International Journal of Innovative Studies in Sciences and Engineering Technology (IJISSET)

ISSN 2455-4863 (Online) **www.ijisset.org** *Volume: 5 Issue: 2 | 2019*

The Kinetic Degradation of the reactive dye Red 198 and Yellow 145 by the Electrochemical using Ferrosilic Electrodes

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Abstract: *Reactive dye aqueous solution is not only a common source in Vietnam but also increases with the market demand. Actually, reactive dye is a non-biodegradable organic compound and toxic to the aquatic system, leading to environmental pollution and ecological imbalance. The reactive dyes could be degraded effectively with the electrochemical process using Ferosilic electrodes. Thereby, both COD and color are removed significantly. Due to the acid media, the electrochemical process creates* OH^* *radical that play as a main function in the dyeing aqueous treatment.* OH^* *oxidizes directly reactive dyes Red 198 and Yellow 145 to* CO_2 *and* H_2O *or intermediate organic compound that can be treated effectively by biological process. This study was conducted to determine the kinetic model of oxidizing reaction of two reactive dyes Red 198 and Yellow 145 by electrochemical process. The results pointed out that the kinetic of Red 198 and Yellow 145 dyes by electrochemical process with Ferosilic anode was the best described by Pseudo -first - order model. The apparent rate constant for degradation of reactive dye Red 198 and Yellow 145 was* $68.2x10^{-3}$*/min and* $88.2x10^{-3}$*/min, respectively.*

Keywords: *Reactive dyes, kinetic reaction, ferrosolic electrode,*

1. INTRODUCTION

According to Butlerove and Alektsev [1], the color of dying aqueous solution depends on the structure of dyes. Actually, the organic colorants contain ethylene, azo, nitroso groups, etc. When electrowinning a dyeing aqueous solution, the organic compounds as well as color binding will be degraded, leading to COD and color decreased. In the electrochemical process using ferrosislic electrodes in acid media, OH^* radicals are not only created but also reacted rapidly with the reactive dye Red 198 and Yellow 145 and formed intermediate organic compounds as the reactive dyes red 198 and yellow 145 as reaction (1.1) and (2.2) [2] that play as main function of reducing COD and color of dying wastewater.

OH^* + dye → intermidicate compound (1.1)

OH^*+ intermidicate compounds→ CO_2 + H_2O + mineralization product (1.2)

The degradation reactive dye Red 198 and Yellow 145 is a complicated process. Firstly, the original reactive dyes were converted to the simple and unstable organic compound through various reactions continuously by OH^* radical, which is generated on the surface of ferrosilic electrode. In the degradation reactive dyes by OH^*, the original dyes were transformed into some durable and non-durable organic compounds. With a complicated reaction, the rate reaction is a function among concentration of reactants, causing difficult to carry out an experimental study. To simplify the function among concentration of reactants, the rate of reaction should be considered as the first reactive equation of COD. The general degradation of reactive dyes is presented as the follow reactions:

Dyes + OH→ nCO_2 + mH_2O + Min.product (1.3)
(Dye: Reative dyes)

The rate of degradation of reactive dyes using electrochemical could be presented as kinetic equation as following:

$$V = -\frac{d[Dye]}{dt} = k*[Dye]^x*[OH^*]^y \quad \text{(Eq.1)}$$

Where:

V: rate of reaction

k: degradation coefficient

x, y: order of reaction

The rate of degradation equation between OH^* and reactive dye Red 198 and Yellow 145, if OH^*concentration is constant then Eq.1 could be alternated to the Pseudo-first order equation. During electrochemical process of Red 198 and Yellow 145 degradation, the rate of OH^* formation was controlled by current density that supplied to electrodes system. When conducting electrolysis of the wastewater containing reactive dyes, assuming in the same conditions of electrode material, current density, pH, concentration of substances in aqueous solution, temperature ... concentration of OH * generated in solution almost unchanged. This assumption has been published in the previous international journal in the field of dyeing wastewater treatment using electrochemical process. Thus, equation Eq.1 could be converted to equation Eq.2 as follow:

$$-\frac{d[Dye]]}{dt} = k' * [Dye]^x \quad \text{(Eq.2)}$$

Where:

$k' = k * [OH^*]^y$: The first - order of apparent rate constant (min^{-1}). The degradation of reactive dyes is assumed followed the first order kinetic equation with x =1, then:

$$V = -\frac{d[Dye]}{dt} = k' * [Dye] \quad \text{(Eq. 3)}$$

$$\Rightarrow -\frac{d[Dye]}{[Dye]} = k' * dt \quad \text{(Eq. 4)}$$

Integral equation Eq.4 from 0 to “t”:

$$-Ln\frac{[Dye]_t}{[Dye]_o} = k' * t \quad \text{(E.q 5)}$$

$$\Rightarrow [Dye]_t = [Dye]_o * e^{-k*t} \quad \text{(Eq. 6)}$$

Where:

$[Dye]_o$: initial dye concentration (t = 0)

$[Dye]_t$: dye concentration at the time “t”.

During degradation of reactive dyes, the COD concentration could be seen as the dyes concentration in the wastewater. Thus, the determination of the first order of rate constant through COD is more appropriate than calculation based on the kinetic model. This method has been applied popular in the previous international publication to determine the rate reaction constant in the degradation of reactive dyes using electrochemical process [3,4,5].

Equation 5 could be converted to equation Eq.7 and Eq.8 as follows:

$$-Ln\frac{COD_t}{COD_o} = k' * t \quad \text{(Eq. 7)}$$

$$\Rightarrow COD_t = COD_o * e^{-k*t} \quad \text{(Eq.8)}$$

Where:

COD_o: Initial COD, mgO_2/l

COD_t: COD at the time “t”, mgO_2/l

t: Degradation time, min

k': The first order of rate coefficient, min^{-1}

Determining the variation of COD of wastewater containing reactive dye Red 198 and Yellow 145 with the electrochemical time. Building chart of $-Ln\frac{COD_t}{COD_o} = k' * t$ equation according to the data obtained to determine *k'* of the degradation reactive dye Red 198 and Yellow 145.

2. EXPERIMENTAL PROCEDURES

1. Dyeing aqueous solution

Dyeing aqueous used in this study was prepared separately in the laboratory by dissolving 0.2 g of reactive dye Red 198 ($C_{27}H_{18}ClN_7O_{15}S_5Na_4$) and Yellow 145 ($C_{28}H_{20}ClN_9O_{16}S_5Na_4$) in a liter of water. The pH of wastewater was adjusted to 11.5 by NaOH 20N solution and heated at 100°C within 2 hours (similar to the actual production). After heating, dyeing aqueous was cooled at room temperature before conducting experiments in this study. The COD and color of wastewater are shown in Table 1.

Table 1. Characteristic of dyeing aqueous contains reactive dyes red 198 and yellow 145

№	Reactive dyes	COD(mg/L)	Color (Pt – Co)
1	Red 198	60	120
2	Yellow 145	70	135

The experimental model of the degradation of reactive dye Red 198 and Yellow 145 using electrochemical included anode (made of Ferrosilic) and cathode (made of 304 steel). The surface area of these electrodes is $13cm^2$ and distance between electrodes is fixed of 2cm. The experimental model is supplied by the direct current power and presented as Figure 1.

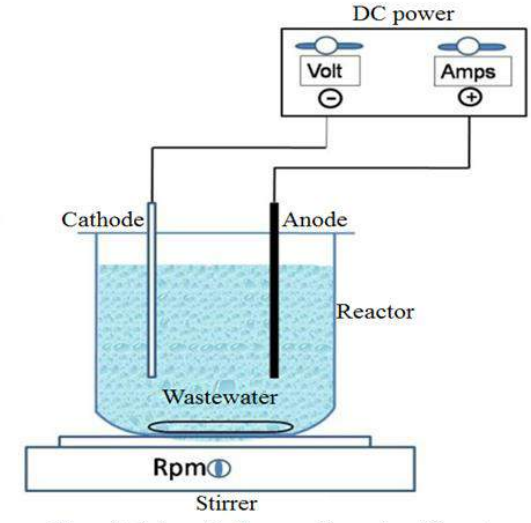

Figure 1. Schematic diagram of experimental system

2. Chemicals and metal solution

All chemical used in this study such as $Fe[SO_4].[NH_4]_2[SO_4].6H_2O$, $K_2Cr_2O_7$, Ag_2SO_4 were purchased from Merck company (Germany).

3. Experiment procedure

Setting up the electrodes in to a reactor with the 200mL of volume. Turning on the stirrer at 100rpm, adjusting pH around 3.0 by concentrate H_2SO_4solution. Adding amount of NaCl (0.5g/L) and turing on power supply. The current density during experiment is controlled at 7.6mA/cm^2. Cl$^-$ ion was removed before analyzing COD

4. Analytical methods

The Color (Pt – Co) and COD were analyzeded according toTCVN6185: 2008 and TCVN6491: 1999

3. RESULTS AND DISCUSIONS

The first order rate of degradation of reactive dye Red 198 and Yellow 145 using electrochemical method is determined and presented as Figure 2 and Figure 3. According to the data presented as Figure 3, the function of $-Ln\frac{COD_t}{COD_o} = k' * t$ is a linear relationship of both reactive dye Red 198 and Yellow 145. It means the COD reduction is followed the Pseudo-first -order reaction. It is the same with the previous studies [3,4,5].

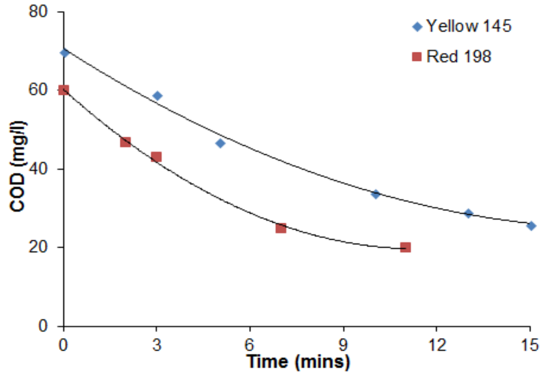

Figure 2. *Kinetic degradation of reactive dyes Yellow 145 and Red 198 using electrochemical mehod*

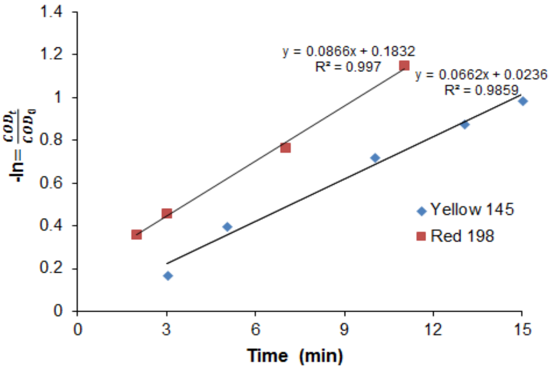

Figure 3. *The first order kinetic of the degradation of reactive dyes Red 198 and Yellow 145*

The results of calculating the first oder reaction constant of the degradation of reactive dye Red 198 and Yellow 145 is shown in Table 2

Table 2. The apparent rate constant *k'* of the degradation of reactive Red 198 and Yellow 145.

Reactive dyes	k'(min^{-1})	R^2
Yellow 145	68.2 .10^{-3}	0.985
Red 198	88.2.10^{-3}	0.997

Both of reactive Yellow 145 and reactive Red 198 are non-biodegradable organic compounds. However, with the higher rate constant (k') of the degradation showed in Table. It pointed that electrochemical process is more effective with reactive dye Yellow 145 than that of reactive dye Red 198. The first - order apparent rate equation of the degradation of reactive dye Red 198 and Yellow 145 was obtained using electrochemical method showed in Table 3.

Table 3. The first order apparent rate equation.

Yellow 145	Kinet-ic equation
	$C_A = C_{A_o} * e^{-k*t} = C_{A_o} * e^{-68.2*10^{-3}*t}$
	Degradation rate equation $-\frac{dC_A}{dt} = k*C_A = 68.2*10^{-3}*C_A$
Red 198	Kinet-ic equation $C_A = C_{A_o} * e^{-k*t} = C_{A_o} * e^{-88.2*10^{-3}*t}$ Degradation rate equation $-\frac{dC_A}{dt} = k*C_A = 88.2*10^{-3}*C_A$

Determination of the errors and verification of the compatibility of kinematic model.

The absolute error S_i between the experimental value and calculation of experimental number *"i"*:

$$S_i = \left| y_i - \hat{y}_i \right| \quad \text{(Eq. 9)}$$

The average error of experimental number N is calculated base on the equation Eq.10:

$$S_{tb} = \frac{\sum_{i=1}^{N} S_i}{\sum_{i=1}^{N} y_i} *100\% = \frac{\sum_{i=1}^{N} \left| y_i - \hat{y}_i \right|}{\sum_{i=1}^{N} y_i} *100\% \quad \text{(Eq. 10)}$$

Where:

y_i :experimental value of experimental number

$\hat{y}_i$: Calculated value by kinetic model

N : Number of experiment

S_i : Absolute error between experimental value and calculation of experimental number *"i"*

S_{tb} : Average erroe of experimental line number N (%)

The benefit of experimental and kinetic model is based on the average error (%). If the average error is less than 10% and the kinetic model of OH* concentration is constant, the first order reaction is accepted [6]. From the data showed in Table 3, the kinetic model of the degradation of reactive dyes could be presented as two equations Eq.11 and Eq.12:

The kinetic equation of the degradation of reactive dye Yellow 145:

$$C_A = C_{A_o} * e^{-k*t} = C_{A_o} * e^{-68.2*10^{-3}*t} \quad \text{(Eq. 11)}$$

The kinetic equation of the degradation of reactive dye red 198:

$$C_A = C_{A_o} * e^{-k*t} = C_{A_o} * e^{88.2*10^{-3}*t} \quad \text{(Eq. 12)}$$

The error results of experimental and kinetic models of the degradation reactive dye Red 198 and Yellow 145 is shown in Table 4 and Table 5.

Table 4. The kinetic error of the degradation of reactive dye Yellow 145with the first order

T	0	3	5	10	13	15
y_i	70	59	47	34	29	26
$\hat{y}_i$	70	57	49	36	29	25
$S_i = \| y_i - \hat{y}_i$	0	2	2	2	0	1

Table 5. The kinetic error of the degradation of reactive dye Red 198 with the first order.

t	0	2	3	7	11
y_i	60	47	43	25	20
$\hat{y}_i$	60	50	45	32	22
$S_i = \| y_i - \hat{y}_i \|$	0	3	2	7	2

The average error of degradation of reactive dye Yellow 145 is calculated according to the equation Eq.13.

$$S_{tb} = \frac{\sum_{i=1}^{N} S_i}{\sum_{i=1}^{N} y_i} *100\% = \frac{\sum_{i=1}^{N} \left| y_i - \hat{y}_i \right|}{\sum_{i=1}^{N} y_i} *100\% = \frac{7}{195} *100\% = 3.5\%$$

(Eq.13)

The average error of degradation of reactive dye Red 198 is calculated according to the equation Eq.14.

$$S_{tb} = \frac{\sum_{i=1}^{N} S_i}{\sum_{i=1}^{N} y_i} * 100\% = \frac{\sum_{i=1}^{N} \left| y_i - \hat{y}_i \right|}{\sum_{i=1}^{N} y_i} * 100\% = \frac{14}{135} * 100\% = 10\%$$

(Eq.14)

The average error of both kinetic models was found to less than 10% it means the first order kinetic can be accepted in this study.

4. CONCLUSSIONS

The data presented in this paper showed that the kinetic model of the reactive dyes (Red 198 and Yellow 145) degradation using electrochemical method with Ferrosilic anode is followed the Pseudo-first - order with the apparent rate constant for degradation of Yellow 145 and Red 198 was 68.2 .10^{-3}min^{-1}and 88.2.10^{-3}min^{-1}, respectively.

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