Response Surface Optimization of Electro-Oxidation Removal of Disperse Red 163 And Reactive Red 196 Synthetic Wastewater

Sirachon Arthasarnprasit, and Orathai Chavalparit

***Abstract*—**The present work the removal of synthetic waste water containing reactive red 196 and disperse red 163 aqueous solution was studied by plug flow electro-oxidation reactor using Pt/Ti as anode and cathode. A response surface methodology was applied to evaluate the single and combine effect of dye concentration current and flow rate. The statistical model analysis of variance (ANOVA) was applied to test the adequacy of model constructed. The model response of color removal (%) and power consumption was examined. The ANOVA results showed that the model was adequate to represents variations of response. The value of R^2 and adjusted R^2 of color removal are 96.83% and 93.98% respectively and are 96.64% and 95.09% for power consumption respectively. The electro-oxidation of synthetic wastewater achieved removal efficiency of 46 to 68% and power consumption of 54 to 84 kWh/kg dye. The graphical model showed that flow rate strongly affect the color removal and power consumption at all range. On the other hand applied current and flow rate affect the color removal and power consumption effectively in some region. The optimization of electro-oxidation treatment was determined for the minimization of power consumption at final concentration of 300 ADMI. The predicted power consumption and experimental power consumption were 75.9 and 78.0 kWh/kg dye respectively.

***Keywords*—**Electro-oxidation, Response surface, Optimization, Synthetic wastewater.

I. Introduction

The textile dyeing and finishing industries effluents have been characterized by strong color, high toxicity and contains large amount of non-biodegradable chemicals such as volatile aromatic carbon which can cause severe health problems [1]. Reactive dyes most commonly used for cotton dyeing, has a low fixation rate and are highly soluble in water. The low fixation of reactive dye results in strong effluent color, which is not easily removed by conventional methods and chemical precipitation. On the other hand, Disperse dye has low solubility in water and can be easily decolorize by chemical coagulation compare to reactive dye [2]. Disperse dye similar to reactive dye requires a large amount of water for application and wash off [3]-[4].

At present, conventional technologies for textile wastewater treatment are chemical coagulation, biological oxidation and activated carbon adsorption [5]. As mention above chemical coagulation methods cannot efficiently remove reactive dyestuffs. Biological oxidation methods failed to remove color due to the toxicity of most commercial dyes [6]. Carbon adsorption methods despite providing efficient color removal for various textile wastewaters are very expensive compare to the other methods [6].

In recent years, the electro-oxidation of textile wastewater has received great attention due to its ability to oxidize toxic and non-biodegradable wastewater [7]. Furthermore, real textile wastewater contains high NaCl concentration to carry out electrochemical process without adding electrolyte to increase organic strength [8]. Unlike electro-coagulation process, the main oxidizing reagent is electron which results in no electrode consumption and no sludge produced. Many researches on electro-oxidation of various textile dyes have been studied in the literature [9]-[12].

To date, mathematical model for electro-oxidation process is hard to achieve due to the complex chemical reactions involve are not completely known. Moreover, the interaction between factors cannot be determined by varying the independent factor while kept the others constant. This conventional experiment method requires many experiment trials, which are time consuming. Response surface methodology (RSM) was proved to effectively for optimizing the process variables when the interactions between variables are present [13]. With RSM, the response of interest can be determined with a minimum number of trials and mathematical model in terms of input parameters can be achieved.

In the present study electro-oxidation of synthetic textile wastewater containing both disperse red 163 and reactive red 196 was investigated. The initial dye concentration (mg/l), waste water flow rate (L/hr) and applied current (A) were selected for the input parameter. The central composite design (CCD) and RSM has been applied to model the response of color removal (%) and power consumption (kWh/kg Dye). The mathematic regression equations have been developed for model simulations. The models were analyzed and optimization approach for minimum power consumption was determined.

Sirachon Arthasarnprasit[1] is a graduate student in the Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

Orathai Chavalparit[2], is an associate professor in the Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand

http://dx.doi.org/10.15242/IICBE.C0915073

II. Materials And Methods

A. Synthetic wastewater preparations

Synthetic wastewater was prepared by adding reactive red 196 and disperses red 163 equally by mass in the range of 20-30 mg/l was completely mixed in tap water by stirring the synthetic wastewater. In order to create conductivity for electro-oxidation process (500 mg/l) Na_2SO_4 and (500mg/l) NaCl was added. The synthetic waste water was stocked and then fed continuously as in Fig.1.

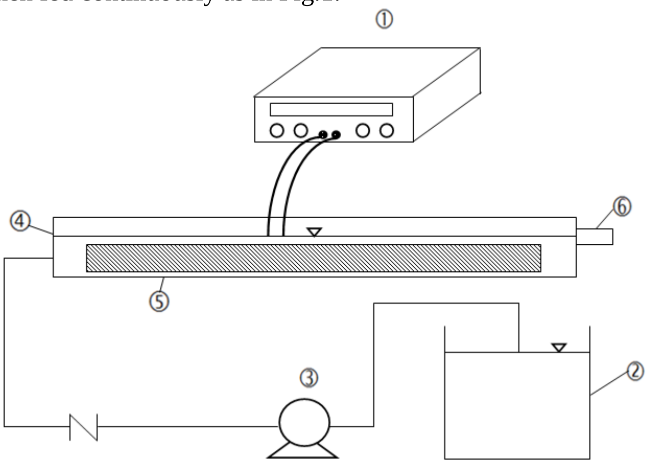

Fig.1: DC-power supply; 2: synthetic wastewater feed stock: 3: influent feed pump; 4: PFR reactor; 5: electrodes; 6: effluent line for sample.

B. Electro-oxidation reactor

The Electro-oxidation process was performed in a plug flow model with effective working volume of 2 L (5 x 50 x 8 cm). The Platinum coated titanium was used as cathode and anode having working dimension of 40 x 5 cm. Three electrode plates were placed with a space of 5 mm in parallel for the experiment. The electrodes were connected with power supply (GPR-6060D) to provide electrical energy. The synthetic wastewater was flowed continuously to the reactor. The initial and final concentration was measured in ADMI unit using DR 6000 UV-Vis spectrophotometer with RFID. The removal efficiency was calculated by following equation:

$$Y_{COL} = \frac{C_{ia} - C_{if}}{C_{ia}} \tag{1}$$

When using C_{ia} initial dye concentration (ADMI) and C_{if} final dye concentration (ADMI). The color removal in fraction can be determined by equation 1.

C. Electro-oxidation experiments

The concentration of effluent wastewater was measured until steady state condition was achieved. The flow rate of synthetic wastewater was between 6.5 and 11.5 L/hr, current was varied between 1.0 and 1.5 A and the initial concentration was varied between 20 and 30 mg/l. The response of energy consumption was calculated using the following equation:

$$P_{dye}\left(\frac{kWh}{kgdye}\right) = \frac{UI}{1000Q(C_i Y_{COL})} \tag{2}$$

Using following terms, current I (A), cell voltage U (V), initial dye concentration C_i (mg/l) and synthetic wastewater flow rate Q (L/hr). The power consumption (kWh/kg dye) can be determined by equation 2.

D. Experimental design for RSM

In the present study, experiment runs were proposed by RSM model using central composite design (RSM). Design Expert 9.0 software were used to create graphical models for the color removal (%) and power consumption (kWh/kg dye) responses. The proposed 16 experimental runs covering the coding factor shown in table 2 were obtained. The α value of 1.682 was chosen to achieve rotatable designs for constant prediction of all points [13]. The statistical significance of models was analyzed by analysis of variance (ANOVA) for testing adequacy of the model. The optimum condition for desired response was predicted and being tested in the last section of this study.

Table II
Symbol and coded factor for three-level RSM design

Factor	symbol	Coded factor		
		-1	0	+1
Concentration (mg/l)	x_1	22	25	28
Applied current (A)	x_2	1.1	1.25	1.4
Flow rate (L/hr)	x_3	7.5	9	10.5

III. Results And Discussions

A. Statistical analysis and modeling

In Electrochemical oxidation process, variables such as current density, flow rate and effluent concentration significantly affected the removal efficiency of target pollutant [14]. In order to study the single and combined effect of these variables response surface and regression method were applied. The Plug flow reactor runs were conducted in CCD experiments. The response models for color removal and power consumption are given in table 2.

The CCD experimental design can be applied to create the regression model. The second order polynomial equations of the output response in terms of input variables can be written as:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1s_3 + a_{23}x_2x_3 + a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 \tag{3}$$

The regression model result for the responses (presented in table 2) regardless of the significant model terms are presented in following equations:

TABLE III
DESIGN RSM OF RESPONSE AND PREDICTED VALUES

Run order	Initial dye concentration (x_1, mg/l)	Applied current (x_2,A)	Flow rate (x_3, L/hr)	Color removal %		Power consumption (kWh/kg dye)	
				actual	predicted	actual	predicted
1	22	1.10	7.5	65.10	63.09	65.53	67.23
2	28	1.10	7.5	60.00	60.80	54.13	53.96
3	22	1.40	7.5	67.90	68.33	84.97	84.80
4	28	1.40	7.5	62.50	61.69	72.53	74.31
5	22	1.10	10.5	51.00	51.01	58.83	58.43
6	28	1.10	10.5	47.80	46.57	51.10	51.64
7	22	1.40	10.5	61.60	60.00	66.10	68.45
8	28	1.40	10.5	50.00	51.21	64.77	64.43
9	20	1.25	9.0	60.45	61.95	72.13	72.67
10	30	1.25	9.0	53.00	52.63	57.67	58.14
11	25	1.00	9.0	50.70	51.76	54.37	52.64
12	25	1.50	9.0	60.00	60.07	80.00	78.17
13	25	1.25	6.5	69.00	69.56	73.57	73.26
14	25	1.25	11.5	50.00	50.58	57.40	57.55
15	25	1.25	9.0	57.59	56.50	63.67	65.41
16	25	1.25	9.0	55.50	56.50	68.07	65.41

TABLE IV
ANOVA RESULT FOR COLOR REMOVAL

source	DF[a]	ANOVA parameter			
		SS[b]	MS[c]	F-Value	P-value
Model	9	666.6	74.07	33.97	<0.0001
Residual	10	21.8	2.18	-	-
Lack-of-fit	5	15.25	3.05	2.33	0.1877
Total	19	688.4	-	-	-

R^2 = 96.83%; adjusted R^2= 93.98%

TABLE V
ANOVA RESULTS FOR POWER CONSUMPTION

source	DF[a]	ANOVA parameter			
		SS[b]	MS[c]	F-Value	P-value
Model	6	1393.2	232.2	62.38	<0.0001
Residual	13	48.39	3.72	-	-
Lack-of-fit	8	19.35	2.42	0.42	0.8701
Total	19	1441.6	-	-	-

R^2 = 96.64%; adjusted R^2 = 95.09%

[a] Degree of freedom.

[b] Sum of squares.

[c] Mean square.

Color removal in percentage

$$Y_C = 56.51 - 2.77x_1 + 2.47x_2 - 5.64x_3 - 1.09x_1x_2 - 0.54x_1x_3 + 0.94x_2x_3 + 0.28x_1^2 - 0.21x_2^2 + 1.26x_3^2 \quad (4)$$

Power consumption

$$Y_P = 65.41 - 4.32x_1 + 7.59x_2 - 4.67x_3 + 0.70x_1x_2 + 1.62x_1x_3 - 1.89x_2x_3 \quad (5)$$

(5)The actual and predicted values of the responses are shown in table 3. These values as well as the model regression equation (4) and (5) were used to construct graphical models

and statistical parameter for the ANOVA as shown in table 4 and table 5.

The adequacy of the responses was evaluated by analysis of variance (ANOVA). The results presented in table 4-5 shows statistical data for validating the precision of the model. The significance of the regression can be determined by F-value and P-value. The F-value of color removal and power consumption were 33.97 and 62.38, respectively. The large number of F-value indicates that the regression models suitably

include variations of response range. Furthermore, relation between P-value and F-value can be used to show whether F-Value is large enough to include the model variations. The P-value less than 0.05 indicate that the model terms are significant at the 95% level of significance.

Moreover, the value of model coefficient of determination (R^2) showed that R^2 and R^2-adj values ware 96.83% and 93.98% for color removal model. However the values for power consumption model were 96.64% and 95.09%, respectively. The values of R^2 more than 80% are desired for good fit of model points.

B. Interpretation of the graphical model

Fig. 2 presents the response surface effect of current and initial dye concentrations on the color removal of disperse red 163 and reactive red 196 dye synthetic wastewater. The effect of current on removal of reactive dye and disperse dye are known to be the most important parameter [15].

In Fig. 2.as the dye removal increased with increase applied current. The effect of Initial dye concentration strongly affect removal efficiency at higher current 1.3-1.5 A (green region) but barely effect the removal efficiency at low current 1.0-1.1 A (dark blue region). Fig. 2 b. presents the effect of current and flow rate on color removal. The color removal are strongly influenced by flow rate of synthetic wastewater but were almost independent of applied current. Fig. 2.c similar to fig. 2.b synthetic wastewater flow rate strongly affects the color-
Removal while color removal slightly increase as initial concentration increases. The graphical model showed same trends for selected initial dye concentration, applied current and flow rate. The color removal was ranged from 46 to 68% and final concentration of effluent ranges from 265 to 540 ADMI.

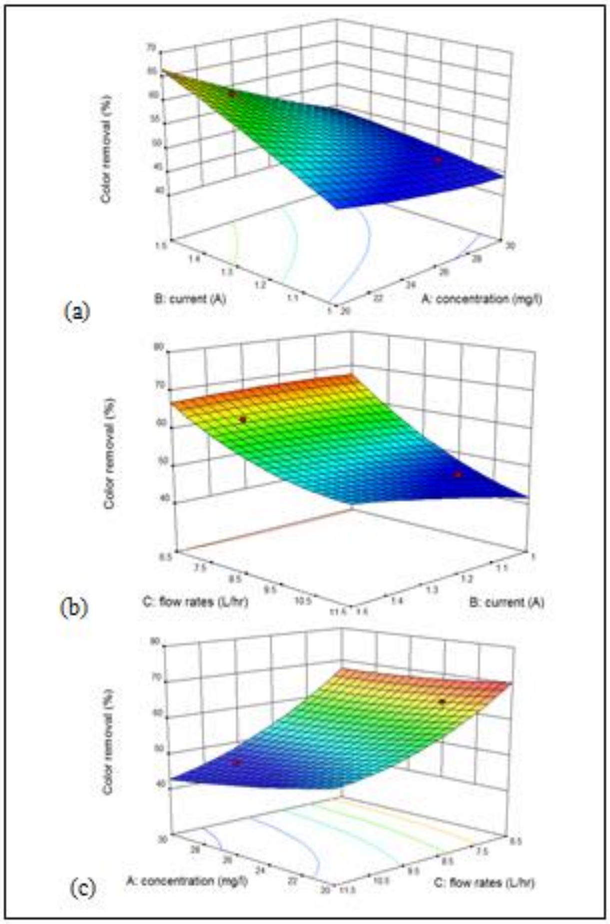

Fig. 2. The effect of input parameter on color removal: (a) Flow rate 10.5 L/hr. (b) Initial dye concentration 28 mg/l. (c) applied current 1.25 A.

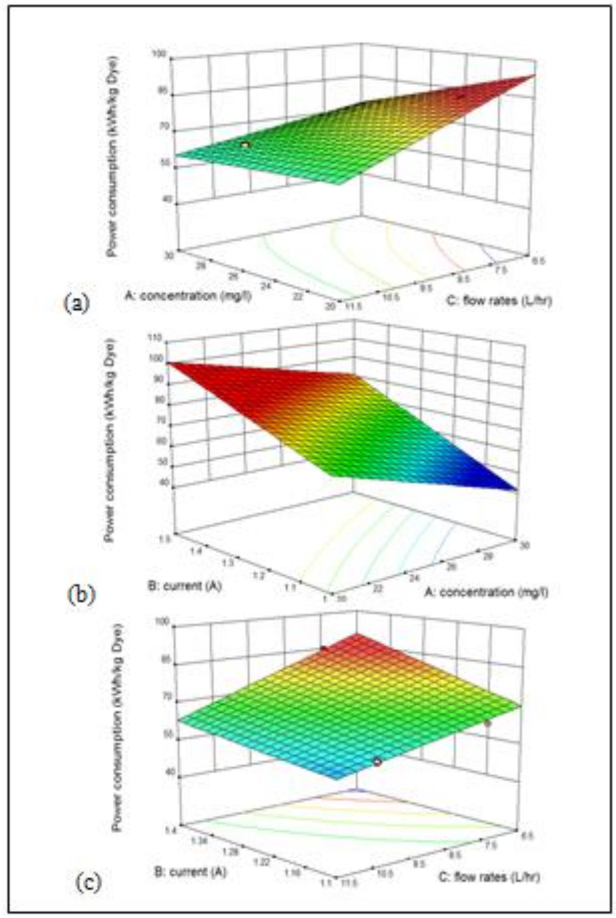

Fig. 3. The effect of input parameter on power consumption: (a) applied current 1.4 A. (b) Flow rate 6.5 L/hr . (c) Initial dye concentration 22 mg/l.

Fig.3. the effect of initial concentration, applied current and flow rate on the power consumption was presented. The graphical model exhibit same trends for each fixed value. Fig 3.a investigates the effect of initial concentration and flow rate. Flow rate affect power consumption as the flow rate increases the power consumption decreases while initial concentration affect the power consumption at low flow rates 6.5 to 7.5 L/hr as shown in red region. Fig. 3.b presents the effect of initial concentration and applied current on power consumption. The model graph shows a linear trend as the applied current increases the power consumption increase. On the other hand, power consumption decreases as the initial concentration increases. Fig. 3.c showed that applied current affect the power consumption at low flow rate 6.5 to 7.5 L/hr (Red region) but barely affect power consumption at low flow rate 10.5 to 11.5 L/hr (light blue region).The model showed that the influence of flow rate on power consumption was not strong compare to fig. 3.a. The power consumption ranges from 51 to 84 kWh/kg dye were achieved for the experiments.

C. Optimization of operating conditions

Operating cost is the response that must be considered prior to implement treatment method [16]. In order to select optimum condition for electro-oxidation treatment minimum-power consumption (kWh/kg dye) is desired. Moreover, the final concentration of wastewater effluent cannot exceed laws and regulations for each country such as Taiwan (400 ADMI), America (200-600 ADMI). Thailand's current law and regulations on wastewater treatment did not include enforcement on ADMI color standard. However, the department of industrial work of Thailand has proposed notification of Ministry of Industry; Subject on wastewater treatment color standard must not exceed 300 ADMI. In present study, the final concentration of 300 ADMI was selected due to the future implemented regulation in Thailand. The results of predicted and experimental parameter were shown in table 6

TABLE VI
OPTIMUM VALUES FOR MINIMIZING

Variables	unit	Optimum values
Initial dye concentration	mg/l	22.6
Applied current	A	1.29
Flow rate	L/hr	7.86
Predicted final concentration	ADMI	300
Experimental final concentration	ADMI	313
Predicted power consumption	kWh/kg dye	75.9
Experimental final power consumption	kWh/kg dye	78.0

http://dx.doi.org/10.15242/IICBE.C0915073

ACKNOWLEDGMENT

This work was supported by the research supporting grant, Faculty of Engineering, Chulalongkorn University, Thailand. The authors would like to thank Nanyang garment Co., Ltd. for providing of disperse red 163 and reactive red 196. This research has been supported by the ratchadaphiseksomphot Endowment Fund 2015 of Chulalongkorn University (WCU-58-020-CC) and the 90th anniversary of Chulalongkorn Fund (Ratchadaphiseksomphot), Thailand

REFERENCE

[1] X. A. Ning, J. Y. Wang, R. J. Li, W. B. Wen, C. M. Chen, Y. J. Wang, Z. Y. Yang, and J. Y. Liu, "Fate of Volatile Aromatic Hydrocarbons in the Wastewater from Six Textile Dyeing Wastewater Treatment Plants", *Chemosphere,* vol. 136, pp. 50-5, 2015.

[2] T. H. Kim, C. Park, J. Yang, and S. Kim, "Comparison of Disperse and Reactive Dye Removals by Chemical Coagulation and Fenton Oxidation", *J Hazard Mater,* vol. 112, pp. 95-103, 2004.

[3] B. K. Korbahti, "Response Surface Optimization of Electrochemical Treatment of Textile Dye Wastewater", *J Hazard Mater,* vol. 145, pp. 277-86, 2007.

[4] B. Merzouk, B. Gourich, K. Madani, Ch Vial, and A. Sekki, "Removal of a Disperse Red Dye from Synthetic Wastewater by Chemical Coagulation and Continuous Electrocoagulation. A Comparative Study", *Desalination, vol.* 272, pp. 246-53, 2011.

[5] O. T. Can, M. Kobya, E. Demirbas, and M. Bayramoglu, "Treatment of the Textile Wastewater by Combined Electrocoagulation", *Chemosphere,* vol. 62, pp. 181-7, 2006.

[6] Robinson, T., McMullan, G., Marchant, R., Nigam, P., "Remediation of dyes in textile effluent: a critical review oncurrent treatment technologies with a proposed alternative". Bioresource Technol. Vol. 77, pp. 247–255, 2001

[7] G. Bhaskar Raju, M. Thalamadai Karuppiah, S. S. Latha, S. Parvathy, and S. Prabhakar, "Treatment of Wastewater from Synthetic Textile Industry by Electrocoagulation–Electrooxidation", *Chemical Engineering Journal,* vol. 144 , pp. 51-58, 2008.

[8] Anastasios Sakalis, Konstantinos Mpoulmpasakos, Ulrich Nickel, Konstantinos Fytianos, and Anastasios Voulgaropoulos, "Evaluation of a Novel Electrochemical Pilot Plant Process for Azodyes Removal from Textile Wastewater", *Chemical Engineering Journal,* vol. 111 , pp. 63-70,2005.

[9] Elisabetta Petrucci, Luca Di Palma, Roberto Lavecchia, and Antonio Zuorro, "Treatment of Diazo Dye Reactive Green 19 by Anodic Oxidation on a Boron-Doped Diamond Electrode", *Journal of Industrial and Engineering Chemistry,* vol. 26 , pp. 116-21, 2015.

[10] José M. Aquino, Romeu C. Rocha-Filho, Luís A. M. Ruotolo, Nerilso Bocchi, and Sonia R. Biaggio, "Electrochemical Degradation of a Real Textile Wastewater Using B-Pbo2 and Dsa® Anodes", *Chemical Engineering Journal,* vol. 251 , pp. 138-45,2014

[11] Vanessa M. Vasconcelos, Francine L. Ribeiro, Fernanda L. Migliorini, Suellen A. Alves, Juliana R. Steter, Maurício R. Baldan, Neidenêi G. Ferreira, and Marcos R. V. Lanza, "Electrochemical Removal of Reactive Black 5 Azo Dye Using Non-Commercial Boron-Doped Diamond Film Anodes", *Electrochimica Acta,* vol. 178 , pp. 484-93, 2015.

[12] Yusuf Yavuz, and Reza Shahbazi, "Anodic Oxidation of Reactive Black 5 Dye Using Boron Doped Diamond Anodes in a Bipolar Trickle Tower Reactor", *Separation and Purification Technology,* vol. 85 , pp. 130-36,2012

[13] S. S. Moghaddam, M. R. Moghaddam, and M. Arami, "Response Surface Optimization of Acid Red 119 Dye from Simulated Wastewater Using Al Based Waterworks Sludge and Polyaluminium Chloride as Coagulant", *J Environ Manage,* vol. 92 , pp. 1284-91,2011.

[14] P. Asaithambi, and Manickam Matheswaran, "Electrochemical Treatment of Simulated Sugar Industrial Effluent: Optimization and Modeling Using a Response Surface Methodology", *Arabian Journal of Chemistry* 2011.

[15] M. Khayet, A. Y. Zahrim, and N. Hilal, "'Modelling and Optimization of Coagulation of Highly Concentrated Industrial Grade Leather Dye by Response Surface Methodolog", *Chemical Engineering Journal,* vol. 167 , pp. 77-83, 2011

[16] T. Olmez-Hanci, Z. Kartal, and I. Arslan-Alaton, "Electrocoagulation of Commercial Naphthalene Sulfonates: Process Optimization and Assessment of Implementation Potential", *J Environ Manage,* vol. 99 , pp. 44-51,2012