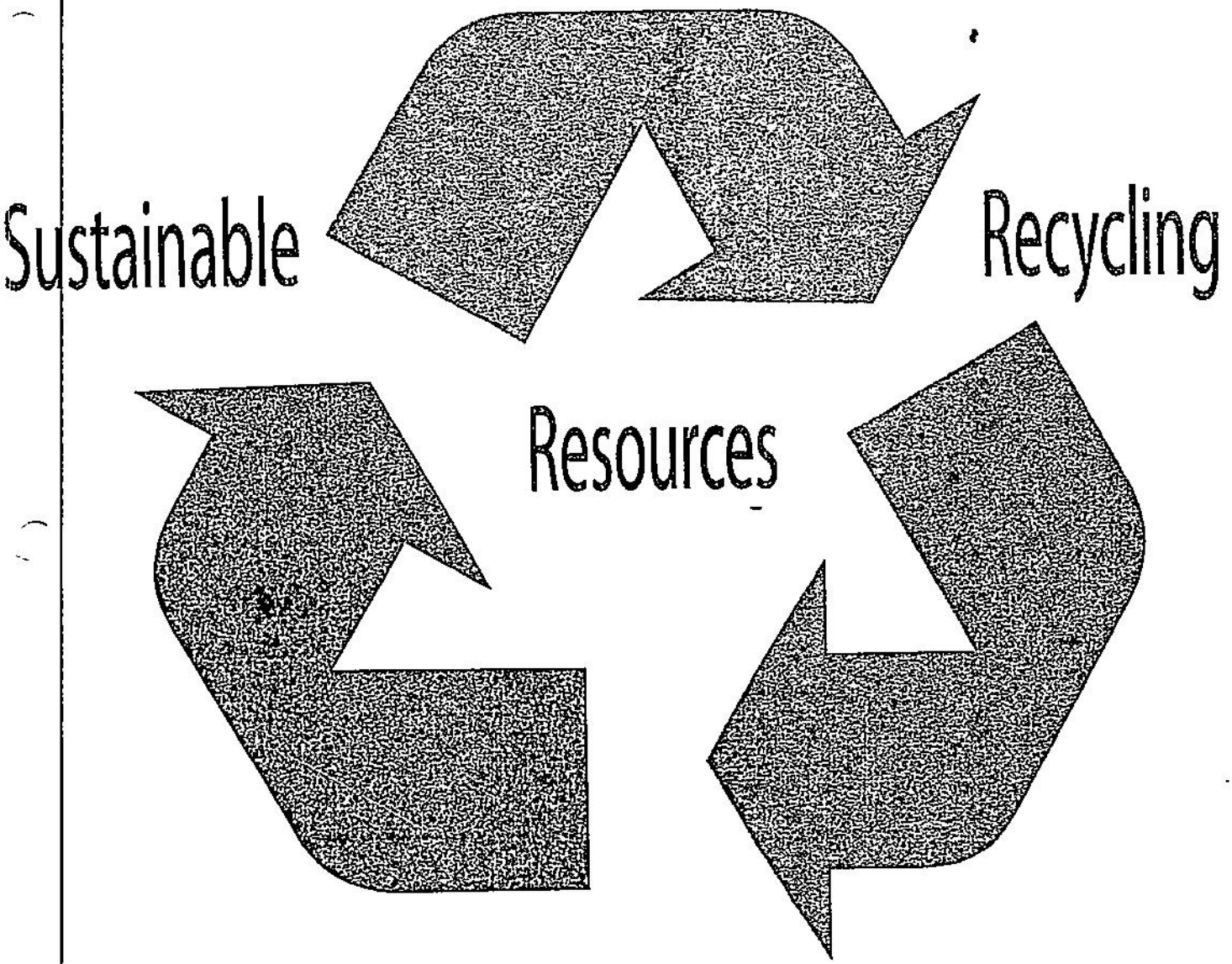
The CBNU-BK21 and KMUTT International Symposium

on

The Sustainable Resource Recycling Technology Development in Environmental and Urban Engineering

11th February 2008, Bangkok, Thailand



BK21 Brain Korea21

CHUNGBUK NATIONAL UNIVERSITY

ESS

Contents

Kinetics of reactive dye with modified starch as carbon source by partially granulated anaerobic mixed culture

Sunantha Laowansiri[1,2*], Soydoa Vinitnantharat[1,*], Pawinee Chaiprasert[3] and Sung-Ryong Ha[4]

[1] Division of Environmental Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi, Bangkok, Thailand
[2]Faculty of Environment and Resource Studies, Mahasarakham University, Mahasarakham, Thailand
[3] Division of Biotechnology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, Bangkok, Thailand
[4] Department of Urban Engineering, Chungbuk National University, Chungbuk, Republic of Korea

Abstract: Color removal and kinetic of reactive dye, reactive red 141 (RR 141), using Modified starch (MS) as carbon source which the concentration of 800 mg COD/l and color concentrations of 50-1000 mg/l by a partially granulated anaerobic mixed culture was studied. Batch test experiments were employed by mixing the 1.8 g MLVSS/l of mixed microorganisms in the solution containing MS and dye. Then they were incubated in an incubator at 37±1 °C for 324 h. Results revealed that RR141 concentrations increased as COD removal decreased. The percentages of COD removal were between 40.4 and 59.4 at steady state while the high color removals ranged between 94.0 and 96.3 at steady state. RR 141 at the concentrations between 50-300 mg/l fitted the first-order and second-order kinetics whereas, RR 141 at the concentrations between 400 and 1000 mg/l fitted zero-order kinetics. The decolorization of RR141 fitted Lineweaver-Burk equation. The values of V_{max} was 9.46 mg/h and K_m was 801 mg/l.

Keywords: Anaerobic treatment, Decolorization, Kinetics, Reactive Red 141e

1. INTRODUCTION

Azo dyes are the most widely used class of dyes in the industrial world market [1]. Approximately 10-15% of all the azo dyes produced are released into the environment [2]. This has a strong negative impact on the aquatic environment because some of the azo dyes or their secondary products have strong toxic, mutagenic and carcinogenic effects on living organisms.

Many different methods have been used for the treatment of textile wastewater. In case of biological treatment, the anaerobic digestion of textile possibly remove high COD and nearly complete decolorization [3, 4], while the traditional aerobic wastewater treatment systems do not substantially decrease the color [5]. Therefore, the objective of this work is to study the color removal and kinetic of reactive red 141 (RR 141) using MS as carbon source which the concentration of 800 mg COD/l and color concentrations of 50-1000 mg/l by a partially granulated anaerobic mixed culture.

2. METHODOLOGY

2.1 Synthetic textile wastewater

Synthetic textile wastewater was prepared by mixing the basal medium and trace elements solution. The basal medium contains (in g/l): NaCl 0.15, $(NH_4)_2SO_4$ 0.28, NH_4Cl 0.23, $Na_3PO_4.12H_2O$ 0.123, Na_2HPO_4 0.38 and $NaHCO_3$ 1.5 g/l. The trace elements solution [6] was prepared in one liter of distillation water. It contains in g/l: $MgSO_4.7H_2O$ 5, $FeCl_2.4H_2O$ 6, $CoCl_3.4H_2O$ 0.88, H_3BO_3 0.3, $ZnSO_4.7H_2O$ 0.1, $CuSO_4.5H_2O$ 0.05, $NiSO_4.8H_2O$ 1, $MnCl_2.4H_2O$ 5, $(NH_4)_6Mo_7O_{24}.4H_2O$ 0.64 and $CaCl_2.2H_2O$ 5. One ml of this solution was added to 1 l of basal medium. The buffer solution contained 1.5 g/l $NaHCO_3$ and the pH was adjusted to 7.00 ± 0.02.

2.2 Carbon sources preparation

The modified starch as carbon sources was used in this study. MS is composed of starch ester. Stock MS solution (20 g/l) was prepared by hydrolysis of the solution in 4% NaOH solution, followed by heating for 2 h at 80 °C.

2.3 Dyestuff preparation

Commercial dye, C.I. Reactive Red 141 (Evercion Red H-E7B) was used in this work and obtained from Winimex Industry Co. Ltd., Thailand. The chemical structure of C.I. Reactive Red 141 is given in Fig. 1. The dye stock solution was prepared by dissolving 10 g of dye in 1000 ml of distilled water. To prepare synthetic textile wastewater using dye concentration of 50-1000 mg/l, the dye from stock solution was dissolved in synthetic textile wastewater.

Corresponding author: sunantha.l@msu.ac.th, soydoa.vin@kmutt.ac.th

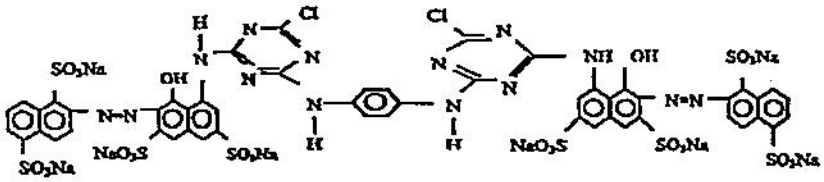


Fig. 1 Chemical structure of C.I. Reactive Red 141

2.4 Microorganisms

The partially granulated anaerobic mixed culture was collected from the UASB treatment plant of textile wastewater and obtained from Thai Textile Development and Finishing Co., Ltd., Thailand.

2.5 Serum bottle batch assay

Experiments were performed in a 120 ml serum bottle. The total working volume of 100 ml was used by mixing a portion of 70 ml of synthetic textile wastewater and 30 ml partially anaerobic granular sludge. The modified starch concentration of 800 mg COD/l with dye concentration of 50-1000 mg/l was used. The concentration of mixed liquor volatile suspended solids (MLVSS) was 1.8 g/l of total working volume. Serum bottles were flushed with nitrogen gas in the headspace and then sealed with butyl rubber stoppers and aluminium crimp seals. The serum bottles were static incubated at 37 ± 1°C and the supernatant of each bottle was taken gradually during incubation.

2.6 Analytical methods

The supernatant from serum bottles were filtered through GF/C and the filtrates were used for analysis of chemical oxygen demand (COD) and color. The MLVSS were also analyzed [7], while the pH was measured by pH meter type CD500 WPA. The color was measured at the maximum wavelength of 520 nm by a DR/3000 HACH spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Color and COD removal efficiencies

Table 1 shows color and COD removal efficiencies containing MS as carbon source (800 mg COD/l) with RR141 concentrations of 50-1000 mg/l. The RR141 concentrations increased the percentages of COD removal decreased. The percentages of COD removal were between 40.4 and 59.4 at steady state (516-660 h). The highest COD removal was 59.4 % at RR 141 concentrations of 50 mg/l. The high color removals were in the range of 94.0-96.3 % at steady state (420-660 h). The pH values were slightly increased at the initial period, after that, the pH dropped to 6.2 and then increased up to 7-7.03 (steady state) by the end of the incubation period. The higher concentration of MS carbon source, the higher acidogenic activity of acetogenic bacteria and deg radation. It is inferred that as consumption of MS concentration increased, the rate of accumulation of organic acids in the medium al so increased. This demonstrates the importance of pH control for decolorization when various biodegradable carbon sources are prese nt in dye wastewater.

Table 1 Color and COD removal containing MS as carbon source (800 mg COD/l) with RR141 concentrations of 50-1000 mg/l

RR 141 concentrations (mg/l)	Color removal (%)	COD removal (%)
50	94.0	59.4
100	95.2	59.3
200	95.1	53.5
300	94.0	53.6
400	94.5	54.4
500	95.0	51.1
600	95.9	49.1
800	96.3	41.4
1000	96.3	40.0

3.2 Decolorization kinetics of RR 141 with respect to color concentrations

Zero-, first- and second-order calculations were plotted in the form of RR 141 concentration (C_t) versus time (t), ln C_t/C_0 versus t, and $1/C_t$ versus t, respectively, in order to determine the decolorization kinetic (Table. 2) (where C_0 is RR 141 concentration at the beginning of the incubation through decolorization and C_t is residual RR 141 concentration at selected time (t) of batch test through decolorization). Zero-order reaction rate did not depend on the concentration of reacting substance. First-order reaction rate did depend on the concentration of only one reacting substance, and for a second-order reaction rate did depend on the concentration of two reacting substance

Table 2 shows Zero-, first- and second order rate constants from decolorization in anaerobic batch tests containing MS as carbon source (800 mg COD/l) with RR141 concentrations of 50-1000 mg/l at 0-84 h. RR 141 at the concentrations between 50-300 mg/l fitted the first-order and second-order kinetics whereas, RR 141 at the concentrations between 400 and 1000 mg/l fitted zero-order kinetics. The decolorization rate constants (k_0) increased as the RR 141 concentrations increased. Meanwhile the decolorization rate constants (k_1) decreased as the RR 141 concentrations increased. It is noted that RR 141 concentration higher than 300 mg/l decolorization rate did not depend on RR 141 concentration. This may caused by the accumulation of inter-metabolites through the

ultaneous degradation and decolorization of dye. The RR 141 concentration ranged between 50 and 300 mg/l decolorization rate depend on RR 141 concentration.

Table 2 Zero-, first- and second order rate constants from decolorization in anaerobic batch tests containing MS as carbon source (800 mg COD/l) with RR141 concentrations of 50-1000 mg/l

RR141 concentration (mg/l)	k and R^2	Zero order (k_0, mg/l-h)	First order (k_1, h^{-1})	Second order (k_2, l/mg-h)
50	k	0.5527	2.46×10^{-2}	1.5×10^{-3}
	R^2	0.8434	0.9151	0.9741
100	k	1.1017	2.19×10^{-2}	5×10^{-4}
	R^2	0.9014	0.9713	0.9691
200	k	1.8036	1.40×10^{-2}	1×10^{-4}
	R^2	0.9432	0.9794	0.9858
300	k	2.3725	1.23×10^{-2}	1×10^{-4}
	R^2	0.9662	0.9732	0.8954
400	k	3.0632	1.24×10^{-2}	7×10^{-5}
	R^2	0.9848	0.9741	0.8982
500	k	3.6204	1.12×10^{-2}	4×10^{-5}
	R^2	0.9850	0.9810	0.9156
600	k	3.8728	9.1×10^{-3}	4×10^{-5}
	R^2	0.9456	0.9689	0.8852
800	k	5.6048	1.08×10^{-2}	3×10^{-5}
	R^2	0.9935	0.9883	0.9007
1000	k	5.6903	8.2×10^{-3}	2×10^{-5}
	R^2	0.9043	0.8368	0.8394

According to the above results (Table 2), Linewever-Burk and Hanes-Woolf equations were plotted in form of zero rate stants (k_0) versus RR 141 concentration at the beginning of the incubation through decolorization (C_0). Linewever-Burk equation plotted in form of $1/k_0$ versus $1/C_0$ (Fig. 2) while Hanes-Woolf equation was plotted in form of C_0/k_0 versus C_0 (Fig. 3). Table 3 ws Linear equations of Lineweaver-Burk and Hanes-Woolf and V_{max} and K_m values. The decolorizations of RR141 fitted for weaver-Burk equation and yielded regression coefficients near 1 ($R^2 = 0.9976$). Lineweaver-Burk equation predicted RR 141 ction. The value of $V_{max} = 9.46$ mg/h and $K_m = 801$ mg/l

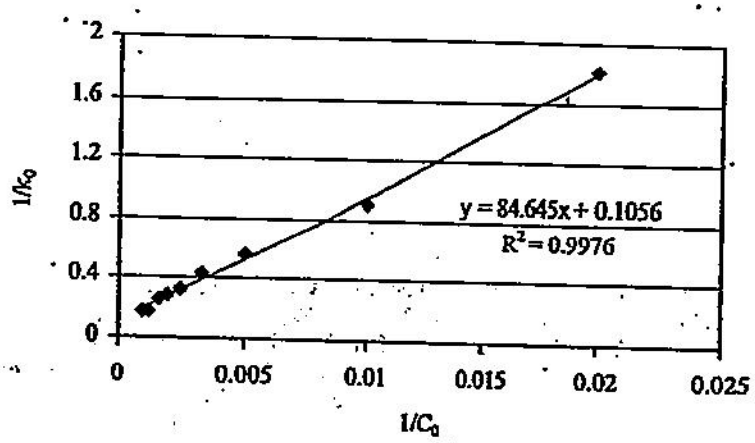


Fig. 2 Linear equation of Lineweaver-Burk

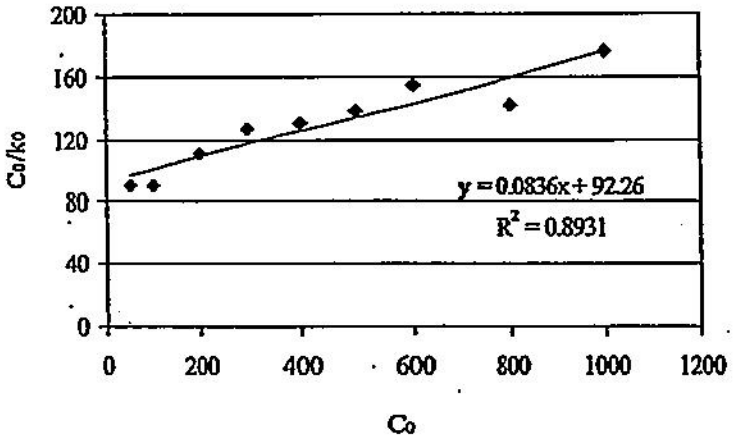


Fig. 3 Linear equation of Hanes-Woolf

Table 3 Linear equations of Lineweaver-Burk and Hanes-Woolf and V_{max} and K_m values

Equations	Linear equations	V_{max} (mg/h)	K_m (mg/l)
Lineweaver-Burk	Y = 84.645x + 0.1056 R^2 = 0.9976	9.46	801
Hanes-Woolf	Y = 0.0836x + 92.26 R^2 = 0.8931	11.96	1103

4. CONCLUSION

Microbial decolorization of RR 141 in anaerobic conditions occurs as a result of reduction and cleavage of the azo bonds. T percentages of COD removal were between 40.4 and 59.4 at steady state while the high color removals ranged between 94.0 a 96.3 % at steady state. RR 141 at the concentrations between 50-300 mg/l fitted the first-order and second-order kinetics where RR 141 at the concentrations between 400 and 1000 mg/l fitted zero-order kinetics. The decolorization of RR141 fitted Lineweav Burk equation. V_{max} (9.46 mg/h) and K_m (801 mg/l) predicted hydraulic retention time and RR 141 reduction for reactor.

5. ACKNOWLEDGMENTS

Authors would like to express their deep gratitude to the Commission on Higher Education and Thailand Research Fund (TF for financial support of this study.

6. REFERENCES

[1] Carliell, C.M., Barclay, S.J., Naidoo, N., Buckley, C.A., Mulholland, D.A., Senior, E. (1995) Microbial decolourisation of a reactive azo dye under anaerobic conditions, *Water SA*, 21, (2), pp. 61-69.

[2] Tan, N.C.G., Borger, A., Slenders, P., Svitelskaya, A., Lettinga, G. and Field, J.A. (2000) Degradation of azo dye Mordant Yellow 10 in a sequential anaerobic and bioaugmented aerobic bioreactor, *Water Science and Technology*, 42, pp. 337–344.

[3] Bell, J. and Buckley, C.A. (2003) Treatment of a textile dye in the anaerobic baffled reactor, *Water SA*, 29, (2), pp. 129–134.

[4] Isik, M. and Sponza, D.T. (2005) Substrate removal kinetics in an upflow anaerobic sludge blanket reactor decolorizing simula textile wastewater, *Process Biochemistry*, 40, pp. 1189-1198.

[5] Supaka, N., Juntongjin, K. and Damronglerd, S. (2004), Microbial decolorization of reactive azo dyes in a sequential anaerobic aerobic system, *Chemical Engineering Journal*, 99, pp.169-176.

[6] Prakash, S.M., Gupta, S.K. (2000) Biodegradation of tetrachloroethylene in upflow anaerobic sludge blanket reactor, *Bioresource Technology*, 72, (1) pp. 47-54.

[7] APHA. (1998) *Standards Methods for examination of water and wastewater.* 20th Edn. APHA, AWWA, WPCF, Washington D USA.