Influence of Temperature and pH on Short-term Estimation of Biochemical Oxygen Demand

Piyarat Premanoch* and Patikon Saensing**

*Department of Environmental Engineering, Faculty of Engineering, Ramkamhaeng University, Bangkok 10240, Thailand **Origin Instrument Co, Ltd., Nakhon Ratchasima 30000, Thailand *E-mail: s piyarat@yahoo.com

Abstract

This research aims to study the influence of temperature and pH on short-term Biochemical Oxygen Demand (BOD $_{\rm st}$) by measuring an oxygen uptake rate of activated sludge sample (microbe) taken from a return sludge pipe in an oxidation ditch at Maharaj Hospital, Nakhon Ratchasima Province, Thailand. The experiment was conducted by filtering solid materials and aerating sludge for not less than 12 hours without adding any substrates for sludge to enter the endogenous respiration condition. 20 mg/mL (13 mg COD/mL) of sodium acetate was used as a readily biodegradable COD substrate (rbCOD) and dosed to 2.2 liters of sludge sample. Final COD concentration was between 3.0-33.9 mg COD/L. Temperature, pH, oxygen and oxygen uptake rate were recorded every 3 seconds using an ultimate hybrid respirometer. Two experimental conditions were conducted, including uncontrolled and controlled conditions. The controlled experiment was conducted at 20 °C, 25 °C and 30 °C (\pm 0.5 °C) and pH was adjusted to 7.8 \pm 0.1 using NaOH 0.05N and HCl 0.05 N, while the uncontrolled experiment was conducted in the range between 25.6-27.6 °C and pH was adjusted to 7.0-9.6.

The experimental results showed the linear relationship between BOD $_{\rm st}$ and COD substrate concentration for each sample of both conditions. The slope of the uncontrolled system was equal to 0.37 ($\rm r^2=0.9917$); while for the controlled system, the average slope was equal to 0.31 ($\rm r^2=0.9950$). In addition, it was also found that when temperature was increased, the experimental duration was shorter from 9.7 minutes (20 °C) to 7.0 minutes (30 °C) at COD concentration was 5.3 mg/L. Furthermore, the research results showed that temperature did not affect the estimated accuracy of BOD $_{\rm st}$, of which the temperature range of 20-30 °C cover increasing temperature of wastewater throughout the year, while pH had a direct effect. Obviously, the findings of this research would be highly beneficial to develop a hybrid respirator system that can be used to analyze BOD $_{\rm st}$ of wastewater and effluent in the activated sludge wastewater treatment system for practical plant operations, which is called the BOD on-line Analyzer.

Keywords: BOD_{st}; Activated sludge; Respiration; Oxygen uptake rate

Introduction

generally known that 5-dav Biochemical Oxygen Demand (BOD₅) is a standard parameter for assessing biodegradable organic compounds contaminated in water that requires 5 days for analysis. There are other alternative methods that take shorter time, for example, Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). However, it is difficult to resign the indication of BOD and do it more precisely than with five-day BOD (BOD₅) in every case [1] as it correlates with a bio-process and concentration level of organic compounds degraded [2]. Short-term Biochemical Oxygen Demand BOD_{st} estimation using a technique of respiration measurement takes a significant shorter time to analyze and it is developed continuously in the measurement tools.

Data from a respiration measurement technique is not only used to estimate BOD_{st}, but also used to estimate kinetic parameters of microbes in the wastewater treatment process of activated sludge widely, [3-8] in the mathematical model development of activated sludge treatment progress [9]. Due to high accuracy of the measurement comparing with an expensive analysis tool, a technique of respiration measurement provides fast result; a duration of 1-1.5 hours can categorize kinetic parameter value of sample sludge without having to analyze concentration of substrate in laboratory [10, 11].

A method to interpret oxygen uptake rate (OUR) of microbes is called Short-term BOD (BOD_{st}), which is conducted by calculating area under the respiration curve called a respirogram (Figure 1). This means an amount of oxygen required to biodegrade organic matter that is easily decomposed per volume of wastewater

and time which takes less than 60 minutes, fast enough to apply in controlling and monitoring progress of activated sludge treatment. The area under the curve of OUR by microorganism under exogenous conditions was evaluated using Equation (1) [12].

$$BOD_{st} = \int_{0}^{tfin} OUR_{ex}(t)dt$$
 (1)

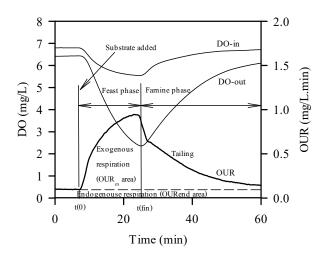


Figure 1 Respirogram

Respirogram is a data of oxygen uptake rate of microbes in sample sludge which consists of 2 parts including endogenous respiration (OUR $_{\rm end}$) and exogenous respiration of microbes under condition without substrate from outside, but activated sludge model 1 (ASM1) explained that endogenous respiration used substrate, part of which is from microbial decay, called Death-regeneration which is a lower part of the graph [13].

After adding acetate to sample sludge, oxygen uptake rate will increase rapidly to the maximum oxygen uptake rate (OUR_{max}) which is related to amount of microbes in the sludge. Exogenous respiration can be divided into 2 phases

including feast, which OUR_{max} level is stable until all substrates are used and after that, oxygen uptake rate will decrease rapidly. Then, it is famine, which oxygen uptake rate gradually decreases to starting value, this graph is called tailing. It's caused by microbes taking back substrate kept in polymer form to use again.

Materials and Methods

Activated sludge samples were taken from the sewage wastewater treatment system (oxidation ditch) in Maharaj Hospital, Nakhon Ratchasima Province. Sludge solid materials samples were filtered and aerated for not less than 12 hours without adding any substrates until reaching the endogenous respiration phase. The remaining substrate in the water would be used by microbes. An initial sludge concentration was 4,995 mg/L. 20 mg/mL (13 mg COD/mL) of sodium acetate of was used as a readily biodegradable COD substrate (rbCOD) and dosed to 2.2 liters of sludge sample. Final COD concentration level was varied into 4 dilutions; 3.0, 5.3, 10.6, 20.4 and 33.9 mg/L. pH was adjusted using NaOH 0.05N and HCl 0.05 N. The OUR data of sludge samples was collected using an ultimate hybrid respirometer. An overview of the instrument of measuring oxygen uptake rate experiment using hybrid respirometer machine is shown in Figure 2. It consisted of the aeration vessel and the respiration chamber with volume of 1.53 and 0.67 L. A pH electrode was placed on the aeration vessel and two polarographic dissolved oxygen electrodes were placed in the measuring chamber. The signal data from all electrodes was computed continuously by Labview 8.2 software package (National Instruments). Record data of temperature, pH, oxygen and OUR were collected in every 3 seconds. The value of OUR was calculated from DO mass balance around the respiration chamber using Equation (2) [12] below:

$$OUR = \frac{dS_{O,2}}{dt} + \frac{Q}{V_2} \left(S_{O,1} - S_{O,2} \right)$$
 (2)

Where Q is sludge circulation rate (L/min) and V_2 is respiration chamber volume (L). $S_{0,1}$ and $S_{0,2}$ are concentrations of oxygen flowing into and out of the respiration chamber [14]. Two experimental conditions were conducted, controlled and uncontrolled including conditions. The controlled experiment was conducted at 20 $^{\circ}$ C, 25 $^{\circ}$ C and 30 $^{\circ}$ C (± 0.5 $^{\circ}$ C) and pH was adjusted to 7.8±0.1 using NaOH 0.05N and HCl 0.05 N, while the uncontrolled experiment was conducted in the range between 25.6-27.6 °C and pH was adjusted to 7.0-9.6. Dissolved oxygen (DO) was controlled at 6-7 mg/L. Experiments were repeated 5 times continuously in each concentration of substrate. At the end of each experiment, the suspended solids of sludge samples, (MLSS) were analysed by following a standard method (American Public Health Association (APHA, 2005)) [15]. The area under the curve of OUR by microorganism under exogenous conditions was evaluated using Equation (2), with Microsoft Excel, Origin Pro and Sigma Plot programs used for computation.

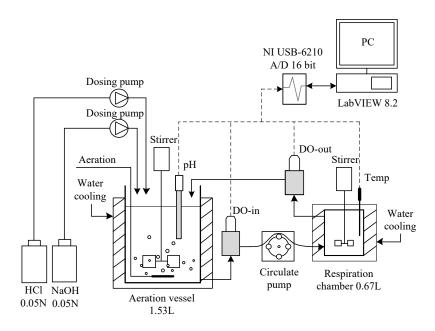


Figure 2 Ultimate hybrid respirometer [5]

Results and Discussion

The OUR data of sludge samples was collected using an ultimate hybrid respirometer. The experiment measuring oxygen uptake rate of uncontrolled sample sludge was conducted at temperature between 25.6-27.6 °C and pH 7.0-9.6, while the controlled experiment was conducted at temperature of 20 °C, 25 °C and 30 $^{\circ}\text{C}$ (±0.5 $^{\circ}\text{C})$ and pH of 7.8±0.1. A sludge sample with an initial concentration of 4,357±461 mg/L was used in the experiment. 20 mg/mL (13 mgCOD/mL) of sodium acetate was used as a readily biodegradable COD substrate (rbCOD) and dosed to 2.2 liters of sludge sample. Final COD concentration level was varied into 5 dilutions; 3.0, 5.3, 10.6, 20.4 and 33.9 mg/L. Figure 3 shows an example of respirogram of oxygen value tendency and oxygen uptake rate from adding substrates with COD concentration of 5.3 mg/L operated at the temperature of 30°C for 5 times continuously. The results of BOD_{st} estimation from all experiments calculated by equation (1) are shown in Table 1.

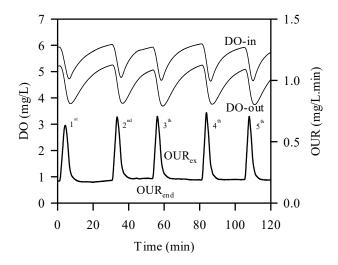


Figure 3 Example of oxygen uptake rate respirogram of 5 continuous experiments (COD substrate = 5.3 mg/L, Temperature = 30°C)

Table 1 Result of BOD_{st} estimation

COD substrate (mg COD/L)	BOD _{st} (mg/L)			
	Uncontrolled (temperature	Controlled temperature and pH 7.8 ± 0.1		
	25.6-27.6 °C and pH 7.0-9.6)	20 ± 0.5°C	25 ± 0.5°C	30 ± 0.5°C
3.0	0.84 ± 0.05	0.91 ± 0.06	0.75 ± 0.03	0.82 ± 0.04
5.3	1.78 ± 0.06	1.80 ± 0.07	1.59 ± 0.15	1.58 ± 0.07
10.6	4.17 ±0.09	3.60 ± 0.07	3.54 ± 0.11	3.29 ± 0.20
20.4	8.13 ± 0.14	6.43 ± 0.34	6.65 ± 0.11	6.79 ± 0.17
33.9	12.07 ± 0.47	9.93 ± 0.25	10.27 ± 0.16	10.05 ± 0.14
Slope	0.3679	0.3022	0.3102	0.3062
r ²	0.9917	0.9931	0.9958	0.9930

According to data in Table 1, it was found that the uncontrolled experiment has lower r² than controlled experiments with 3 temperature levels. Higher slope was found to be significantly different from the controlled experiment. The slope of controlled condition for all experiments was similar meaning that temperature has lower effect on reliability of BOD_{st} estimation than pH. Therefore, pH should be constant control throughout the experiment. For the uncontrolled experiments, pH changed in the wide range from 7.0 to 9.6. Figure 4 is comparison of linear relations of the uncontrolled and controlled experiments, showing the linear relationship between BODs and COD substrate concentration for each sample. It was found that the controlled experiments at temperature of 20-30°C had an average slope of 0.3062. R² for all experiments was high and similar $(r^2 = 0.9930-0.9958)$. Reliability and validity of BOD_{st} estimation were also considered from the Yield (Y), which could be calculated from Y = 1 - Slope [16]. The experiments of uncontrolled and controlled temperature and pH would have Y equal to 0.63 and 0.69 mg cell (COD)/mg COD. It can be

seen that the controlled experiment had value of Y that was close to the yield referred in the activated sludge model 1 (ASM no.1) of 0.67 mg cell (COD)/mg COD at the standard temperature of 20°C [13] and the results were consistent with the study by Saensing, P. and Kanchanatawee, S. [5], Premanoch, P. [7] and Muller et al. [16] of 0.69 mg cell (COD)/mg COD.

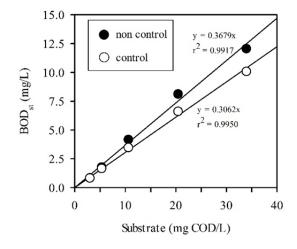


Figure 4 Comparing linear relations of uncontrolled and controlled experiments

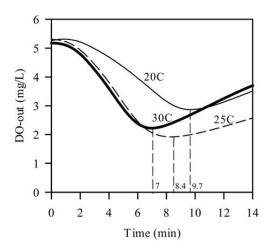


Figure 5 Influence of temperature on experimental duration

Moreover, the temperature affected to a duration of experiment that could reflect by DO-out peak in Figure 5. It was found that when temperature increased, it made experiment duration shorter. When comparing the experimental results with COD of 5.3 mg/L at 20 $^{\circ}$ C, 25 $^{\circ}$ C and 30 $^{\circ}$ C, the experiment duration would be equal to 9.7, 8.4 and 7.0 minutes, respectively.

Conclusions

In conclusion, the findings indicated that controlling pH has higher influence on the reliability and validity in BOD_{st} estimation using respiration measurement than controlling temperature. The experiment of uncontrolled temperature and pH has lower linear relation ($r^2 = 0.9917$) than controlled experiment ($r^2 = 0.9950$). It shows that BOD_{st} estimation requires controlling stable pH while increasing temperature will reduce the duration of OUR measurement without any influence on BOD_{st} estimation.

The reliability and validity could be considered from the Yield of 0.69 mg cell (COD)/mg COD of experiments with the controlled temperature and pH which was close

to the referred value in activated sludge model 1 (ASM1) [13] at the standard temperature of 20°C equal to 0.67 mg cell (COD)/mg COD. The results of this experiment were consistent with the previous researchers [5, 7, 15] using the same principles and techniques (0.69 mg cell (COD)/mg COD). However, the development of instrumentation is needed. For example, an oxygen electrode with automatic computation functions will further reduce the time consumed in experimentation and provide greater accuracy as well as increased stability, ease of use and convenient maintenance.

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