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Statistical optimization of Rhodamine B removal by factorial design using reaction rate constant in electrochemical reaction

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Abstract−This study elucidates the reduction of Rhodamine B (RhB) color through electrochemical oxidation technique. Effects of current density, electrolyte type, electrolyte concentration, air flow rate and pH on the RhB color removal were investigated. The 2^4 full factorial design was used to investigate the individual and combined effects of the current density, NaCl concentration, air flow rate, and pH. Also, this study tested the reaction constant rate (k) regression models as an alternative response surface model for the optimization of operating conditions. Increase of pH decreased the RhB color removal efficiency. At the same time, the increase of current density, NaCl concentration, air flow rate also increased the RhB color removal efficiency. From the 2^4 factorial design, it was found that the individual main effects and four interaction effects (combined effects) of the independent variables were statistically significant ($p<0.05$). Also, the prediction results of the RhB concentration using the k regression models showed a nonlinear pattern which was similar to the actual experimental results. In the RhB color removal reactions, the 1^{st} order k regression model showed a smaller prediction error than the 2^{nd} order k regression model.

Key words: Factorial Design, Reaction Rate Constant, k Regression Model, Rhodamine B, Electrochemical Treatment, Ru-Sn-Sb Electrode

INTRODUCTION

The textile industry causes considerable water pollution by discharging effluents into public sewers, ponds, rivers and irrigation lands. The effluent of the textile manufacturing process contains a large variety of pollutants such as dyes, surfactants, detergents and suspended solids. The conventional treatment process for these wastewaters generates a large amount of sludge, and in some cases the removal efficiencies are not enough to achieve the discharge limits, and hence further treatment is necessary [1]. Thus, a study about advanced wastewater treatment is needed for the stable treatment of industrial wastewater including textile industry effluent.

Recently, the advanced oxidation processes (AOPs) such as ozone oxidation, Fenton oxidation, electron beam, photo-catalytic and electrochemical processes have been studied in order to solve these problems. Especially, the use of electrochemical oxidation appears to be a promising alternative to solve the environmental problem generated by the discharge of textile effluent. Electrochemical oxidation is a complex phenomenon involving the coupling of an electron transfer reaction with a dissociate chemisorption step when electrodes are dipped in electrolyte solution at a definite potential difference. Therefore, the electrolytes present in wastewater dissociate into ions, and oxidation of electrons occurs at the anode.

The efficiency of the method is a function of several parameters such as potential difference, nature of electrodes and pH. Electrochemical methods offer many distinctive advantages such as environmental compatibility, versatility, energy efficiency, safety, selectivity and amenability to automation and cost effectiveness [2]. Several researchers have investigated the feasibility of electrochemical degradation of dyes with various electrode materials for wastewater treatment such as titanium-based electrodes [3], platinum electrode [4], diamond and metal alloy electrodes [5], and boron-doped diamond electrodes [6,7]. Applications of this method for textile wastewater have been tested on a lab scale and a good removal of organic substances at various operating conditions has been obtained [8,9].

Conventional methods of studying an electrochemical process by maintaining other factors constant do not depict the combined effect of all the factors involved. These methods are also time consuming and require a number of experiments to determine the optimum level, which is unreliable [10]. A statistical technique, commonly named response surface methodology (RSM), as a powerful experimental design tool has been used to optimize and understand the performance of complex systems. RSM is a collection of mathematical and statistical techniques used for developing, improving and optimizing processes that can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions for the system or to determine a region that satisfies the operating specifications [11].

This study concerns the current density, electrolyte type, electrolyte concentration, air flow rate and pH, which are the main parameters that influence the performance of the electrochemical oxidation process in textile wastewater on laboratory scale. Also, we have attempted to optimize the color removal of Rhodamine B (RhB) using a reaction rate constant. The optimization of the reaction rate

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constant has been performed for factorial design. A 2^4 factorial design is employed for the independent and combined optimization of various factors.

EXPERIMENTAL

1. Electrochemical Experiments

The electrochemical reactor employed in this study consists of Ru-Sn-Sb oxide coated titanium mesh (11 cm×6.3 cm) electrodes. The anode and cathode were positioned vertically and parallel to each other with an inter electrode gap of 2 mm. The experiments were done using 1.0 L of Rhodamine B solution with constant stirring at 150-200 rpm using a magnetic stirrer to maintain uniformity throughout the system. The area of electrode exposed for the electrolysis was fixed to be 69.3 cm^2.

RhB color removal efficiency was measured as a decrease in optical density measurement at 554 nm for the sample before and after electrolysis.

2. Factorial Design

The most important factors that affect the electrochemical oxidation process are current density (C), NaCl concentration (N), air flow rate (A) and pH (P). To study the combined effect of these factors, experiments were conducted at the conditions of different combination of parameters. The design of experiments chosen for this study was the 2^4 full factorial design for the four independent variables, and the treatment conditions for the 2^4 full factorial design are given in Table 1. The RhB concentrations were measured during 9 minutes.

To test the combined effects of the four independent variables, ANOVA (analysis of variance) procedure was conducted. Because there are nine data points in the experiment, the time variable (2 and 4 minutes) was added to the independent variables in the ANOVA procedure.

Table 1. Treatment conditions for RhB color removal in 2^4 full factorial design

Run number	Current density, C (mA/cm^2)	NaCl concentration, N (g/L)	Air flow rate, A (L/min)	pH, P (−)
1	14.43	0.5	0	3
2	14.43	0.5	0	9
3	14.43	0.5	2	3
4	14.43	0.5	2	9
5	14.43	1.75	0	3
6	14.43	1.75	0	9
7	14.43	1.75	2	3
8	14.43	1.75	2	9
9	43.29	0.5	0	3
10	43.29	0.5	0	9
11	43.29	0.5	2	3
12	43.29	0.5	2	9
13	43.29	1.75	0	3
14	43.29	1.75	0	9
15	43.29	1.75	2	3
16	43.29	1.75	2	9

3. k-Regression Model for Optimization

The factorial design helps to develop a statistical model of a reaction by performing the minimum number of well chosen experiments and to determine the optimal values of process parameters. Krishna Prasad and Srivastava [12] have used the 2^4 factorial design method to optimize the combined effects of four factors (current density, dilution, time of electrolysis, pH) for color removal and chemical oxygen demand (COD). They developed the regression models based on the data of factorial design experiments, and determined the optimal combination of the four independent variables. However, they used the 'time of electrolysis' as an independent variable in the regression models and treated the relationships between the time and the dependent variables (color removal and COD reduction) as linear. However, most electrochemical reaction shows a non-linear pattern in the time course of reaction.

To incorporate the non-linear relationship between the time and the RhB color removal, the regression models fitting the reaction rate constant (k) for the RhB color removal were suggested as response models in the optimization procedure. The k regression model development was conducted in two stages. The 1^{st} and 2^{nd} order reaction rate constants were calculated based on the experimental data by integral method [13]. The integral method is most often used when the reaction order is known and it is desired to evaluate the specific reaction rate constants.

Then, the reaction rate constants were regressed using the four independent variables. The stepwise regression method in the SAS package was used in the development of the k regression models. Using the k regression models, the RhB color removal were predicted in the experimental time domain (0-9 minutes), and the prediction errors were calculated and compared.

RESULTS AND DISCUSSION

1. Effect of Current Density

Fig. 1 shows the RhB color removal efficiency with different cur-

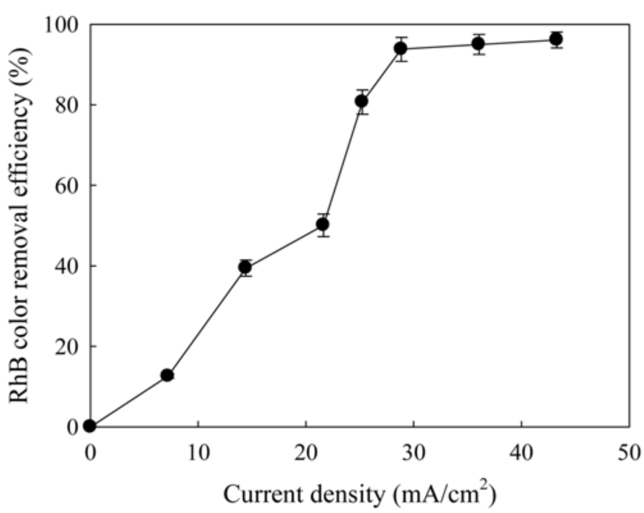

Fig. 1. Effect of current density on the RhB color removal efficiency in the electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, NaCl concentration 1.0 g/L, air flow rate 2.0 L/min).

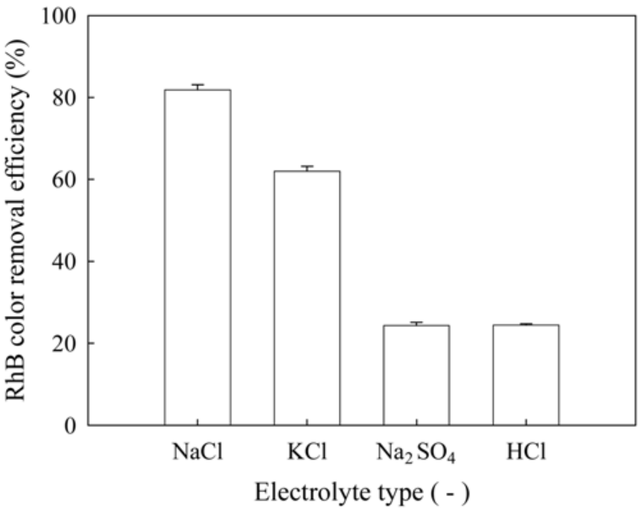

Fig. 2. Effect of electrolyte type on the RhB color removal efficiency in the electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm², air flow rate 2.0 L/min).

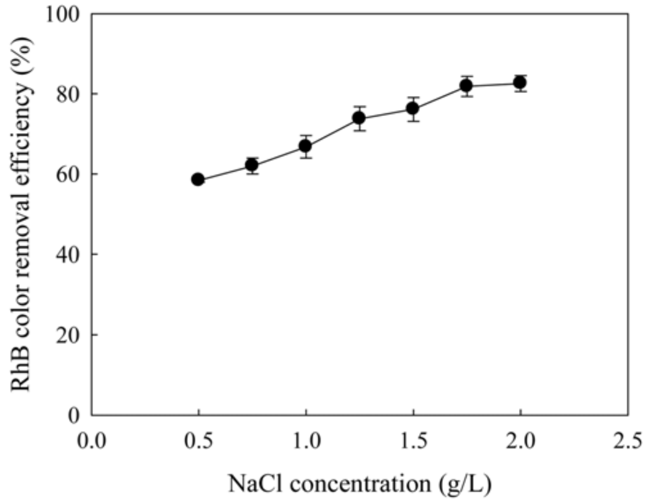

Fig. 3. Effect of NaCl concentration on the RhB color removal efficiency in the electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm², air flow rate 2.0 L/min).

rent density. The current density was varied from 7.2 to 43.3 mA/cm^2 using 1.0 g/L NaCl as electrolyte and 2.0 L/min air flow rate at pH 7. The RhB color removal efficiency increased by increasing the current density because the increment of current density increased the over potential required for the generation of several oxidants (O_3, free chlorine, ClO_2, H_2O_2, OH radical etc.). The concentration of several oxidants by the electrochemical reaction could be increased by the increment of current density [14]. The RhB color removal efficiency was almost proportional to the current density under the current density of 28.9 mA/cm^2. The RhB color removal increased up to 28.9 mA/cm^2 and beyond this current density the increase had no further significant contribution on the RhB color removal efficiency.

2. Effect of Electrolyte Type

Fig. 2 shows the effect of electrolyte type (NaCl, KCl, Na_2SO_4, HCl) on the RhB color removal efficiency. The RhB color removal efficiency using NaCl as an electrolyte was higher than that using any other electrolyte. And the color removal efficiencies of RhB with Na_2SO_4 and HCl as supporting electrolyte were very low, which was similar to the study of Li et al. [15]. Li et al. [15] suggested that NaCl, which could be oxidized to form a strong oxidant of HOCl, could promote the degradation of phenol. Also, the production of other oxidants (O_3, H_2O_2, ClO_2 etc.) using NaCl was higher than that using HCl, KCl and Na_2SO_4 [14].

Also, Li et al. [16] showed that phenol in Na_2SO_4 solution decreased from 490 mg/L to 0 mg/L in 35 h with Ti/RuO_2 at current density of 20 mA/cm^2. However, phenol solution with 1.0 g/L NaCl as supporting electrolyte was degraded from 80 mg/L to 0 mg/L in 130 min at current density of 10 mA/cm^2 [16]. In this study, it was observed that NaCl is the best electrolyte in the RhB color removal using electrochemical reaction.

3. Effect of NaCl Concentration

In this electrochemical degradation of RhB color, NaCl concentration was varied from 0.5 to 2.0 g/L using current density 28.9 mA/cm^2 and 2.0 L/min air flow rate at pH 7.0. The results are presented in Fig. 3. Increasing the NaCl concentration increases the RhB color removal efficiency due to the increased mass transport of chloride ions to the anode surface and also the increased diffusion in the diffusion layer of the anode. As a result, a larger amount of several oxidants will be generated, which results in the increased RhB color removal efficiency.

4. Effect of Air Flow Rate

To enhance RhB color removal efficiency, the dosage of oxygen was adjusted. The effect of air flow rate on the RhB color removal efficiency is illustrated in Fig. 4. It appears that the RhB color removal efficiency in the air flow rate of 2.0 L/min was a little higher than that of 0 or 1.0 L/min. Nonetheless, an identical RhB color removal efficiency was found between those of 2.0 and 4.0 L/min,

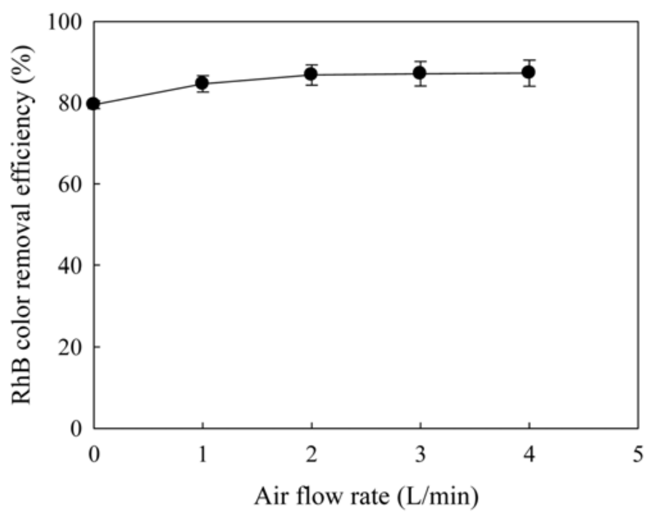

Fig. 4. Effect of air flow rate on the RhB color removal efficiency in the electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: initial pH 7, current density 28.9 mA/cm², NaCl concentration 1.0 g/L).

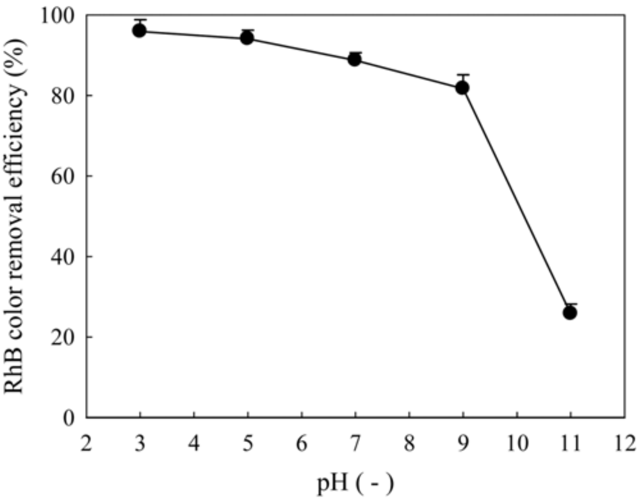

Fig. 5. Effect of initial pH on the RhB color removal efficiency in the electrochemical process using Ru-Sn-Sb electrodes (Operating conditions: current density 28.9 mA/cm^2, NaCl concentration 1.0 g/L, air flow rate 2.0 L/min).

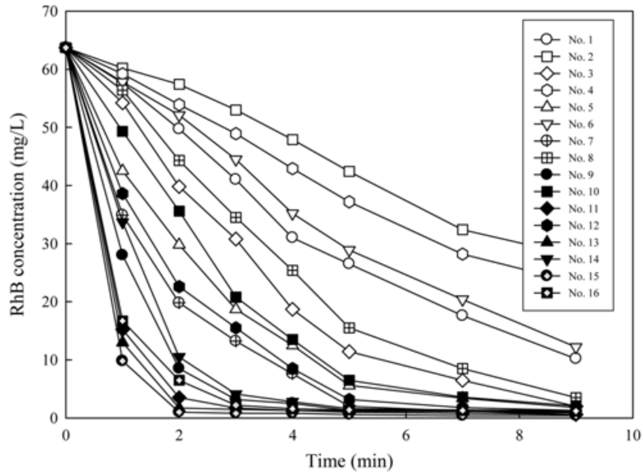

Fig. 6. Experimental results of RhB concentration in the RhB color removal by electrochemical process.

which means the aeration process is not an economical choice for the enhancement of RhB color removal efficiency regardless of accelerating mass transfer. This observation was in agreement with that reported by Chen and Liang [17] and Sudoh et al. [18], who stated that the production of electro-generated H_2O_2 was proportional to the mass transfer rate of dissolved oxygen to the cathode surface. The report of Chen and Liang [17] clearly indicated that the TOC removal efficiencies in electrochemical reaction without dosage of oxygen were slightly lower than those with dosage of oxygen because H_2O_2 could be synthesized by cathodic reduction of oxygen derived from anodic oxidation of water even in oxygen free solution.

5. Effect of pH

The RhB color removal efficiency decreased with the increase in the initial pH of the solution as shown in Fig. 5. The RhB color removal efficiency decreased drastically when the initial pH was 11.0. And the COD removal efficiencies were shown as 88.2%, 83.2% and 76.5% at the pH value of 3, 7 and 11, respectively. The chlorine/hypochlorite generation was stable at given current density. However, at the higher pH value the hypochlorite acid converts itself into chlorate or hypochlorate according to the reactions mentioned in Eqs. (1) and (2). This results in the reduced availability of hypochlorite at higher pH, which causes a reduction in RhB color removal.

$$6HOCl+3\ H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^- \quad (1)$$

$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \quad (2)$$

Another reason may be that at acid pH the chlorine is present in the solution in the form of hypochlorous acid, which is having higher oxidation potential (1.49 V) than that of hypochlorite (0.94 V) [12]. The hypochlorite is prevalent in the alkaline condition [3].

6. The Results of the 2^4 Factorial Experiment

The experimental results of RhB color removal according to electrolysis time are given in Fig. 6. To test the effects of the independent variables (four control variables and time) on the RhB color removal, an ANOVA procedure was conducted (Table 2).

Table 2. The results of the ANOVA procedure. Only statistically significant effects were presented (five-way interaction effect was used as an error source)

Source	df	SS	MS	F	p
Current density (C)	1	6210.6	6210.6	749.4	0.0001**
NaCl concentration (N)	1	1062.6	1062.6	128.2	0.0015**
Air flow rate (A)	1	275.0	275.0	33.2	0.0104*
pH (P)	1	1670.4	1670.4	201.6	0.0008**
Time (T)	1	1048.8	1048.8	126.6	0.0015**
CxP	1	149.6	149.6	18.1	0.0239*
CxT	1	144.5	144.5	17.4	0.025*
CxNxP	1	162.9	162.9	19.66	0.0213*
CxPxT	1	87.8	87.8	10.59	0.0473*

**p<0.01, *p<0.05

The five independent variables showed statistically significant main effects (p<0.05) as in Fig. 7. The current density of 3 mA/cm^2 showed the lower RhB concentration compared to 1 mA/cm^2. Also, NaCl concentration of 1.75 g/L, and air flow rate of 2 L/min, pH of 3 resulted in the lower RhB concentration compared to other conditions.

Among interaction effects, the two 2-way interaction effects (CxP and CxT) were statistically significant (p<0.05, Fig. 8). The difference of RhB concentration between pH 3 and pH 9 became smaller in the current density of 3 mA/cm^2 than that in the current density of 1 mA/cm^2.

Also, the two 3-way interaction effects (CxNxP and CxPxT) were statistically significant (p<0.05). Fig. 9 shows the three-way interaction effect of CxNxP. When the current density was 1 mA/cm^2, the difference of RhB concentration between pH 3 and pH 9 showed a bigger value under the condition of the NaCl concentration of 1.75 g/L than that of 0.5 g/L. But, when the current density was raised to 3 mA/cm^2, the difference between pH 3 and pH 9 of NaCl 0.5 g/L showed almost the same value, while the difference became much smaller when the NaCl concentration was 1.75 g/L.

These statistically significant interaction effects reveal that the com-

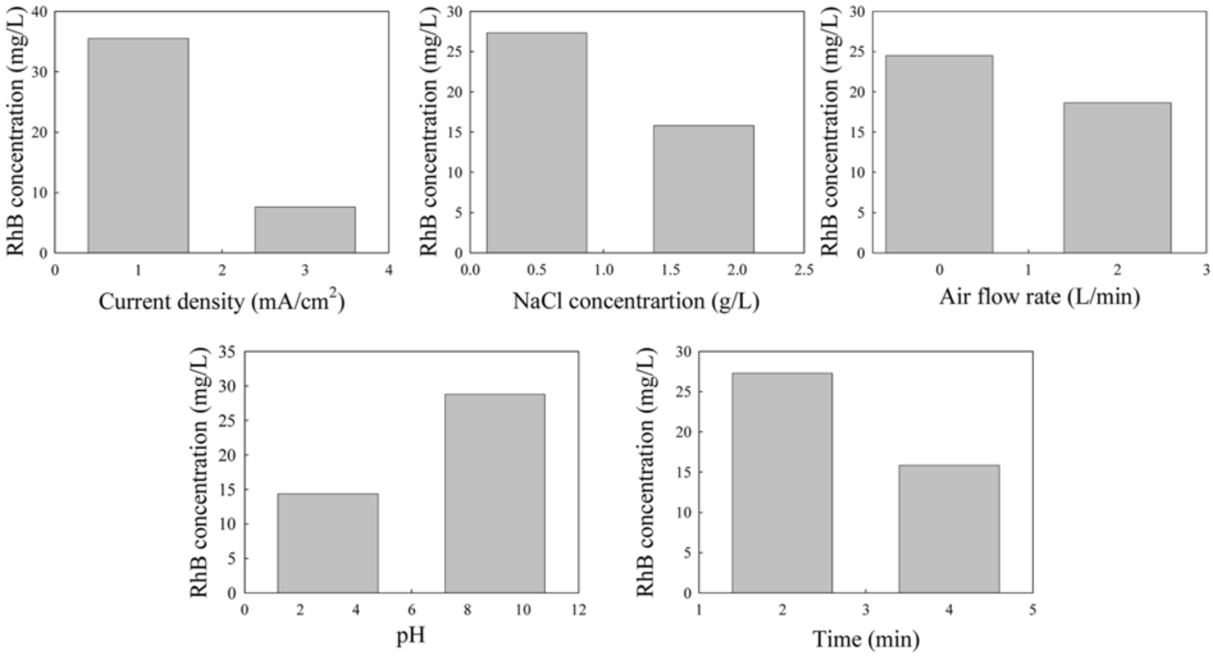

Fig. 7. The main effects of the five independent variables.

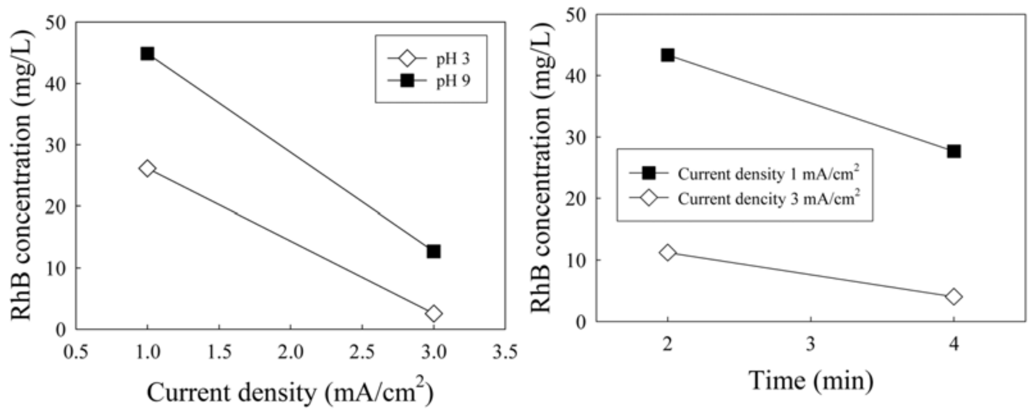

Fig. 8. The two-way interaction effect between current density and pH.

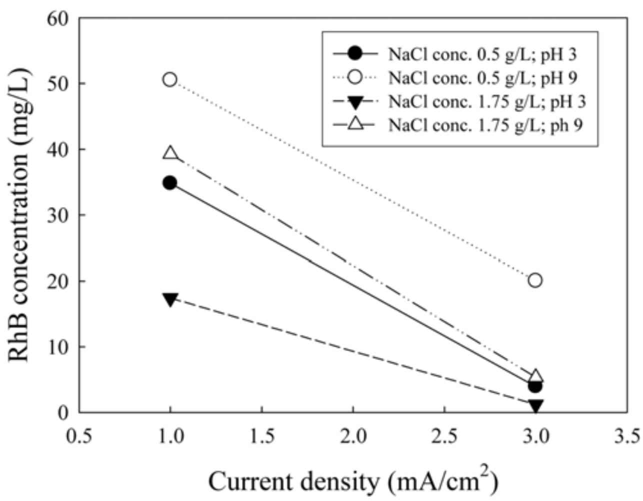

Fig. 9. The three-way interaction effect of C*N*P.

bined effects of the independent variables should be considered when investigating the RhB color removal efficiency and optimizing the RhB color removal set-up conditions.

7. Prediction of the RhB Concentration Using the k Regression Models

To predict the RhB concentration in the time domain, the k (reaction rate constant) regression model was used. The development of the k regression models was conducted in two stages. First, reaction rate constants were calculated based on the experimental data. Then, the reaction rate constants were regressed using the four independent variables.

From Fig. 6, it was assumed that the reaction was the 1^{st} or 2^{nd} order. Using the experimental data, the reaction rate constants (k) for the 1^{st} and 2^{nd} orders were calculated (Table 3). From the r^2 criterion, the 1^{st} order reaction showed the high r^2 values (r^2=0.960-0.985) when the current density was 14.43 mA/cm^2 (No. 1-8). While the 2^{nd} order reaction showed the high r^2 values (r^2=0.700-0.985)

Table 3. Reaction rate constants (k) calculated from experimental data for the 1st and 2nd orders

Run number	Current density C (mA/cm^2)	NaCl concentration, N (g/L)	Air flow rate, A (L/min)	pH, P (-)	1st Order		2nd Order	
					k	r^2	k	r^2
1	14.43	0.5	0	3	0.187539	0.976*	0.00673	0.815
2	14.43	0.5	0	9	0.087208	0.963*	0.00195	0.912
3	14.43	0.5	2	3	0.345436	0.965*	0.03194	0.618
4	14.43	0.5	2	9	0.109306	0.985*	0.00265	0.932
5	14.43	1.75	0	3	0.415496	0.985*	0.04344	0.789
6	14.43	1.75	0	9	0.166104	0.967*	0.00543	0.820
7	14.43	1.75	2	3	0.557590	0.969*	0.12748	0.750
8	14.43	1.75	2	9	0.289888	0.960*	0.01912	0.683
9	43.29	0.5	0	3	0.609397	0.705	0.12014	0.934*
10	43.29	0.5	0	9	0.395690	0.982*	0.03800	0.801
11	43.29	0.5	2	3	0.687186	0.475	0.18261	0.985*
12	43.29	0.5	2	9	0.485407	0.960*	0.06847	0.834
13	43.29	1.75	0	3	0.655910	0.067	0.13731	0.700*
14	43.29	1.75	0	9	0.568240	0.715	0.09158	0.925*
15	43.29	1.75	2	3	0.792898	0.233	0.33518	0.965*
16	43.29	1.75	2	9	0.609765	0.424	0.10920	0.867*

*: Higher r^2 value between 1st and 2nd order

Table 4. Stepwise regression results for the 1st order k model

Step	Variable entered	Variable removed	Variables in model	r^2	F	p
1	C		C	0.9133	158.1	<0.0001
2	N		C, N	0.9443	118.58	<0.0001
3	NxP		C, N, NxP	0.9752	170.21	<0.0001
4	NxA		C, N, NxP, NxA	0.9843	187.62	<0.0001
5	P		C, N, P, NxP, NxA	0.9888	194.4	<0.0001
6	CxN		C, N, P, CxN, NxP, NxA	0.993	235.3	<0.0001
7		NxP	C, N, P, CxN, NxA	0.992	274.19	<0.0001
8	A		C, N, A, P, CxN, NxA	0.9949	322.88	<0.0001
9		NxA	C, N, A, P, CxN	0.9949	425.17	<0.0001
10	AxP		C, N, A, P, CxN, AxP	0.9963	444.83	<0.0001

Table 5. Parameter estimation results for the 1st order k model

Variable	Parameter estimate	Standard error	SS*	F	p
C	0.01404	0.00088476	0.35322	251.76	<.0001
N	0.18029	0.02281	0.08765	62.47	<.0001
A	0.08452	0.01913	0.0274	19.53	0.0013
P	−0.02571	0.00378	0.06474	46.15	<.0001
CxN	−0.00216	0.00078449	0.01064	7.59	0.0203
AxP	−0.00566	0.00291	0.00532	3.79	0.0801

SS*: sum of square

when the current density was 43.29 mA/cm^2 (No. 9-16).

In the second step, the stepwise regression procedures were conducted to build the k regression models using the current density (C), NaCl concentration (N), air flow rate (A), pH (P), and all the interaction terms as independent variables. The stepwise regression results for the 1st order model are shown in Table 4 and Table 5.

Then, the k regression model for the 1st order was derived from the parameter estimation (Table 5) as in Eq. (3). Using the same method at the 1st order model, the 2nd order k regression model was set up as Eq. (4).

$$k_{1st}=0.01404C+0.18029N+0.08452A-0.02571P-0.00216CxN-0.00566AxP \quad (3)$$

$$k_{2nd}=0.00283CxN+0.00238CxA-0.00019505CxNxP-0.00022467CxAxP \quad (4)$$

After k values for the 16 experimental conditions were predicted by using Eq. (3) and Eq. (4), the RhB concentration were calculated using 1st or 2nd order reaction equations in the time domain of 0-9 min. Figs. 10 and 11 show the predicted results of RhB concentration by the 1st order and 2nd order k models, respectively.

Table 6 shows the prediction errors by the 1st and 2nd order k regression models in different experimental conditions. The total average error value of the 1st order model (3.9 mg/L) was lower than that of the 2nd order model (9.9 mg/L). Thus, in the aspect of the prediction error criterion, the 1st order k regression model is more

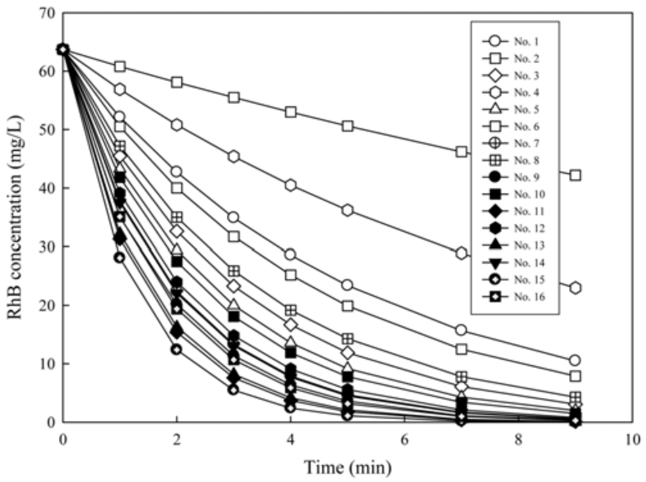

Fig. 10. Predicted results of RhB concentration by the 1st order k model.

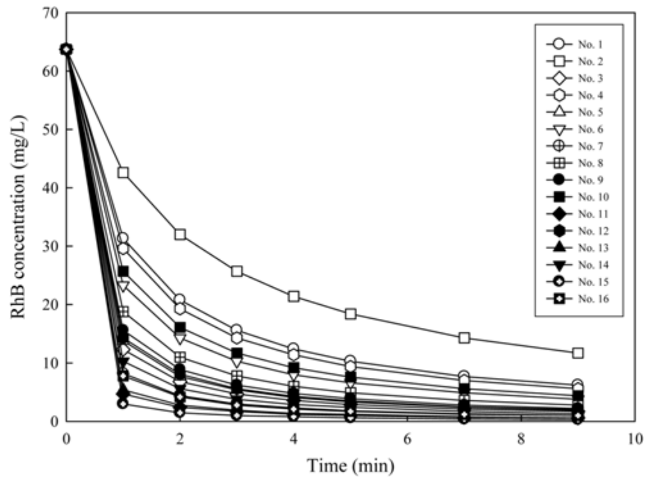

Fig. 11. Predicted results of RhB concentration by the 2nd order k model.

suitable as the response surface model for the RhB color removal optimization.

Radha et al. [19] carried out kinetic studies about the electrochemical oxidation for the treatment of textile industry wastewater. They calculated the rate constants for different current densities. However, they could not calculate the rate constants which had the independent and combined effects of several variables. And they did not use the calculated rate constants for the prediction of removal efficiency.

Factorial design has been used to optimize the process parameters (current density, dilution, electrolysis time, pH) on the electrochemical degradation of distillery spent wash [12]. The decolonization equation for the prediction of removal efficiency was calculated by 2^4 full factorial design. However, electrolysis time was used as an independent variable. This means that the reaction curves were assumed to be linear in the time course, which, in general, is not true. Many reactions show curvilinear shapes.

In this study, to overcome the limitation of the previous studies, the k regression model was used to predict the RhB concentration. First, the reaction rate constant (1st or 2nd order) was predicted using four independent variables (current density, NaCl concentration, air flow rate, pH) and their interaction terms. Second, RhB concentration or removal efficiency in the whole time course was calculated using the predicted rate constant and the reaction equation.

CONCLUSIONS

The present study clearly demonstrated the usefulness of elec-

Table 6. The average prediction errors in the different experimental conditions

No.	Current density (mA/cm^2)	NaCl concentration (g/L)	Air flow rate (L/min)	pH (−)	Average prediction error (mg/L)	
					1st Order model	2nd Order model
1	14.43	0.5	0	3	3.3	16.1
2	14.43	0.5	0	9	5.6	19.4
3	14.43	0.5	2	3	3.4	16.2
4	14.43	0.5	2	9	1.7	24.6
5	14.43	1.75	0	3	1.0	9.5
6	14.43	1.75	0	9	7.9	22.5
7	14.43	1.75	2	3	1.1	7.3
8	14.43	1.75	2	9	4.5	16.6
9	43.29	0.5	0	3	4.3	3.0
10	43.29	0.5	0	9	2.8	7.8
11	43.29	0.5	2	3	4.8	1.5
12	43.29	0.5	2	9	0.8	6.8
13	43.29	1.75	0	3	5.7	1.2
14	43.29	1.75	0	9	4.1	3.7
15	43.29	1.75	2	3	4.6	1.0
16	43.29	1.75	2	9	5.9	1.6
		Total average			3.9	9.9

trochemical treatment of Rhodamine B using titanium mesh coated Ru-Sn-Sb oxide electrode. The existence of interactions among the four factors (current density, NaCl concentration, air flow rate, pH) was investigated for the response of RhB color removal using 2^4 factorial experimental design. Also, this study tested the reaction constant rate (k) regression models as an alternative response surface model for the optimization of the operating conditions. To consider the curvilinear reaction pattern, this study predicted the RhB concentration in the time domain using the well-known reaction equations. The k regression models for the 1^{st} and 2^{nd} order reaction were constructed using the four factors and their interaction terms. For the RhB color removal reactions (color removal), the 1^{st} order k regression model shows the better prediction of the RhB concentration than the 2^{nd} order k regression model. However, it should be noticed that this study was restricted to the color removal of RhB. The method of this study should be verified under various conditions including the RhB COD removal.

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