Sulphide removal from liquid using biofilm on packed bed of salak fruit seeds

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Abstract. This study focused on the removal of sulphide from liquid solution using biofilm on packed bed of salak fruit seeds. Bio-filter operation of 444 hours consists of 6 phases of operation. Each phase lasted for approximately 72 hours to 82 hours and run at various inlet concentration and flow rate. The highest removal efficiency is 92.01%, at the end of phase 7 at the inlet concentration of 60 ppm and the flow rate of 30 mL min-1. Mathematic model of sulphide removal was proposed to describe the operation of bio-filter. The model proposed can be applied to describe the removal of sulphide liquid using bio-filter in packed bed. The simulation results the value of the parameters in process. The value of the rate maximum specific growth is 4.15E-8 s^{-1} , Saturation constant is 9.1E-8 g cm^{-3}, mass transfer coefficient of liquid is 0.5 cm s^{-1}, Henry's constant is 0.007, and mass of microorganisms growth to mass of sulphide consumed is 30. The value of the rate maximum specific growth in early process is 0.00000004 s^{-1}.

1 Introduction

Sulphide compounds are causing problems for the environment. For example, under anaerobic wastewater conditions, sulphides combine with hydrogen to produce hydrogen sulphide which in environment can be oxidized to sulphuric acid. Then the sulphuric acid formed reacts readily with the alkaline components of the concrete structures such as sewer pipes and manholes [1].

Several processes available to remove sulphide, such as physical, chemical, and biological processes. The physical and chemical processes such as absorption, combustion, and scrubbing have been used to remove sulphide from industrial waste water streams. But those physical and chemical methods need high energy requirements, high chemical disposal, and high costs [2]. A prospective biological process for sulphide removal is bio-filtration [3]. This paper report a study on the use of bio-filtration for sulphide removal from liquid. In this method microorganisms living in a support matrix were applied to degrade the pollutant. It is expected that this process is inexpensive. Furthermore this method is very attractive for low concentration gas streams due to the relatively moderate operating cost and minimum by-product generation [4].

The support matrix for the microorganism or packing material is an important factor in the design of a bio-filtration unit. The support matrix for the microorganism or packing material is an important factor in the design of a bio-filtration unit. The material need high porosity, high water retention capacity, and also nutrient presence and availability [4].

Organic materials have both the presence of nutrients and high water holding capacity than in organic packing materials. Most bio-filter media commonly applied are peat and compost with inert bulking agents such as activated carbon, wood chips or beads [5]. Composts are used frequently as they over dense and have more varied microbial population as well as good water holding capacity and nutrients. However, composts have low porosity, so the pressure drop in the bio-filter will be high. Soils are prone to short circuiting and clogging [4]. Activated carbon is good, but very expensive [6].

In this study, the removal of sulphide in liquid by bio-filter on packed bed of salak fruit seeds (SFS) in a column was investigated. These materials offer some advantages such as low cost, porous, and high water retention capacity. To quantitatively describe the process, a mathematical model considering liquid to bio-film mass transfer and bio-oxidation in the bio-film was developed and tested.

There were several mathematical model to describe the phenomena in bio-filter. Spigno and Nicolella [7] presented the model consist of mass balance equations and accounting for reaction, mass transfer and axial dispersion to describe the steady-state degradation of phenol in a bio-filter. Meanwhile Jaber et al. [8] were derived the αlump parameter which enables the performance of the bio-filter as a whole to be characterized whatever its composition (mixture or layers of different packing materials) and whatever the EBRT (empty bed residence time).

Removal of hydrogen sulphide on wastewater by chemical reaction was studied by Santos et al. [9] which compares four different empirical expressions. Biodegradation and oxidation were found to be the two

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main removal mechanisms in bio-filter. Even though biodegradation was the main mechanism responsible for the H_2S removal from the liquid phase, however oxidation being the most important one.

Agarwal and Goshal [10] worked on phenol removal in wastewater, claimed that their model has been able to predict the dynamics of the bio-filtration process. The system and condition of operations were input of substrates concentration, mass transfer coefficients in liquid phase, size reduction, Henry"s constants, flow rate of inlet, bed void fraction, growth and half saturation constants [10]. Inlet substrate concentration, inlet velocity, growth and half saturation constants and liquid phase mass transfer coefficients significantly control the operational dynamics.

The kinetics of microbial growth and the biodegradation of methanol and toluene in bio-filter and bio-trickling filters, packed with inert materials, has been studied and analysed by Ramirez et al. [11]. The specific growth rate was found to be a function of the methanol and toluene concentrations in the biofilm. In the bio-filter (BF) used for treating methanol, was found to be affected by the nitrogen concentration present in the nutrient solution, and the kind of packing material employed. A Michaelis-Menten model type provided a good fit for the elimination capacity (EC) of the Bio-trickling filter treating methanol, while a Haldane model type provided a good fit to the EC of the BF treating methanol and toluene.

Micro-kinetic models were expressed as functions of operating parameters such as the concentration of volatile organic compounds (VOCs) in the gas phase. Bio-filters treating methanol have shown that was also a function of the concentration present in the nutrient solution and the kind of packing material employed. The models of Michaelis-Menten and Haldane have been adapted to estimate the elimination capacities of the bio-filters, both with and without percolation.

The Michaelis-Menten model type was fitted to the EC of bio-trickling filters treating methanol. The Haldane model type has been fitted to the EC of bio-filters treating methanol and toluene, because these bio-filters presented inhibition by VOC concentration. The carbon dioxide production rate presented a linear correlation with the content of volatile solids in the biofilm, and with the difference of temperature between the packed bed and the environment. The carbon dioxide production rate was also identified as being an indicator of the energy generated during the VOC biodegradation.

In this research the sulphide to be removed was from liquid solution. The samples for sulphide observation were taken at the outlet of the column at various time and the process was done at 6 phases at different sulphide inlet concentration and debit (total operation time was 6 x 72 hours). Mathematical model proposed assumed no intra-film-gradient of sulphide concentration. A study on sulphide removal from gas phase at different conditions applying different mathematical model is presented by Lestari et al. [12].

2. Theoritical Development

2.1. Theoritical Development

Including figures and tables. SFS can be schematically shown in figure 1. The biofilm is attached on packing material and the liquid contain sulphide flows from the top of the column through outside the biofilm.

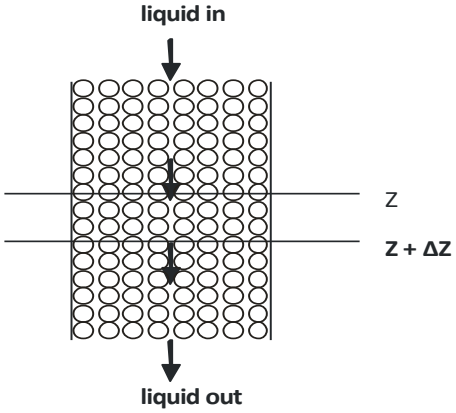

Figure 1. Schematic diagram of packed bed system

The detailed diagram of the mass transfer around the biofilm is taken from Lestari et.al. [12] and shown in figure 2. The sulphide move from the bulk of the liquid to the surface of the biofilm through the liquid film. Then the sulphide diffuses to the inner part of the biofilm. While diffusing part of the sulphide is consumed by the microorganism in the biofilm. So, the fundamental processes involved are the transfer of sulphide from liquid stream to the surface of the bio-film, sulphide diffusion in the bio-film, and bacterial action in the bio-film to degrade the sulphide compounds.

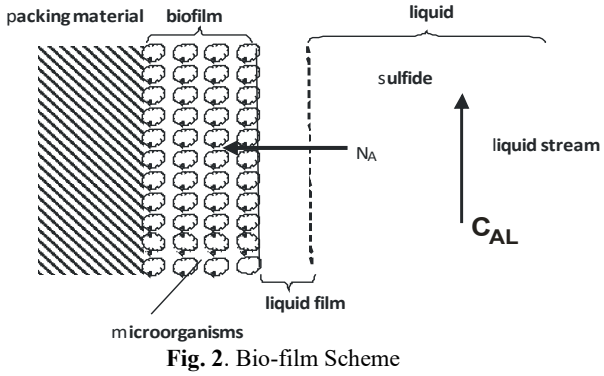

Fig. 2. Bio-film Scheme

The following kinetics model proposed is essentially similar to the model by Lestari et al. [13], in which the assumptions taken are as follows: 1. Sulphide concentration in the bio-filter for a given height is considered to be uniform because bio-film thickness (δ) is relatively small, so the diffusion is relatively fast. 2

The microorganism concentration in the bio-film at certain axial position in the bed is also assumed to be uniform. Based on these assumptions, the concentration profile in the biofilm system can be schematically simplified as in Figure 3.

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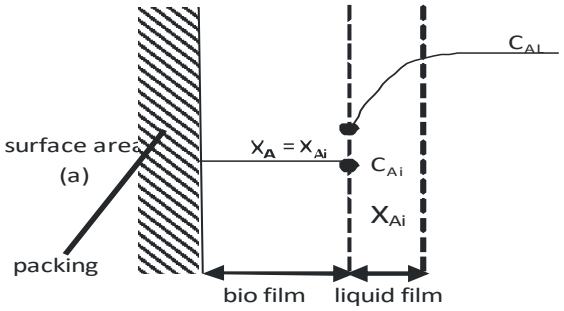

Fig. 3. Profile of concentration sulphide in the model

The mass balance of sulphide in liquid stream in the bed of thickness of Δz as in Lestari et al. [14] based on figure 1 is as follows:

$$F_V \frac{\partial C_{AL}}{\partial z} + k_C (C_{AL} - C_{Ai}) a_s S = -S\varepsilon \frac{\partial C_{AL}}{\partial t} \quad (1)$$

Similar assumption, pseudo steady-state as in Lestari et al. [13] is also taken. So in the liquid phase = 0, and equation (1) becomes:

$$\frac{F_V}{\varepsilon S} \frac{dC_{AL}}{dz} + \frac{k_C a_S}{\varepsilon} (C_{AL} - C_{Ai}) = 0 \quad (2)$$

$$\frac{dC_{AL}}{dz} = -\frac{k_C a_S S}{F_V} (C_{AL} - C_{Ai}) \quad (3)$$

The mass balance of sulphide in the bio-film at certain z position (figure 3) as in Lestari et al. [13] is as follows:

$$\frac{d X_A}{dt} = \frac{k_C}{\delta} (C_{AL} - C_{Ai}) - r_A \quad (4)$$

Because C_{Ai} is in equilibrium with X_{Ai}, and the equilibrium is assumed to follow the model of distribution coefficient, the correlation between C_{Ai} and X_{Ai} is as the following:

$$C_{Ai} = K_A * X_{Ai} \quad (5)$$

Since the bio-film thickness is δ, the rate of increase of the mass of microorganisms is [13]:

$$\frac{dm}{dt} = Y_{X/S} . r_A . a . \delta \quad (6)$$

where Y is contaminant yield coefficient (the ratio of mass of microorganism growth to mass of sulphide consumed). Since the mass of microorganism m = ρ a δ, where ρ is mass of microorganism per volume of bio-film, equation (6) becomes:

$$\frac{d\delta}{dt} = \frac{Y_{X/S}}{\rho} . r_A . \delta \quad (7)$$

All in all, the mathematical model representing the sulphide removal from liquid using biofilm on packed bed of SFS is the set of equation of 2, 3, 4, 5 and 7. The model developed was solved by the finite difference approximation method. Experimental data will be applied to verify the accuracy of the mathematical model.

3 Methodology

3.1 Materials and Methods

3.1.1 Materials

The material preparation was conducted according to Lestari et al. [15]. Salak fruit seeds were harvested from Sleman, Yogyakarta, Indonesia. The salak fruit seeds were washed and then dried in an oven at 55° C to eliminate all volatile impurities and the water. The microbes were isolate 12 which results of isolation from the sludge of the municipal waste water treatment plant in Srandakan, Bantul, Yogyakarta, Indonesia. For the growth of microbes, the sulphur oxidizing bacteria (SOB) medium of 0.4 g/l NH_4Cl, 0.2 g/l MgCl .$6H_2O$, 0.2 g/l KH_2PO_4, 0.2 g/l K_2HPO_4, 0.2 g/l yeast extract and 8 g/l $Na_2S_2O_3.5H_2O$ was added [15]. Medium and equipment were autoclaved and sterilized at 121°C, 1.2 atmospheric for 15 min.

3.1.2 Methods

One ose of isolate was used as starter on 5 ml of medium SOB in 250 ml erlenmeyer flask, then was shaker at 180 rpm for overnight. The starter was added by 50 ml of medium SOB and was shaker at 180 rpm for overnight again, then added by 450 ml medium SOB and was shaker as before procedure. The method of bio-filter experiment was conducted according to Lestari et al. [15]. Isolate 12 was then immobilized on SFS. Approximately 2.5 kg of dried SFS and 3000 ml of SOB medium was mixed in a flask and was autoclaved. The mixture was then sterilized at 121°C and 1.2 atmospheric for 15 min. The sterilized mixture was then mixed with 300 ml of isolate 12, and was kept at 30° C at atmospheric pressure, for 6 days to let the biofilm grow on SFS surface. The SFS covered by biofilm was then used as packing material in the sulphide removal column. Prior to the continuous experiments, the SOB medium was added to the bio-filter to feed the microorganism.

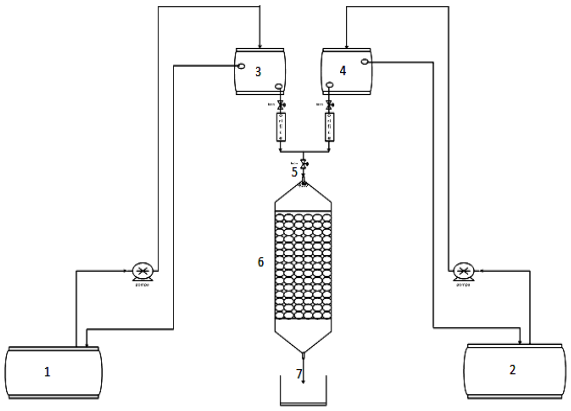

Fig. 4. Experimental set-up: (1) sulphide tank; (2) nutrient tank; (3) sulphide feeder tank; (4) nutrient feeder pump; (5) valve; (6) bio-filter, and (7) outlet port

Table 1. The operating conditions of the Bio-filter in each Phase

Phase	Duration (hours)	Inlet Concentration (ppm)	Fow rate (mL/min)
I	72	15	50
II	72	30	50
III	72	45	50
IV	74	60	50
V	82	60	40
VI	72	60	30

4 Results and Discussions

4.1 Performances of Bio-filter at Sequential Operations

The effects of operating conditions on outlet concentration and removal efficiency are shown in Fig 5. The time shown in Figure 5 is the operating time only, the switching time between phases is not counted. In phase 1 (acclimatization period), inlet concentration of H_2S solution was 15 ppm and the flow rate was 50 mL min-1. It was observed that removal efficiency as 8.24 % at the end of 24th hour. It increased with time and reached 87.94% at the end of phase 1. The increase of sulphide removal by increasing time suggests that there is microbial growth during this period.

In phase 2, the inlet concentration of H_2S solution was increased from 15 ppm to 30 ppm while the flow rate was kept to be constant of about 50 mL min-1. It was observed that by increasing inlet concentration, the removal efficiency decreased from 87.94% to 66.98%. This phenomena is conceivable since at the higher sulphide concentration the amount of sulphur to be removed was higher, so less portion of sulphide can be removed by the microbes. But by increasing time the microbes grew, so more sulphide can be removed. As a result, the removal efficiency increased by time and reached 95.63% at the end of phase 2. During phase 3, the inlet concentration was 45 ppm while the flow rate was 50 mL min-1. Similar phenomena were observed as in phase 2. The initial removal efficiency was 54.78% while the one at the end of this phase was 83.62%. During phase 4, the inlet concentration was increased to 60 ppm, but the flow rate was kept to be the same as in phase 3, which was 50 mL min-1. Again similar phenomena were observed in which the initial removal efficiency 53.23% while at the end of the phase, the removal efficiency was 70.06%. The effect of the increase of inlet concentration to the decrease of RE in early of each phases were similar to the study by Majumder et al. [16] that describes the Cu(II) removal using bio-filter. When the inlet concentration of Cu(II) was increased from 20 mg L^{-1} to 27.5 mg L^{-1}, the RE was decreased from 97.5% to 64.7%.

In phase 5, the inlet concentration was kept to be the same as in phase 4, which was 60 ppm, while the flow rate was decreased to 40 mL min^{-1}. The removal efficiency at the initial phase was 63.58%, while the one at the end of phase was 87.46%. These data show that the decreased of removal efficiency at the time of period change from phase 4 to phase 5 is smaller than the ones before. This is logical since the flow rate at phase 5 is lower than the ones before, so the residence time in the column is longer. As a results the sulphide removal is more effective. In phase 6, the inlet concentration was 60 ppm while the flow rate was decreased to 30 mL min-1. The removal efficiency at the initial phase was 73.22%, while the one at the end of phase was 92.10%.

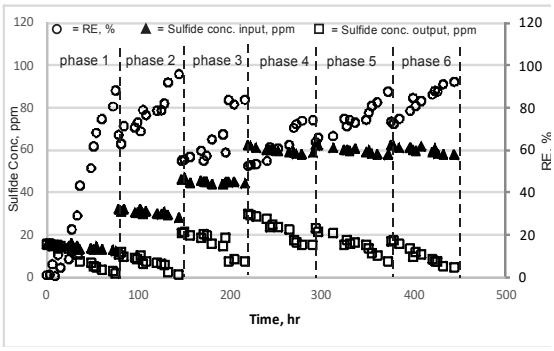

Fig 5. Performance of bio-filter at various flow rates and inlet concentrations

It was observed also that there is a drop in sulphide removal during every switching of operation. This may be caused by the shut-down of the bio-filter for approximately 3 hours, in which part of the microbes died so the removal capability becomes lower. It was also observed that drop of RE in the change of flow rate are relatively less than the one in change of inlet concentration. This phenomenon suggests that the disturbance caused by change of flow rate is less significant than the one caused by change of concentration. However as time progresses, the RE gradually increased as seem in figure 5. Figure 5 also shows that the lower the flow rate, the higher the RE would be. This result is similar to the research of Jaber et al. [8] which showed that decreasing the loading rate from 39.6 g m^{-3} h^{-1} to 9.9 g m^{-3} h^{-1} could increase RE from 45% to 100%.

4.2 Simulation Results

The comparison of simulation results and experimental data are shown in figure 6. The values of the parameters involved were obtained by curve fitting. During the entire operations the values of the parameters are constant, except for the first phase (acclimatization). The differences are due to the lower activity of the microbes during acclimatization.

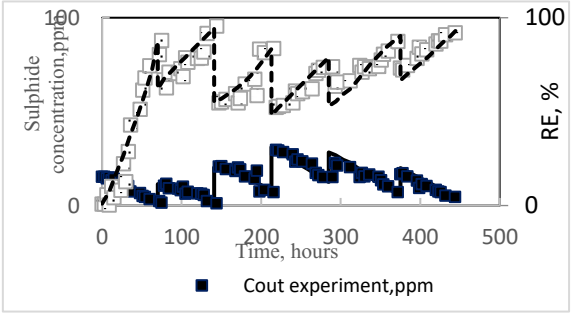

Figure 6. Concentrations and removal efficiency versus time from experiment and modelling

The thickness of the biofilm needs to be adjusted every switching of operations because of the death of part of the microbes during the shut-down period. Figure 6 shows that the model proposed can quantitatively describe the performances of the bio-filter.

Curve fitting resulted the appropriate values of the parameters for all phases as follows: μ_{max} = 0.0000000415 s^{-1}, α= 0.000000091 g cm^3, k_C = 0.5 cm s^{-1}, K_A = 0.007, and $Y_{X/S}$ = 30, except in early process, in which the value of μ_{max} is 0.00000004 s^{-1}, smaller than value of μ_{max} in the other phases. It is expected that the proposed model can be applied to quantitatively predict the performance of the sulphide removal at various condition (inlet sulphide concentration, flow rate, and removal efficiency).

Bio-filter column using the same packing material and microbes can also be applied to remove sulphide from gas phase [12]. The gas studied was biogas with sulphide content of 10 ppm to 79 ppm. The values of the parameters involved were found to be μ_{max} = 0.0000007 s^{-1}, K_S = 0.0000039 g cm3, k_G = 0.0086 cm s^{-1}, H_S = 0.9 and $Y_{X/S}$ = 10. The comparison shows that the values of rate of maximum specific grow and half saturation constant for liquid phase are smaller than the ones of gas phase. However the values of mass transfer coefficient, Henry's constant and yield of microorganisms growth to mass of sulphide consumed for liquid phase were higher than the ones of the gas phase. Those suggest that the biofilm in gas environment is more active than the one in liquid environment (higher μ_{max}). The mass transfer coefficient from the liquid to the biofilm is higher than the one of the gas. This is in accordance with mass transfer theory. The higher K_A in the gas phase implies that sulphide in the gas is less absorbed in the biofilm than the sulphide in liquid phase.

4.3 Rate of degradation

The correlation between sulphide concentration in the biofilm and the rate of degradation modelled by Monod's equation using parameter obtained in this study are shown in figure 7. It is observed that the correlation is non linear. Hence, simplification of Monod equation to linear form is not recommended. Different conclusion was obtained by Ottengraf and Van den Oever [15] which reported that the correlation can be simplified to zero-order.

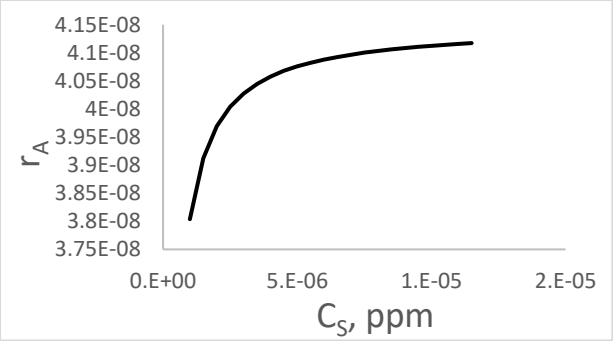

Figure 7. Effect of sulphide concentration in the biofilm to the rate of sulphide degradation by kinetic modelling

5 Conclusion

During every switching of operation, the sulphide removal efficiency drops. The drop of removal efficiency in the change of flow rate are relatively less than the one in change of inlet concentration. The highest removal efficiency is 92%, at the end of phase 6 at the inlet concentration of 60 ppm and the flow rate of 30 mL min^{-1}.

Monod's equation is recommended to applied for elimination of sulphide by biofilm on packed bed of salak fruit seeds. The model can quantitatively describe the performances of the bio-filter. Curve fitting resulted the appropriate values of the parameters for all phases as follows: μmax = 0.0000000415 s^{-1}, α= 0.000000091 g cm^3, k_C = 0.5 cm s^{-1}, K_A = 0.007, and $Y_{X/S}$ = 30, except in early process, in which the value of μ_{max} is 0.00000004 s^{-1}.

The value of μ_{max} at the first phase (acclimatization) is lower than the ones of the other phases because during the acclimatization, the performance of the microbes has not achieved the normal one. The values of μ_{max} and half saturation constant for liquid phase sulphide removal was found to be relatively lower than the ones of gas phase. Meanwhile, the values of mass transfer coefficient, Henry's constant and yield of microorganisms growth to mass of sulphide consumed for liquid phase were higher than the ones of the gas phase.

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