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Oxygen Transfer Rate in an Aerated Tank for Pharmaceutical Wastewater Treatment

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ABSTRACT

The treatment of pharmaceutical non-penicillin wastewater was conducted in the biological aerobic process. The oxygen transfer rate played the major role to reduce the organic pollutants of the wastewater by removing gases, oils, volatile acids and odour. The microbial culture used in the experiment was the ethanol producers, isolated from the wastewater. Optical density, COD and concentration of chemicals equivalent to carbohydrate were measured in a time period of 3-4 days of aeration. The propagation of bacteria was monitored and its growth rate was determined. Oxygen transfer rate and mass transfer coefficients were found to be affected by airflow rate, bubble size and agitation rate. Dissolved oxygen was shown as an indication of microbial growth and limitation of mass transfer. The dissolved oxygen was about 7.89 ppm from the starting point and then it dropped to 2 ppm by the end of the first day. After the second day of aeration the oxygen depletion was obviously observed since the DO meter showed 0.14 ppm. Aeration rate was 0.2 – 1.3 liters per minute for working volume of 3 liters and 5-10 liters per minute for 15 liters aerated tank. Maximum optical density was obtained with high aeration rate at the first day of aeration, 0.95 g/l, as the aeration was reduced the cell propagation was also reduced. The maximum cell growth was obtained by the end of 3 days of aeration with minimum airflow rate. The maximum COD and carbohydrate reduction was 58 and 90 percent respectively with 1.15 liter/min airflow rate in the 3 liters aeration system. The bubble size affected the mass transfer coefficient (K_La), as the contact surface of gas exposure to liquid increased the mass transfer coefficient was increased. As the dissolved oxygen concentration dropped the K_La was also decreased. The values of K_La for the 5 and 10 liters/min airflow rate for 15 liters aerated tank were 0.055 h^{-1} and 0.3975 h^{-1} respectively.

Key Words: aeration, aerobic treatment, oxygen transfer, mass transfer coefficient, wastewater

ABSTRAK

Rawatn untuk air sisa farmaseutikal bukan penisilin telah dijalankan dalam proses aerobik biologi. Kadar pemindahan oksigen memainkan peranan penting dalam mengurangkan bahan pencemar organik dalam air sisa dengan menyingkirkan gas, minyak, asid meruap dan bau. Kultur mikrob yang digunakan dalam eksperimen ini merupakan mikrob penghasil etanol yang dipisahkan daripada air sisa. Ketumpatan Optik, Keperluan Oksigen

Kimia (KOK) dan kepekatn kimia bersamaan kandungan karbohidrat diukur dalam masa pengudaraan selama 3-4 hari. Pembiakan bakteria diawasi dan kadar pertumbuhan diukur. Kadar pemindahan oksigen dan pekali pemindahan jisim dipengaruhi oleh kadar pengaliran udara, saiz buih udara dan kadar pengadukan. Oksigen terlarut ditunjukkan sebagai tanda pertumbuhan mikrob dan batas pemindahan jisim. Kandungan oksigen terlarut adalah lebih kurang 7.89 bpj pada permulaan dan jatuh kepada 2 bpj di akhir hari pertama. Selepas hari kedua pengudaraan, pengurangan kandungan oksigen jelas diperhatikan kerana meter oksigen terlarut menunjukkan 0.14 bpj. Kadar pengudaraan adalah 0.2-1.3 liter per minit bagi isipadu kerja sebanyak 3 liter manakala kadar pengudaraan 5-10 liter per minit untuk tangki pengudaraan sebanyak 15 liter. Ketumpatan optik mencapai maxima untuk kadar pengudaraan tinggi pada hari pertama pengudaraan ,0.95 g/l, apabila pengudaraan dikurangkan, pembiakan sel juga dikurangkan. Pertumbuhan sel maxima didapati di akhir pengudaraan selama 3 hari dengan kadar pengaliran udara minima. KOK maxima dan pengurangan karbohidrat ialah 58 dan 90 peratus masing-masing bagi kadar pengaliran udara 1.15 liter/minit dalam sistem pengudaraan 3 liter. Saiz buih udara mempengaruhi pekali pemindahan jisim (K_La) , apabila permukaan sentuhan gas yang terdedah kepada kepada cecair ditambahkan, kadar pemindahan jisim juga bertambah. Apabila kepekatan oksigen terlarut dikurangkan, K_La untuk kadar pengaliran udara 5 liter/min dan 10 liter/ minit bagi tangki pengudaraan 15 liter masing-masing ialah 0.055 j^{-1} dan 0.3975 j^{-1}.

Kata Kunci: Pengudaraan, rawatan aerobik, pemindahan oksigen, pekali pemindahan jisim, air sisa

INTRODUCTION

Aerobic wastewater treatment processes remove dissolved and colloidal organic matter in industrial wastewater. The growth and the propagation of the microorganisms will consume oxygen in the liquid phase. Thus it causes the dissolved oxygen to be depleted when the microorganisms are in exponential growth phase. However, the specific oxygen uptake of bacterial increases only slightly with increasing oxygen concentration above a certain critical concentration. In order to achieve the optimum oxygen transfer rate (OTR) several parameters such as airflow rate, bubble size, nature of the wastewater, agitation rate, temperature, reaction rate and propagation of the microorganisms, which influence the mass transfer rate, have to be taken into consideration.

The activated sludge process for domestic wastewater treatment was introduced to the world in 1914 (Eckenfelder 2000). Since then considerable amount of studies have been conducted to improve the oxygen transfer efficiency. Among the aeration devices introduced were porous diffuser, filter type diffuser, mechanical aeration device, orifice type diffuser and fine pore air diffuser. The aeration market is in a substantial state of flux in the U.S. today. Emphasis on high efficiency has led to many intensive research programmes aimed at evaluating the design, operation, and control processes in relation to improving overall system performance.

The transfer of oxygen from the gas phase to the microorganism takes place in several steps. Firstly, the oxygen must travel through the gas to the gas-liquid interface, then through the bulk liquid, and finally into the microorganisms. Some researchers believe that oxygen transfer occurs significantly during bubble formation when the interfacial area exposed to the liquid is constantly renewed (Bailey & Ollis 1986). On the other hand, there are also other researchers who believe that oxygen transfer occurs very significantly during the bubble's ascent (Scragg 1991). However it is well understood that regardless of where the transfer really occurs, the rate of transfer is proportional to the contact time and area of contact between the liquid and gas. It is found that the overall gas transfer coefficient, K_L.a, increased while bubble size decreased until the bubble diameter approached 2.2 mm, further reduction in bubble size resulted in decreasing K_L.a, although smaller bubbles may increase oxygen transfer efficiency (Deronzier et al. 1998).

Modeling of oxygen transport in the aeration system is important, for it can be used as a reference for overall process performance improvement as well as process design and simulation. The oxygen transfer process mentioned above is based on the concentration gradient between the oxygen concentration in the gas phase and in the microorganism. The basic model for oxygen transfer in a dispersed gas-liquid system is given (Scragg 1991):

$$N_a = K_L (C^{\circ}-C_L) \tag{1}$$

For the gas side, mass transfer can be similarly defined in terms of the gas partial pressure as follows:.

$$N_a = K_g (P-P^{\circ}) \tag{2}$$

Since it is usually impossible to measure the local and interface concentrations anywhere in a bioreactor, average values of the concentrations or dominant bulk concentrations and overall mass transfer coefficients are used. In order to know the total oxygen transfer rate in a vessel, the total surface area available for oxygen transfer has to be determined. Thus an overall mass transfer coefficient incorporating the surface area of the bubble is used, namely

$$N_a = K_L a (C^*-C) \tag{3}$$

The $K_L a$ value is dependent on the physicochemical properties of the bioreactor media, the physical properties of the bioreactor and operating conditions of the vessel. The magnitude of $K_L a$ can be controlled by the agitation rate and the airflow rate. Oxygen is a substrate, which enhances microbial growth; however, above a certain concentration, the microbial growth will become independent of oxygen concentration.

In a short time period, the dynamic model shown in equation 4 at quasi steady state condition, OTR to microbial cell would be equal to oxygen molar flow transfer to liquid phase (Badino et al. 2000).

$$\frac{dC}{dt} = K_L a(C^* - C) - Q_{O_2} X \tag{4}$$

At steady state condition the oxygen concentration profile would be an exponential model shown below:

$$\frac{C - C^*}{C_o - C^*} = e^{-K_L at} \tag{5}$$

In reality, oxygen concentration would never reaches to the concentration defined in the proposed model, since the microbial activities at optimal and maximum cell density would reach at the point where oxygen depletion may take place (Jia-Ming Chern et al. 1997).

The mass transfer coefficient, $K_L a$ for a continuous stirred tank bioreactor can be correlated by power input per unit volume, bubble size, which reflects on interfacial area and superficial gas velocity (Scragg 1991; Bailey et al. 1986). The general form of the correlations for evaluating $K_L a$ is defined in the following polynomial equation.

$$K_L.a = x\ (P_g/V_L)^y\ (v_g)^z \tag{6}$$

The mass transfer coefficient is expected to relate gas power per unit volume and gas terminal velocity. Measurement of gas bubble velocity is some what troublesome in the experimental stage of aeration. Extensive research has been conducted for the explanation of the above correlation. For the gas liquid mass transfer in low viscosity fluids in agitated vessels have been reviewed and summarized as follows (Scragg 1991):

1. For coalescing air-water dispersion, when liquid is relatively pure, the mass transfer coefficient was expected to be:

$$K_L a = 2.6\text{x}10^{-2}\ (P_g/V_L)^{0.4}\ (v_g)^{0.5} \tag{7}$$
$$V_L \leq 2.6\text{m}^3;\ 500 < P_g/V_L < 10000$$

2. For non-coalescing air-electrolyte dispersion, once there is a small amount of electrolyte in the system, the mass transfer coefficient was also correlated as:

$$K_L a = 2\text{x}10^{-3}\ (P_g/V_L)^{0.7}\ (v_g)^{0.5} \tag{8}$$
$$V_L \leq 4\text{m}^3;\ 500 < P_g/V_L < 10000$$

3. These correlations may not be valid for non-Newtonian behaviour of biological fluids, nor the effect of antifoam and the presence of solids. A correlation may be true for aerobic non-Newtonian fluid filamentous media of fermentation broth was proposed as (Scragg 1991):

$$K_L a = x\ (P_g/V_L)^{0.33}\ (v_g)^{0.56} \tag{9}$$

The industrial wastewater used in the experiment is considered as non-coalescing air electrolyte dispersion, thus the equations discussed above

would be examined as theoretical model for estimation of oxygen transfer rate in liquid phase and compared with the experimental data obtained.

MATERIALS AND METHOD

The non-penicillinic wastewater from a pharmaceutical company (S. Pharmaceutical M, Sdn. Bhd., Perak, Malaysia) was collected and used in the batch aeration wastewater treatment experiments. The pharmaceutical wastewater was clear orange colur, strong odour, containing toxic chemicals and COD value in the range of 3000-30,000 mg per liter. The pH of the wastewater was neutralized and monitored for each experimental run, as the bacteria would have a higher rate of propagation at neutral pH.

Two different sizes of aerated tanks with working volumes of 3 and 15 liters were used. An air blower, aerator unit model 8500, 6W, with low, medium and high rate of oxygenation was used for small tank. A gas flow meter, Cole Parmer 0-70 ml/min model 6G08 R4 was used for setting the desired airflow rate. Air bubbles entered to the bottom of the tank through a gas sparger and maintained the wastewater highly aerated. A mixer-stirrer Cafamo digital model RZR2000 for the range of 100-600 rpm was used for complete aeration in the small aeration tank. Also a 15 liters aeration unit, model TR01 with a stirrer model RW20DZM.n, 72W, KIKA from Labortechnik, Malaysia was used for the large aeration tank. High shear dispersing impeller with the diameter of 82 mm was used in this large system. Dissolved oxygen meter model HI9145 microprocessor, Hanna Instrument, Portugal, was used to detect and measure the level of dissolved oxygen in the large aeration tank. The characteristics and operating conditions for the aeration systems are summarized in Table 1.

The fungus isolated from wastewater was used as a seed culture. The media for seed culture as a starter of each experimental run was prepared by using 1.0 g of glucose and 1.0 g of peptone in 100 ml of distilled water. The nutrients and minerals were obtained from Merck. The media was sterilized in autoclave at 121°C, 15 psig steam pressure for 20 minutes.

TABLE 1. Aeration test conditions in two different aeration systems

Aeration Tank	Small size	Large size
Volume of wastewater, liter	3	15
Diffuser type	Coarse bubble	Fine bubble
Air flow rate, liter/min.	0.2 – 1.6	5 & 10
Agitation Rate, rpm	200	300
Liquid temperature, °C	25 – 28	28 – 30
pH of wastewater	6 - 8	6 – 8
Inoculating volume, seed culture, ml	50	250
Nutrients & trace minerals		
Yeast Extract, g	0.9	4.5
Glucose, g	0.9	4.5
Calcium Chloride, g	10	50

Periodic samples were taken at starting point right after introducing the inoculums on the first, second and third day of each experimental run. The optical cell density, COD, total reduced carbohydrate concentration and dissolved oxygen were monitored for various air flow rates. The COD was measured by a closed reflux colorimetric method at 600 nm with spectrophotometer using potassium dichromate as reducing reagents (Greenberg et al. 1992). All organic chemicals that are present in waste water would be detectable as equivalent to carbohydrates by a chemical reducing agent 3,5-dinitrosalycilic acid (DNS) which was detected by the spectrophotometer at 540 nm wavelength (Summers 1924; Thomas et al. 1980).

RESULTS AND DISCUSSION

Experimental run had been conducted to study the effect of airflow rate in the 3 liters aeration wastewater treatment tank. Nutrients were added in the treatment tank to ensure sufficient bacterial growth. In each experiment, the cell optical density, COD and the concentration of chemicals equivalent to carbohydrates were monitored for the duration of aeration.

Based on the experimental results as shown in Figure 1, the COD curves showed sharp reduction in the first day of the treatment and the rates were gradually reduced when the aeration was extended until the third day. From the obtained data, it had shown that higher reduction of COD was achieved with higher airflow rate. An airflow rate of 1.3 liter/min yields the highest percentage of COD reduction, about 58 percent. On the other hand, the percentage of carbohydrate consumption also presents the similar trend with the airflow rate. Reduction of chemical equivalent to carbohydrate for small aeration tank with airflow rates of 0.22, 0.83 and 1.3 liter/min are shown in Figure 2. The highest percentage of carbohydrate reduction, 90 percent was obtained with an airflow rate of 1.3 liter/min. The results indicated that the aerobic wastewater treatment process with the airflow rate of 0.22 to 1.14 liter/min were under oxygen transfer limitation, thus further process improvement can be achieved by increasing the airflow rate.

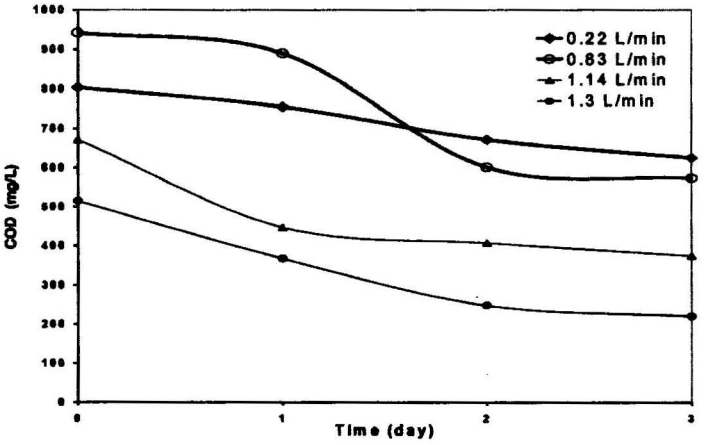

FIGURE 1. COD reduction for small aeration tank with various airflow rates

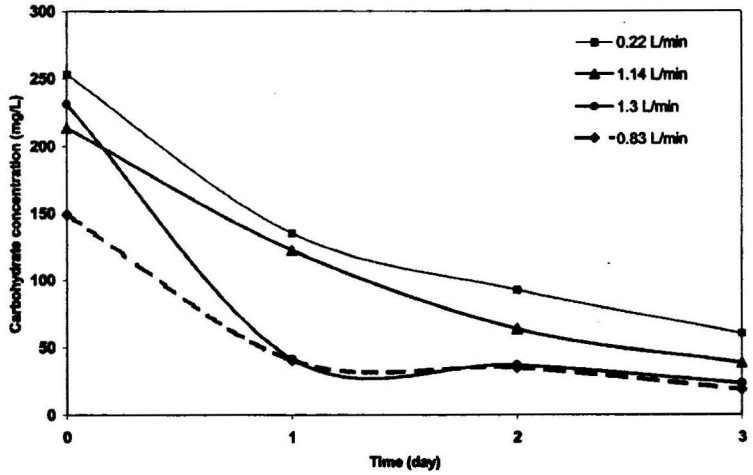

FIGURE 2. Reduction of chemical equivalent to carbohydrate for small aeration tank with various airflow rates

Further experiments were conducted in a large aeration tank, 15 liters batch system to study the dry weight cell density, COD, carbohydrate, dissolved oxygen and oxygen transfer modeling. Two different airflow rates, 5 and 10 liters/min were applied. However due to the failure and operation limitation of the system, the system can only provide oxygenate for 8 hours a day. The COD, dry cell weight, carbohydrate and dissolved oxygen concentrations for each experimental run with airflow rate of 5 and 10 liters/ min were presented in Figures 3 and 4, respectively

It was expected that the dissolved oxygen for the 5 liters /min system decreased with respect to time as the system was running in an oxygen limitation condition. The concentration of the oxygen approached zero at the third day of the experiment. Even though the system was running in an oxygen transfer limitation condition, the microbial achieved a maximum

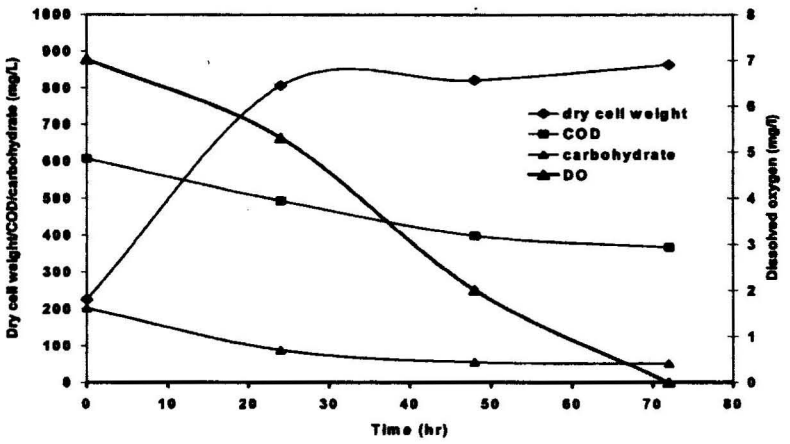

FIGURE 3. COD, dry cell weight, carbohydrate and dissolved oxygen concentration in 15 L aeration system with air flow rate of 5 liters/min.

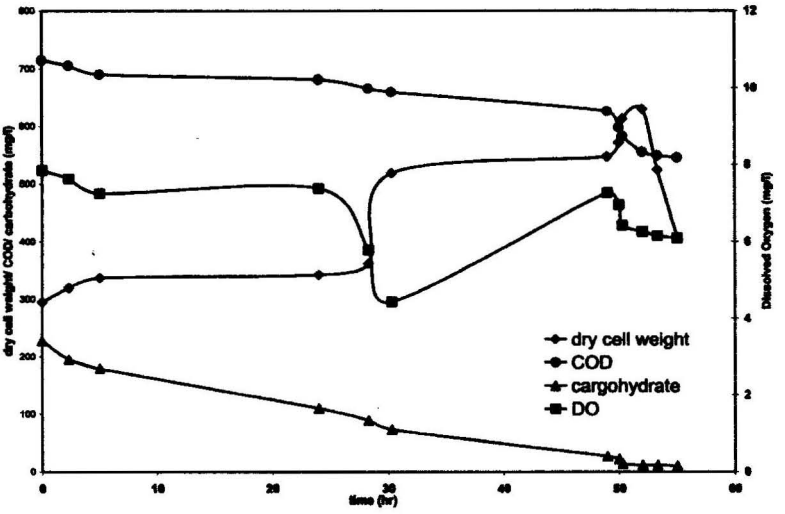

FIGURE 4. COD, dry cell weight, carbohydrate and dissolved oxygen concentration in 15 L aeration system with air flow rate of 10 liters/min.

growth at 24 hours. The reduction of COD and carbohydrate were 40 and 74 percent, respectively. The experimental results showed that the system required more aeration. Therefore an airflow rate of 5 liters /min was not sufficient and the calculation of $K_L a$ may cause error.

When the airflow rate was doubled, there was sufficient oxygen for optimum microbial growth. Theoretically under sufficient aeration condition, the concentration of dissolved oxygen in the system should be constant, however due to the reason as mentioned above, the dissolved oxygen curve has shown a drop in oxygen concentration from 24 to 30 hours. The dissolved oxygen was available at around 5 – 8 mg/liters during aeration. The COD reduction was only 22.5 percent. Nevertheless, the rate of carbohydrate consumption was 95 percent. The cell density increased gradually as oxygen was consumed. At the third day of operation, the cell density was decreased since the cell death rate was high and the nutrient was depleted.

The oxygen transfer coefficient $K_L a$, for the above system can be estimated by applying the following mathematical model:

$$\frac{dC_L}{dt} = K_L a(C^* - C_L) - rX \qquad (10)$$

A graph of C_L against $(rX + dC_L/dt)$ was plotted as presented in figure 5 for 15 L aeration tank system with 5 and 10 liters/min airflow rates. The validity of $K_L a$ analyzed for 5 liters/min was under dissolved oxygen limitation. The experimental data as presented in Figure 5 showed a good agreement for 10 liters /min airflow rate.

The oxygen transfer coefficient for 5 and 10 liters /min airflow rate were 0.0509 h^{-1} and 0.3918 h^{-1}, respectively. The superficial gas velocity (v_g) for turbulent flow region were predicted around 0.18 m s^{-1} and 1.3 ms^{-1} for

P, P_0 = Oxygen partial pressure in the gas (bulk and interface respectively), bar
P_g = agitator power under gassing conditions, W
$Q_{O2}X$ = Oxygen uptake to the microbial cell, mol/L.hr
r = Specific rate of oxygen uptake, mol/L.hr
V_L = liquid volume without gassing, m^3
v_s = superficial gas velocity, m/s
x = constant

REFERENCES

Badino, Jr., C. A., Facciotti, M. C. R. & Schmidell, W. 2000. Improving K_La determination in fungal fermentation, taking into account electrode response time. *J. Chem. Technol. Biotechnol.* 75: 469-474.

Bailey, J. & Ollis, D. F. 1986. *Biochemical engineering fundamentals*. New York: McGraw Hill, 494.

Deronzier, G., Duchene, P. H. & Heduit, A. 1998. The optimization of oxygen transfer in clean water. *Wat Sci Technol.* 38(3): 35-42.

Eckenfelder, W. W. 2000. *Industrial water pollution control*, 3rd. Ed. New York : McGraw Hill, 341.

Greenberg, A. E., Clesceri, L.S. & Eaton, A. D. 1992. *Standard methods for the examination of water and wastewater*, 18th Ed. Washington D.C. : American Public Health Association, American Water and Wastewater Association & Water Environment Federation.

Jia-Ming Chern & Cheng-Fu Yu. 1997. Oxygen transfer modeling diffused aeration systems. *Industrial Engineering and Chemical Research* 36: 5447-53.

Scragg, A. H. 1991. *Bioreactor in biotechnology*. New York: Ellis Horwood.

Summers, J. B. 1924. The estimation of sugar in diabetic urine, using dinitrosalicylic acid. *J. Biol. Chem.* 62(2): 248-254.

Thomas, L. C. & Chamberlain, G. J. 1980. *Colorimetric chemical analytical methods*. Salisbury : Tintometer Ltd., 31.

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