Korean J. Chem. Eng., **25**(3), 553-557 (2008)

Non-steady state estimation of biodegradability of dyeing wastewater using respirometer

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(*Received 31 July 2007 • accepted 20 September 2007*)

Abstract−Dyeing wastewater is notorious for its non-readily-biodegradability because it contains various kinds of refractory chemicals. To set up a strategy for controlling the dyeing wastewater discharged into conventional wastewater treatment plants, obtaining bio-kinetic information such as maximum specific growth rate (μ_{max}) and half saturation constant (K_s) should first be done. To estimate the biodegradability of the dyeing wastewater, bio-kinetic constants of the artificially formulated dyeing wastewater containing 33 different dyes and auxiliaries were determined by using a respirometer. Activated sludge acclimated to the artificial dyeing wastewater was inoculated to the respirometer and the bio-kinetic constants were determined from oxygen uptake data. The μ_{max} was found to 0.06 hr^{-1}, which is 3 to 15 times smaller than that of the typical activated sludge for sewage treatment. The K_s was found to 210 mg/L, which was 3.5 to 21 times higher than that of the normal activated sludge.

Key words: Auxiliaries, Biodegradability, Bio-kinetics, Dyeing Wastewater, Respirometer

INTRODUCTION

Textile industry is notorious for discharging huge amounts of pollutants into receiving water bodies. Wastewater in the textile industry is generated mainly from washing and finishing steps after dyeing processes. Dyeing wastewater is usually treated by conventional wastewater treatment processes: physico-chemical, and then biological treatment. However, it has been known that the dyeing wastewater is hardly degraded biologically because the dyes and auxiliary chemicals used in dyeing processes have a complex and refractory molecular nature.

Many studies have mainly focused on development of new technologies to treat the dyeing wastewater effectively, for example, the advanced oxidation processes using an oxidants such as ozone [1] and biological treatment using cell immobilization [2] etc. However, in order to treat the dyeing wastewater properly and effectively, information on the bio-degradability of the dyeing wastewater should first be obtained. But there has been little literature reporting the biodegradability of the dyeing wastewater.

Bio-kinetic information on the dyeing wastewater can be determined by using a respirometer. Based on monitoring microbial oxygen consumption rate, bio-kinetic parameters of dyeing wastewater could be achieved, which could help us to understand degradation characteristics of refractory materials quantitatively [3,4].

Monod kinetics had been used as a basic tool analyzing system performance of biological wastewater treatment. Although there are many parameters characterizing the microorganisms and substrates, the half saturation constant (K_s) and maximum specific growth rate (μ_{max}) are most important parameters for understanding biodegradability, affinity and compatibility of substrates to microorganisms. Both parameters were determined by the respirometer in this study. Therefore, the aim of this study was to provide quantitative information on the biodegradability of the dyeing wastewater.

MATERIALS AND METHODS

1. Determination of Bio-kinetic Constants by Using a Respirometer

Bio-kinetic constants of the dyeing wastewater were determined by using a respirometer. Fig. 1 shows the schematic of the experimental setup for the respirometer (COMPUT-OX Respirometer, Model 00-14, US). Temperature was controlled to 20±2 °C with a water bath, and pH was also controlled to 7±0.5.

Synthetic dyeing wastewater (preparation will be explained in section 2.3) was poured into the respirometer which was already inoculated with activated sludge acclimated to the synthetic dying wastewater. The respirometer was connected to an oxygen cylinder and then sealed. The sludge in the respirometer generated carbon

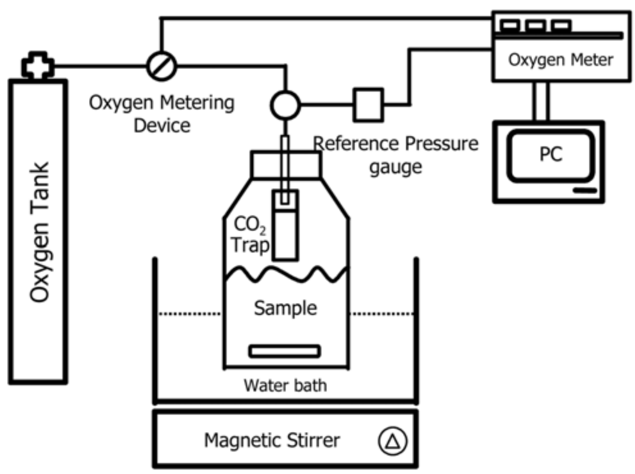

Fig. 1. Schematic of the respirometer system.

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dioxide (CO_2) during the dissimilation of the substrates, i.e., respiration began. The CO_2 was absorbed to potassium hydroxide (KOH) pellets located inside the respirometer, which made inner pressure of the respirometer decreased. Pressure sensor detected the pressure drop, and it made the regulator open the valve of the oxygen cylinder to release oxygen into the respirometer until the supplied oxygen compensated for the pressure drop. The amounts of released oxygen were recorded and saved on a personal computer. Accumulated oxygen uptake curve as a function of time was drawn with these data, and then bio-kinetic constants could be obtained.

2. Cultivation of Activated Sludge and Acclimation to Synthetic Feed Solution

Activated sludge was sampled from a sewage treatment plant. The sludge was immediately delivered to the laboratory and inoculated to a 10 L bioreactor. It had been cultivated with synthetic feed solution. Table 1 shows the components of the synthetic feed solution. The main source of carbon and nitrogen in the feed solution was glucose and ammonium sulfate, respectively. The bioreactor was run by the fill and draw method, i.e., like a sequencing batch reactor. F/M ratio was controlled to 0.29-0.33 kgCOD/kgMLSS. HRT was 12-24 hr and SRT (Solid Retention Time) was 4-8 day. For the purpose of aeration and mixing, 3 L/min of air was supplied to the bioreactor. Temperature was controlled to 20±2 °C.

The synthetic dyeing wastewater was fed to the bioreactor after 3 weeks of acclimation to the synthetic feed solution. Diluted synthetic dyeing wastewater was fed to the bioreactor at first. Increasing loading rate of the synthetic dyeing wastewater gradually, the activated sludge in the bioreactor was acclimated to the synthetic dyeing wastewater. Activated sludge reached steady state after 3 months of operation. The activated sludge was taken out from the bioreactor and then transferred to the respirometer to obtain oxygen uptake data.

Table 1. Composition of feed-water for acclimation of activated sludge

Components	Concentration (mg/L)
Glucose	150
Peptone	45
Yeast extract	120
$(NH_4)_2SO_4$	96
KH_2PO_4	44
$MgSO_4 \cdot 7H_2O$	24
$MnSO_4 \cdot 4\text{-}5H_2O$	2.16
$FeCl_2 \cdot 6H_2O$	0.12
$CaCl_2 \cdot 2H_2O$	2.40
$NaHCO_3$	30

3. Synthetic Dyeing Wastewater

33 different dyes and auxiliaries typically used in the textile industry were selected for preparing the synthetic dyeing wastewater. Representative 5 reactive dyes and 9 disperse dyes were selected. 0.15 g of each dye was dissolved to 1 liter of water. 19 different auxiliaries used for dyeing cottons and polyesters were selected. All dyes and auxiliaries were kindly delivered from the textile industry and they are all commercially available. Tables 2 and 3 show the characteristics of each component of the dyes and auxiliaries used in preparation of the synthetic dyeing wastewater. Table 4 shows the concentration of pH, total organic carbon (TOC), conductivity, color, total dissolved solids (TDS) and COD_{cr} of the synthetic dyeing wastewater. The measured water quality was quite similar to that of the dyeing wastewater generated from a real textile industry.

4. Analytical Methods

Water quality (TDS, BOD_5, COD_{cr}, and COD_{Mn}) of the synthetic wastewater, influents and effluents of the bioreactor was measured according to the analytical methods described in Standard methods [5,6]. TOC and color were measured by TOC analyzer (Phoenix 80000, Tekmer Dohrmann, USA) and UV/VIS/NIR spectrometer (Varian Cary 5000, USA) respectively. Electric conductivity was measured by conductivity meter (K612, CONSORT, Belgium).

THEORY

To get bio-kinetic information on the biological wastewater treat-

Table 2. Characteristics of the dyes formulated in artificial dyeing wastewater

Types	Commercial names of dyes	Dissolution (g/L)	Concentration (mg/L)			
			TOC	COD_{Mn}	COD_{cr}	BOD_5
Reactive dye	Cibacron Yellow C-RG	0.15	34	40	104	3.6
	Cibacron Red C-2BL	0.15	42	51	143	3.6
	Cibacron Blue CR	0.15	38	42	113	4.0
	Cibacron Navy CB	0.15	37	46	121	1.2
	Cibacron Black CNN liq.	0.15	9	8	48	2.2
Disperse dye for pale dyeing	Miketon Yellow R-SE	0.15	54	83	150	30
	Miketon Red RSE	0.15	54	83	148	66
	Miketon Blue R-SE	0.15	52	73	146	50
Disperse dye for medium to dark dyeing	Foron Y/Brown S-2RFL	0.15	56	80	182	104
	Foron Rubine S-2GFL	0.15	56	95	162	40
	Dianix Blue S-2G	0.15	55	84	161	30
Disperse dye	Esperese N/Blue MD	0.15	51	77	143	46
	Foron Black RD-3G	0.15	52	88	131	78
	Lumaron Black RD-3G	0.15	54	86	157	66

Table 3. Characteristics of the auxiliaries formulated in synthetic dyeing wastewater

(a) Auxiliaries used for cotton dyeing

Commercial names/function	Dilution factor	Actual concentration after dilution (mg/L)			
		TOC	COD_{Mn}	COD_{cr}	BOD_5
lnvatex SA/chelating agent	×1000	143	150	130	118
Ultravon PL/wetting agent for continuous process	×1000	324	352	1,300	78
Tinoclarite CBB/H_2O_2 stabilizer	×1000	55	101	153	56
lnvadine MR/wetting agent for mercerization	×1000	259	128	1,068	74
lrgapadol PR/wetting agent for dyeing	×1000	358	120	1,536	114
Cibapon R/soaping agent	×1000	150	89	429	189
Alvatex FFC/de-foaming agent	×1000	328	148	1,547	232
Cibafluid P/anti-friction agent	×1000	156	185	348	1.6
Cationic Softener	×1000	73	102	278	2.0
Silicon Softener	×1000	99	98	447	46

(b) Auxiliaries used for polyester dyeing

Commercial names/function	Dilution factor	Actual concentration after dilution (mg/L)			
		TOC	COD_{Mn}	COD_{Cr}	BOD_5
Imerol Xn/scouring agent	-	30	32	94	20
Leophen FR-M/wetting agent	×1000	426	300	954	140
Neocrystal KO/oligomer dispersing agent	×1000	100	71	251	185
Imerol DKK/scouring agent	×1000	265	192	883	230
Ladicuest 1097/chelating agent	×1000	50	45	128	12
Modarez Acf/anti- friction agent	×1000	118	62	393	220
Acid PEA/pH buffering agent	×1000	198	257	509	105
Dispel DT/dispersing agent	×1000	269	323	886	120
Unidyne TG 473/water/oil repellent	×1000	230	95	656	135

Table 4. Characteristics of the synthetic dyeing wastewater

Water quality parameter	Actual concentration
COD_{cr}	14,800 mg/L
TOC	3,770 mg/L
Color	59,400 (Pt/Co)
Conductivity	1369 μS/cm
TDS (Total Dissolved Solids)	19,800 mg/L
pH	3.3

ment, first, the half saturation constant (K_s) and the maximum specific growth rate (μ_{max}) should be determined. Based on Monod kinetics, both parameters are important for understanding the biodegradability, affinity and compatibility of substrates. Both parameters were determined by the accumulated oxygen-uptake data obtained from the respirometric experiments [7]. The procedure was as follows.

As shown in Eq. (1), all metabolized COD in the respirometer (ΔCOD) is channeled into either oxygen uptake (O_2 Uptake) or into microbial cell COD (ΔCOD_{cells}), i.e., the amount of substrate removal is accounted for as the amount of COD that has been oxidized (O_2 Uptake) plus that which has been incorporated into the cells (ΔCOD_{cells}). The O_2-Uptake in Eq. (1) represents the amounts of oxidized COD and the ΔCOD_{cells} means the amounts of COD channeled into new synthesized biomass cells.

$$\Delta COD = O_{2Uptake} + \Delta COD_{cells} \tag{1}$$

ΔCOD : the amounts of substrate removal in an aerobic biological system (mg)
O_2 Uptake : the accumulated oxygen uptake (mg)
ΔCOD_{cells} : the amounts of COD that has been incorporated into the cell (mg)

ΔCOD and ΔCOD_{cells} can be obtained through the Eq. (2) for biomass yield (Y) and the Eq. (3) for unit cell mass (O_x), respectively.

$$\Delta COD = \frac{\Delta X}{Y} \tag{2}$$

$$\Delta COD_{cells} = \Delta X \cdot O_x \tag{3}$$

ΔX : the amount of cells produced (mg cell)
Y : Yield (mg cell/ mg substrate)
O_x : unit COD of cell mass (mg O_2/mg cell)

Recognizing that $\Delta X = X_t - X_o$ and substituting the Eq. (2) and (3) into the Eq. (1), the following Eq. (4) is obtained.

$$\frac{(X_t - X_o)}{Y} = O_{2Uptake} + (X_t - X_o)O_x \tag{4}$$

X_t : cell concentration at time arbitrary time t (mg/L)

X_o : initial cell concentration (mg/L)

Rearranging and simplifying Eq. (4) yields Eq. (5)

$$X_t = X_o + \frac{O_{2Uptake}}{1/Y - O_x} \quad (5)$$

Since the O_x and Y are available from separate batch experiments, Eq. (5) can be used to convert oxygen uptake data into biomass growth curves, i.e., time vs. biomass concentration. This graph can be analyzed to determine growth rates for different initial wastewater concentration.

Specific growth rate (μ=(1/X)(dX/dt)) is defined as the growth rate per unit biomass. Integrating it gives the following Eq. (6).

$$\mu = \frac{\ln(X_2 - X_1)}{t_2 - t_1} \quad (6)$$

X_1, X_2 : cell concentration at arbitrary time (mg/L)
t_1, t_2 : time

If we plot the biomass concentration obtained from Eq. (5) on semi-logarithmic paper as a function of time, i.e., $\ln X_t$ vs. t, we can get a straight line. As shown in Eq. (6), the slope of the line is specific growth rate (μ). If different waste concentrations are used in this procedure, several different m values could be obtained. Plotting the μ values as a function of waste concentration (S or COD), we can have a typical growth curve (S vs. μ), where we can finally obtain the maximum specific growth rate (μ_{max}) and half saturation constant (K_s).

RESULTS AND DISCUSSIONS

1. Effluents of the Bioreactor

The activated sludge was acclimated to the synthetic dyeing wastewater for 3 months. After reaching steady state, water quality of the influent and effluent was compared (Fig. 2). Removal efficiencies of the COD_{cr} and BOD_5 were 39% and 86%, respectively, which means that the non-biodegradable organics still remained in the effluents. Since the BOD_5 removal was relatively high, it looks like a large portion of the organics in the influent was degraded biologically. However, there was still 61% of COD_{cr} that remained undegraded. To see how much of the non-biodegradable organics remained in the effluents, a ratio of COD_{cr} and BOD_5 was calculated.

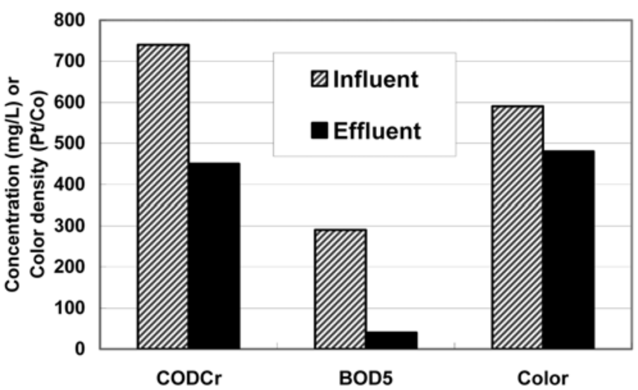

Fig. 2. Biological removals of COD, BOD and color of the synthetic dyeing wastewater.

The ratio of synthetic dyeing wastewater, ($COD_{cr}-BOD_5$)/COD_{cr}, was 61%, but the effluent's ratio increased to 89%, indicating that significant amounts of non-biodegradable organic compounds still remained in the effluent.

On the other hand, only 18% of the color of the synthetic dyeing wastewater was removed by the activated sludge, suggesting that the color components were much more recalcitrant than the components of the COD_{cr} and BOD.

2. Determination of Bio-kinetic Constants of the Dyeing Wastewater

Bio-kinetic constants, μ_{max} and K_s for the dyeing wastewater were determined through the same way described in the previous section. The dyeing wastewater was diluted to have different concentration of 40, 60, 80, and 100%. The concentration of the diluted dyeing wastewater was expressed as %: the concentration of undiluted dyeing wastewater was 100%. The diluted and undiluted synthetic dyeing wastewaters having different concentration were inoculated to 4 separate respirometers. Each respirometer was run simultaneously and the accumulated oxygen uptake data were achieved. Fig. 3 shows the cumulative O_2-Uptake data as a function of time according to four different waste concentrations. The oxygen uptake increased as the waste concentration increased.

On the other hand, to get a yield coefficient, Y, a separate batch reactor was run. Activated sludge acclimated to the synthetic dyeing wastewater was inoculated to the batch reactor. The synthetic dyeing wastewater was spiked and the reactor was aerated. Initial soluble-COD and MLSS concentrations were 723 and 5,160 mg/

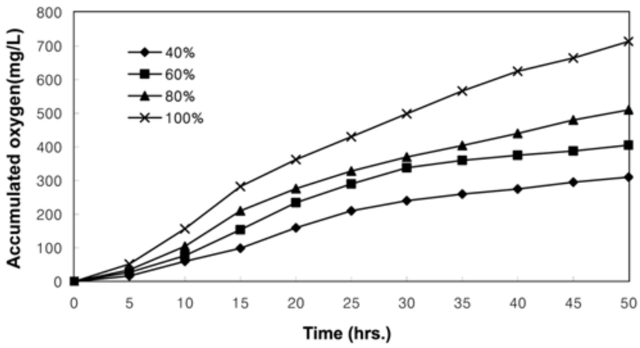

Fig. 3. Accumulated oxygen uptakes as a function of time according to different dyeing wastewater concentrations.

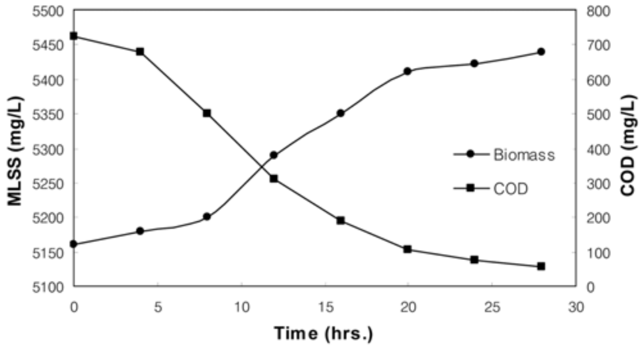

Fig. 4. Variation of the COD and MLSS concentration of the batch reactor as a function of time.

L, respectively. Soluble-COD and MLSS concentrations were monitored as a function of operation time (Fig. 4). Since Y is defined as the ratio of generated biomass to oxidized substrates, Y could be computed as $\Delta X/\Delta COD$. The computed Y value from the data in Fig. 4 was 0.42 mg MLSS/mg COD; Y=(5440-5160)/(723-56)=0.42 mg MLSS/mg COD.

Determination O_x value is also needed to calculate the X_t in the Eq. (5). It is well known that the experimentally determined value of O_x is very close to 1.42 mg COD/mg MLSS, which is theoretically calculated according to following stoichiometric equation [8].

$$C_5H_7NO_2+5O_2 \leftrightarrow 5CO_2+2H_2O+NH_3 \quad (7)$$

Molecular weights: 113 g 160 g (=5×32)

$C_5H_7NO_2$ is a typical molecular formula representing microorganisms of activated sludge. Therefore, the calculated O_x value, 1.42 g COD/g MLSS (=160 g/113 g) was used in this study instead performing a separate batch experiment.

Based on the procedure described in the Theory, μ_{max} and K_s values for the dyeing wastewater were determined by using the accumulated oxygen uptake data shown in Fig. 3. The μ_{max} and K_s were determined to 0.06 hr^{-1}, and 210 mg/L, respectively. Considering that μ_{max} and K_s values of the activated sludge in domestic wastewater treatment plants typically range from 0.2 to 0.9 hr^{-1}, and from 10 to 60 mg/L, respectively [9], both values of the dyeing wastewater seemed to be significantly different with them. The μ_{max} of the dyeing wastewater was 3-15 times smaller than that of sewage treatment plant. The K_s of the dyeing wastewater was 3.5-21 times greater than that of normal activated sludge. In general, the greater μ_{max}, the more affinity to wastewater biomass has. The smaller K_s, the more biodegradable wastewater is. Therefore, the synthetic dyeing wastewater used in this study could be classified as very non-readily-biodegradable and recalcitrant.

The dyeing wastewater is not readily biodegradable as is well known, so that the result of this study was not so surprising. However, quantitative analysis of their non-biodegradability has not been reported in the literature. Therefore, the result of this study is important for developing a new strategy for management of the wastewater treatment plants dealing with dyeing wastewater. Using the bio-kinetic data, the engineering parameters such as hydraulic retention time (HRT) and recycling flow ratio (α) of returned activated sludge (RAS) can be controlled to optimize the wastewater treatment plants [10]. Moreover, further accumulation of bio-kinetic data of various kinds of dyes and auxiliaries using the method used in this study can contribute to development of environmentally friendly dyes and auxiliaries.

CONCLUSION

To investigate the biodegradability of the dyeing wastewater, synthetic dyeing wastewater was made of 33 different dyes and auxiliaries typically used in the textile industry. After three months of acclimation, the removal efficiencies of COD_{cr} and BOD_5 were 39% and 86%, respectively. The ratio of COD_{cr} and BOD_5 of the synthetic dyeing wastewater, $(COD_{cr}-BOD_5)/COD_{cr}$, was 61%, but the ratio of effluent increased to 89%, indicating that significant amounts of non-biodegradable organic compounds still remained in the effluent. Bio-kinetic constants of the acclimated activated sludge, μ_{max} and K_s, were determined by using a respirometer. The determined μ_{max} and K_s values were 0.06 hr^{-1}, and 210 mg/L, respectively. The synthetic dyeing wastewater used in this study could be classified as very non-readily-biodegradable and recalcitrant. Results of this study could be used as basic criteria for improving the system performance of wastewater treatment plants dealing with dyeing wastewater.

ACKNOWLEDGMENT

The authors would like to offer appreciation to the “Chung-Nam Environmental Technology Development Center” and “Ministry of Environment” (Projects: Establishment of evaluation tool for clean dyestuffs and evaluation of eco-friendliness of dyestuffs developed) for their support of this study.

NOMENCLATURE

μ_{max} : maximum specific growth rate [hr^{-1}]
ΔCOD : the amounts of substrate removal in an aerobic biological system [mg]
ΔCOD_{cells} : the amount of COD that has been incorporated into the cell [mg]
ΔX : the amount of cells produced [mg cell]
K_s : half saturation constant [mg/L]
$O_{2Uptake}$: the accumulated oxygen uptake [mg]
O_x : unit COD of cell mass [mg O_2/mg cell]
X_1, X_2 : cell concentration at arbitrary time [mg/L]
Y : yield [mg cell/mg substrate]

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