous media, and specie concentration balance. The continuity equation and Navier – Stokes equation were used to represent the momentum transfer through the wet-scrubber, -i.e.

$$\nabla \cdot u = 0 \tag{2}$$

$$\rho \frac{\partial}{\partial t} u + \nabla \cdot (-\eta(\nabla u + (\nabla u)^T) + pI) = -\rho(u \cdot \nabla)u \tag{3}$$

where ρ represented the bulk-density of biogas (kg/m^3), u referred to the bulk velocity $(\mathrm{m/s})$, η represented the dynamic viscosity $(Pa \cdot s)$, and P was defined as static pressure (Pa), while biogas diffusion through the pack-bed was be determined by utilizing the Brinkman equation,

$$\frac{\rho}{\varepsilon_P}\frac{\partial u}{\partial t} + \nabla \cdot (-\frac{\eta}{\varepsilon_P}(\nabla u + (\nabla u)^T) + pI) = -\frac{\eta}{\kappa}u \tag{4}$$

where ε_P represented the porosity of the packed bed, and κ referred to the diffusivity of porous packed bed (m^2). The boundary condition of flow at the inlet and outlet were $u \cdot n = u_0$ and $p = 0$, respectively. Since the outlet was the minimum pressure surface, then the reference pressure equaling to zero was applied. The no-slip condition was applied on the solid wall of the reactor.

In order to determine the concentration change of sulfur dioxide in synthesis biogas, the mass convection and diffusion relation was applied as,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i + c_i u) = R_i \quad (5)$$

where D_i referred to diffusivity (m^2/s), c_i referred to concentration of each specie (mol/m^3) and R_i represented the chemical reaction rate $(\mathrm{mol}/\mathrm{m}^3 \cdot s)$. The boundary condition of concentration distribution throughout the reactor were at time 0 sec, inlet concentration 5.3 mol/m^3 and diffusivity $5.77x10^{-5}$ m^2/s and at time 4 hours, outlet concentration 0 mol/m^3

In order to solve the two-dimension transient problems involving continuity, momentum and mass transfer relations, the Parallel Direct Sparse Solver (PARDISO) which is relied on the LU decomposition technique was selected. Grid generation study was performed until the change in the norm of concentration was less than 2%. The validation was done by comparing with the numerical results with the previous experimental results by Lestari [18]. The validation results are reported in the following section.

3. Chemical Reaction Rate

The hydrogen sulfide reduction in the bioscrubber could be determined by balancing the concentration of hydrogen sulfide absorbed in adsorbent liquid and the concentration of residual hydrogen sulfide in biogas.

3.1 Concentration of Hydrogen Sulfide in Adsorbent Liquid

The hydrogen sulfide reduction process started with the adsorption of hydrogen sulfide in adsorbent liquid. Later the hydrogen sulfide was digested in the microbial reduction. The concentration change of the hydrogen sulfide soluble in the adsorbent liquid could be determined by the typical mass transfer relation. For simplicity, the solution of hydrogen sulfide in adsorbent liquid is homogeneous and completely mixed. The model of concentration balance could be expressed as follows [19],

$$V_L\left(\frac{dC_L}{dt}\right) = \mathrm{R}_{ab} + R_{bio} \quad (6)$$

where V_L represented the effective liquid volume of the bioreactor (L), C_L referred to the concentration of each compound in the fluid phase (mg/L). R_{ab} and R_{bio} represented the rate of removal $(\frac{mg}{min})$ by liquid absorption and bio-digestion, respectively. The absorption rate of gases in liquid could be determined from [20],

$$\mathrm{R}_{ab} = K_L a_S \cdot \left(\frac{\mathrm{C}_{G_{in}}}{H} - C_L\right) \quad (7)$$

where $\mathrm{C}_{G_{in}}$ referred to the concentration of the compound in the influent gas stream (mg/L), $K_L a_S$ represented the mass transfer coefficient (min^{-1}), and H was defined as the Henry's law constant (-). The Henry's law constant could simply be determined from the solubility of hydrogen sulfide in the adsorbent liquid according to the Weiss relation [21],

$$K_{H_2S} = e^{\left(-41.0563+\left(66.4005\cdot\frac{100}{T}\right)+\left(15.106\cdot\ln\left(\frac{T}{100}\right)\right)\right)} \quad (8)$$

$$H = K_{H_2S} \cdot RT \quad (9)$$

where T represented chemical reaction temperature (K), and R was defined as gas constant, which are commonly equal to 0.08205746 $(\frac{L \cdot atm}{K \cdot mol})$, and the bio-digestion rate by the SOB could be expressed as,

$$R_{bio} = u_{\max} \cdot V_L \cdot \frac{X}{Y_{X/S}} \cdot \gamma_{bio} \tag{10}$$

where $u_{\max}$ represented the maximum specific growth rate ($\min^{-1}$), $Y_{X/S}$ represented the yield coefficient of microorganisms digesting hydrogen sulfide (mg-dry weight/mg-S), X referred to the microbial density in the liquid phase (mg-dry weight/L), and γ_{bio} represents the biomass growth kinetic (-), while the microbial growth rate was based on the Monod relation [22] - [23].

$$\gamma_{bio} = \frac{C_{LS}}{C_{LS} + K_S} \tag{11}$$

where K_S referred to the half saturation constant of hydrogen sulfide (mg/L), C_{LS} referred to the hydrogen sulfide concentration in the liquid (mg/L). When combining equation (10) and equation (11), the rate of bio-digestion of the SOB in the reactor could be illustrated as follows,

$$R_{bio} = u_{\max} \cdot V_L \cdot \frac{X}{Y_{X/S}} \cdot \frac{C_{LS}}{C_{LS} + K_S} \tag{12}$$

The yield coefficient of the SOB strain by the H2S oxidation, $Y_{X/S}$ could be calculated by using the ratio between the weight of the SOB and the concentration of hydrogen sulfide in the liquid.

$$Y_{X/S} = \frac{dX}{dC_{LS}} \tag{13}$$

By combining all the above equation, the overall mass balance for hydrogen sulfide in the liquid phase of the reactor could finally be expressed as shown by equation (14),

$$R_{i,L} = \frac{dC_{LS}}{dt} = K_L a_S \cdot (\frac{C_{GS_{in}}}{H_S} - C_{LS}) - (\frac{1}{Y_{X/S}} \cdot u_{\max} \cdot X \cdot \frac{C_{LS}}{C_{LS} + K_S}) \tag{14}$$

where $C_{GS_{in}}$ represented influent concentrations of hydrogen sulfide (mg/L).

3.2 Concentration Change of Hydrogen Sulfide in Biogas

The The change in concentration of hydrogen sulfide in biogas could be estimated by applying the mass transfer relation of hydrogen sulfide adsorption behavior in liquid. The mass transfer behavior of hydrogen sulfide in biogas involved the advection and the adsorption of hydrogen sulfide in adsorbent liquid. Therefore, the concentration change of hydrogen sulfide in biogas could be determined from

$$R_{i,G} = \frac{dC_{G_{out}}}{dt} = \frac{Q}{V} \cdot (C_{GS_{in}} - C_{GS_{out}}) - K_L a_S \cdot (\frac{C_{GS_{in}}}{H_S} - C_{LS}) \tag{15}$$

where V represented the volume of bioreactor (L), and $C_{GS_{in}}$ referred to the concentrations of H_2S in the gas stream (mg/L).

When solving the mass transfer relation in Eq. (14) and (15) simultaneously with the governing equations mentioned in previous section, the concentration change in bioreactor and the hydrogen sulfide removal performance could be evaluated. Therefore, the microbial density [24] and the hydrogen sulfide digestion rate were included in this proposed computational model.

4. Results and Discussion

The numerical results obtained from the proposed model were compared with the experimental results presented by Lestari [18]. The controlled parameter for comparison are the inlet volumetric flow rate at 30 L/min of synthesis biogas with the composition of 0.02% hydrogen sulfide, and 99.98% nitrogen,

the controlled hydrogen sulfide in supplied biogas at 180 ppm and the process duration of 4 hours. The comparison was done by comparing the concentration level of hydrogen sulfide at the pack-bed height of, 0, 20, 40, 60 and 80 cm, respectively.

The parametric study on the effect of mass transfer coefficient of the bubble swarm for hydrogen sulfide, $K_L a_s$ on the removal efficiency was done at the specified controlled parameters similar to the experiment by Lestari [18], such that $u_{\max} = 0.0000007\,(s^{-1})$, $K_s = 3.9$ (mg/L) and $Y_{x/s} = 0.093$ (mg dry weight/mg-S). The simulation results at the end of 4 hour reaction period shows that the decrease of hydrogen sulfide content along centerline of reactor as shown in Figure 3. For the validation of the mathematical model, the local removal efficiency can then be demonstrated in comparison with the experimental results presented by Lestari [18] as in Figure 4. The simulation results match the experimental results when $K_L a_s$ is equal to 0.012 (1/s), in which the removal efficiency is the highest.

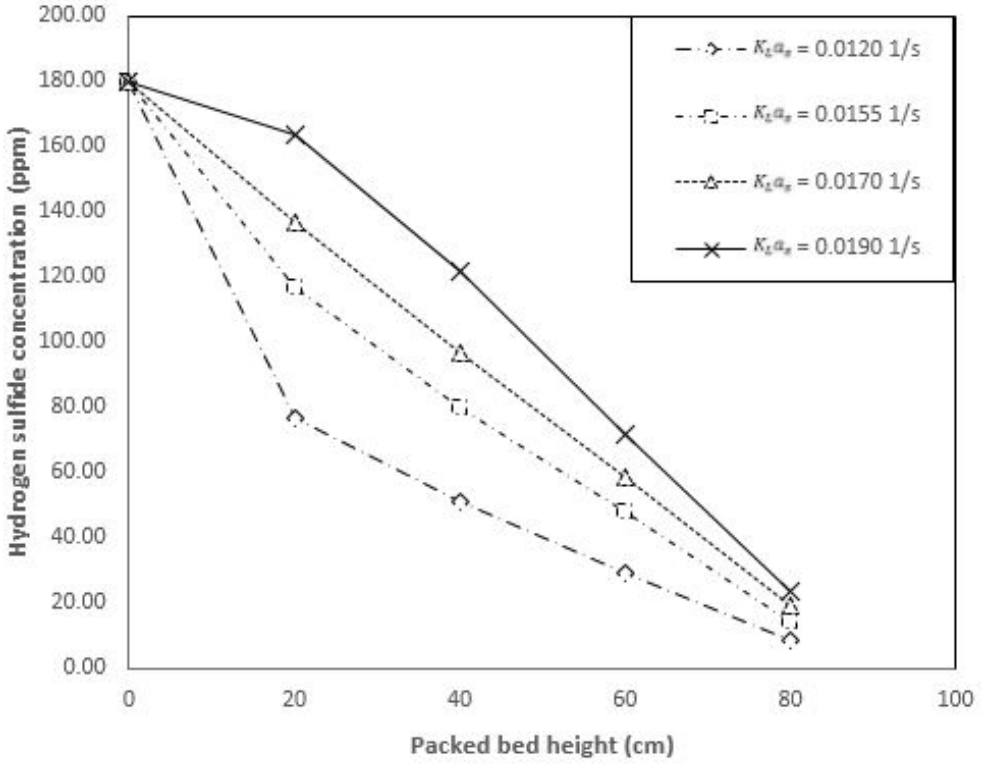

Figure 3. The hydrogen sulfide concentration in gas phase at 4 hour along the centerline of reactor at various $K_L a_s$

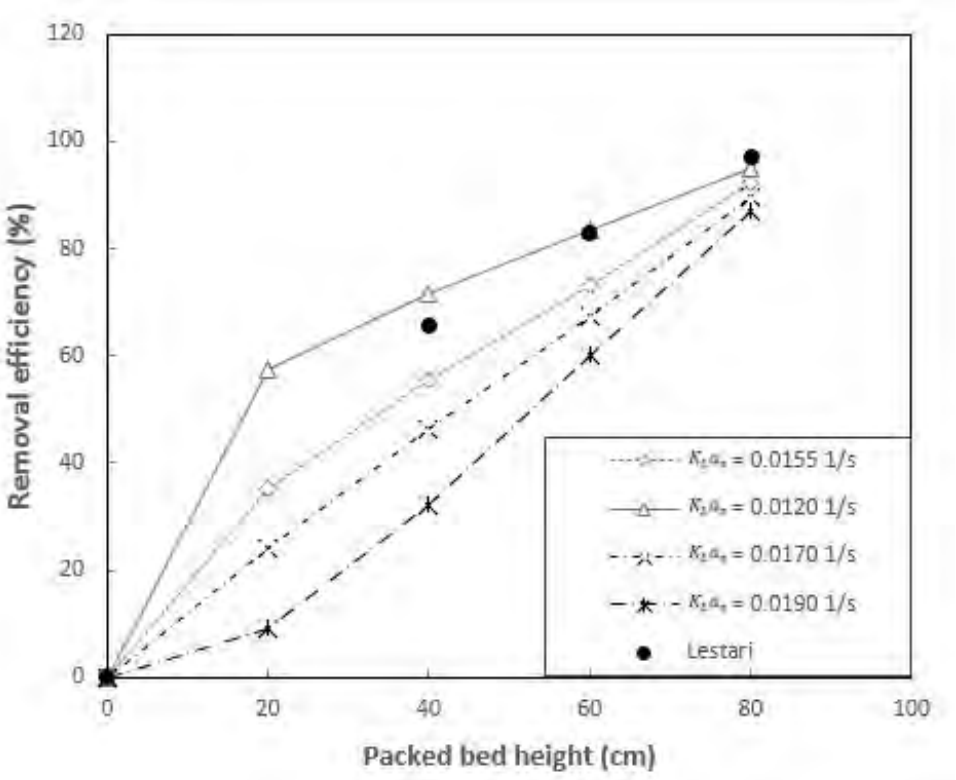

Figure 4. The removal efficiency of hydrogen sulfide along the centerline of reactor at various $K_L a_s$

Further investigation on the distribution of hydrogen sulfide concentration throughout the reactor has been done as shown in Figure 5, which demonstrate the bulk velocity profile and the concentration contour of hydrogen sulfide. The maximum concentration of hydrogen sulfide appears at the reactor inlet on the bottom part of reactor. The concentration of hydrogen sulfide drops drastically along the centerline of the reactor. This implies that the reaction activity along the centerline is more rigorous than those near the reactor wall.

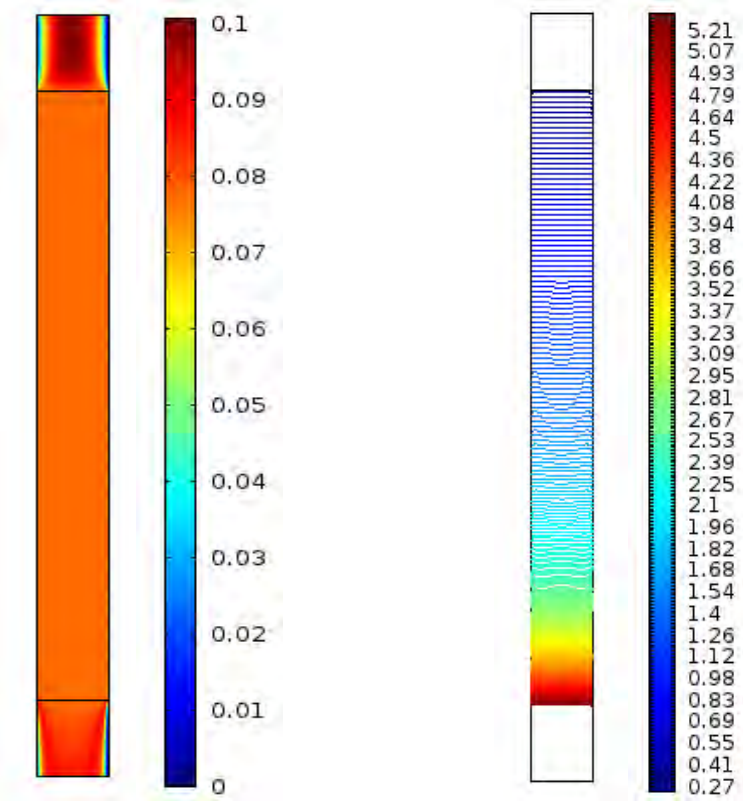

Figure 5. The bulk velocity profile and the concentration contour of hydrogen sulfide in the bioscrubber.

5. Conclusion

This paper proposed the computational model for predicting the concentration distribution and hydrogen sulfide removal efficiency of a bioscrubber. The proposed computational model has included the effects of hydrogen sulfide adsorption rate in adsorbent liquid and the digesting rate of SOB. The model was validated by comparing with the experimental results by Lestari [18]. In Lestari's experiment, the removal efficiency after 4 hours of operation was reported to reach 97.15%, while the prediction result from the proposed model was expected to be 95.09%. The computational results showed the nonuniformity of hydrogen sulfide in radial direction of the reactor. The proposed computational model can be further utilized in designing and performance improving of the large scale bioscrubbers.

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