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DECOLORATION OF REACTIVE BLACK 5 IN AQUEOUS SOLUTION BY ELECTRO-FENTON REACTION

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ABSTRACT

In a three-electrode electrochemical reactor, oxygen and Fe^{3+} were reduced into H_2O_2 and Fe^{2+} by appropriate working electrode voltage in aqueous solution, initiating and facilitating Fenton reaction to proceed a combined reaction named as electro-Fenton reaction. Reactive black 5 (RB5) dye was chosen as the target compound to evaluate the efficiency of electro-Fenton reaction in this study. The results revealed that an optimal decoloration efficiency of RB5 (η_{RB5}) was achieved at the working electrode voltage of -550 mV/(Ag/AgCl), and the ionic strengths of KNO_3 and $Fe^{3+}$of the solution of 0.1 M and 20 mg L^{-1}, respectively. Furthermore, when Fe^{3+} in the reaction solution was substituted by Cu^{2+}, about the same η_{RB5} can also be achieved. A first-order kinetic model was adopted to describe the decoloration of RB5 by the electro-Fenton process, yielding the reaction rate constant expressed as $k = 165.5(C_{Fe^{3+},0})^{0.55}$, where the units of k, initial concentration of Fe^{3+} ($C_{Fe^{3+},0}$), and 165.5 are min^{-1}, mg L^{-1}, and $min^{-1}(mg\ L^{-1})^{-0.55}$, respectively.

INTRODUCTION

Azo dyes are the most widely used commercial reactive dyes in the dyeing processes with the world-wide production of more than 7×10^5 tons per year [1]. Approximately 10-15 wt% of the dye is lost during the dyeing process which contributes to the organic concentration of the effluent [1]. It has been shown that neither simple chemical nor biological treatment can achieve the desirable decoloration and depletion of dye organic matter [2,3]. The value of ratio of BOD_5/COD normally indicates the extent of the biological degradability of the organics, and that of dyes is usually less than 0.1 [4]. Therefore, the destruction of biologically recalcitrant organics in the textile wastewater has to be accomplished by those methods which enhance the biological degradability of the organics, such as advanced oxidation processes (AOPs) [5,6].

The application of the Fenton process to decompose organic pollutants has attracted extensive attention because of its satisfactory performance [7-9]. The Fenton reaction involves the reaction of H_2O_2 with iron salt, which generates strong oxidizing radical ($\cdot OH$) to decompose the organics. The main reaction is as follows [10,11]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad (1)$$

Fenton reaction using Fe^{2+} can achieve good treatment efficiency, but the precipitate of ferric hydroxide that requires additional separation and disposal limits its application.

The electrochemical technologies have attracted a great attention because of their versatilities and environmental compatibilities. Organic pollutants can be destructed by the electrochemical reactions which possess abilities of oxidation and reduction. However, when working electrode is directly used to oxidize or reduce the organic pollutants (direct mode), the reaction efficiency is inhibited because of the low contact surface area between the electrode and target pollutants [12]. In order to overcome this drawback, organic pollutants can be decomposed by an indirect electrolysis, which generates reactive chemical reactant (indi-

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rect mode). Panizza et al. [13] added chloride ions into the solution, of which the purpose was to electrolyze chloride ions to produce ClO^- ions to further oxidize the organic compounds in the solution enhancing the treatment efficiency of an electrochemical system.

Combing an electrochemical reaction with a Fenton reaction in one integrated process, which is so called an electro-Fenton reaction [14], gives an electrode potential capable of continuously reducing the dissolved oxygen (DO) and Fe^{3+} of the solution to form H_2O_2 [15] and Fe^{2+}, respectively. Therefore, the Fenton reaction of this indirect mode proceeds with continuous re-installation without the external addition of Fe^{2+} and H_2O_2. Recently, numerous studies have investigated the application of electro-Fenton reaction to decompose the aromatic compounds and refractory pollutants with satisfactory efficiencies [16,17].

The aim of this study was to investigate the decoloration of Reactive black 5 (RB5) by means of the electro-Fenton reaction system. Major factors affecting the values of η_{RB5} were examined. These included the working electrode potential (E_{WE}), the ionic strength (I), the $C_{Fe^{3+},0}$, and the value of pH. Because other metal, e.g., Cu^+, can also initiate the Fenton reaction [18], the effect of Cu^{2+} on η_{RB5} was also evaluated in this study. Further, a first-order kinetic expression was derived based on the observed experimental results.

MATERIALS AND METHODS

RB5, supplied by Aldrich (USA), was used as the target substance in this study. Its molecule structure is shown in Fig. 1. $Fe(NO_3)_3$, $Cu(NO_3)_2$, and KNO_3 were purchased from Sigma (St. Louis, MO, USA). All the other chemicals used in this study are reagent grade obtained from several suppliers. Deionized water from a Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all buffers and sample solutions.

Figure 2 shows the schematic diagram of the reaction system. A potentiostate-galvanostate electrochemical apparatus (Radiometer's multipurpose model PGP 201) was used for electrolyses. Electrolyses were carried out in a three-electrode electrochemical cell, of which the volume is 200 cm^3 with a magnetic stirrer. Furthermore, DO was supplied by purging oxygen. The value of pH of the solution was controlled by the addition of 0.05 N HNO_3/NaOH and maintained at a constant value during the entire reaction period. The material of working (WE) as well as counter (CE) electrode was platinum. CE was placed in the anodic compartment containing saturated KNO_3 solution. A porous glass was used to separate the anodic compartment and the bulk solution of WE. The reference electrode (RE) was Ag/AgCl electrode (silver/silver chloride electrode, SSCE). The standard reduction potential of SSCE with saturated KCl is 197 mV/NHE [19], with NHE denoting normal hydrogen electrode.

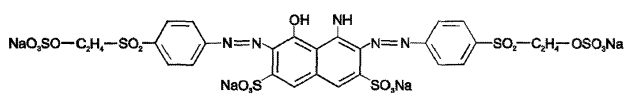

Fig. 1. The molecular structure of RB5 with molecular formula of $C_{26}H_{21}N_5O_{19}S_6Na_4$.

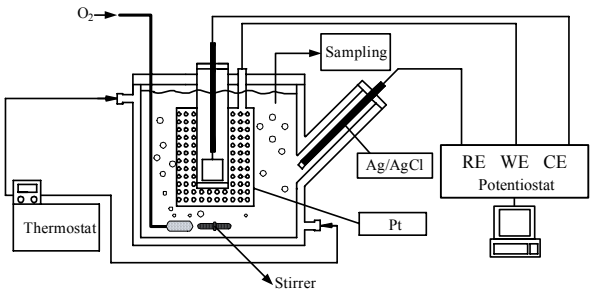

Fig. 2. The experimental apparatus sketch. RE, WE, CE: reference (Ag/AgCl), working (Pt), and counter (Pt) electrodes.

The concentration of RB5 was determined by the UV-Vis spectrophotometer (Perkin Elmer, Lambda 25). The intensity measured at the maximum visible absorbance wavelength (i.e., $A_{\lambda max}$ with wavelength of 595 nm) of RB5 by the UV/Vis spectrophotometer was used to calculate the decoloration efficiency. The relative standard deviation of analyses of RB5 samples via UV/Vis with triple measurements was below 5%. The concentration of DO was determined by an oxygen electrode (Model 97, Orion Research Inc.)

RESULTS AND DISCUSSION

1. Optimal E_{WE}

DO and Fe^{3+} in the solution can be reduced to H_2O_2 and Fe^{2+} by electrochemical reaction, respectively. The standard reduction potentials to reduce DO and Fe^{3+} versus SSCE are 573 and 498 mV, respectively, as shown in Eqs. 2 and 3.

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

$$E^0 = 573 \text{ mV/SSCE} \qquad (2)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$E^0 = 498 \text{ mV/SSCE} \qquad (3)$$

From Eqs. 2 and 3, the quantities of H_2O_2 and Fe^{2+} depend on the applied E_{WE}, as well as the electron-Fenton reaction efficiency. Hence, the optimal E_{WE} can be found by noting the relationship between η_{RB5} and E_{WE}. The result of $C_{RB5}/C_{RB5,0}$ vs. E_{WE} for RB5 is shown in Fig. 3, where $C_{RB5,0}$ and C_{RB5} are the concentrations of RB5 at time t = 0 and t, respectively.

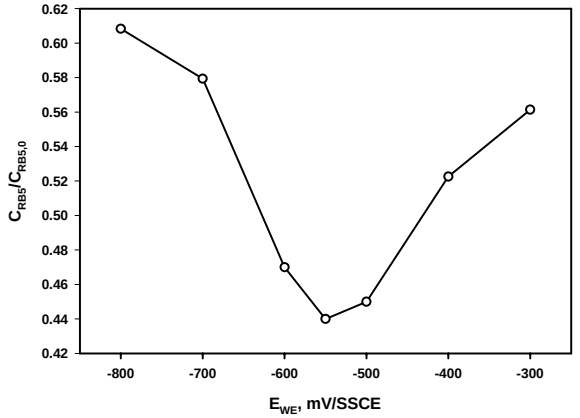

Fig. 3. Variation of $C_{RB5}/C_{RB5,0}$ of RB5 with E_{WE}. Experimental conditions: $C_{RB5,0}$ = 20 mg L^{-1}, I of KNO_3 = 0.1 M, $C_{Fe^{3+},0}$= 20 mg L^{-1}, initial pH = 3, reaction time = 25 min, T = 298 K. C_{RB5}, $C_{Fe^{3+},0}$: concentrations of RB5, Fe^{3+}. T = reaction temperature. 0: initial condition. E_{WE}: working electrode voltage. I: ionic strength.

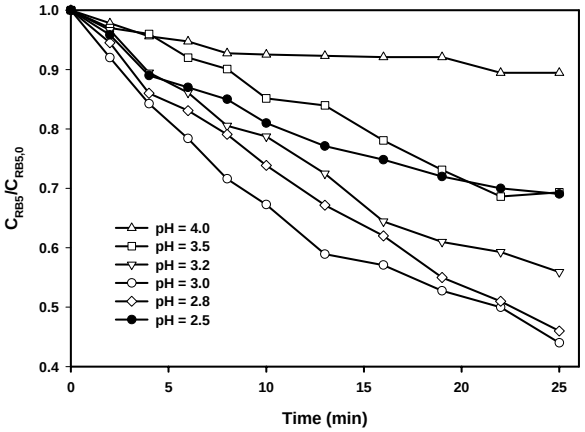

Fig. 4. Time variation of $C_{RBR}/C_{RB5,O}$ of RB5 at various initial pH values. Experimental conditions: E_{WE} = -550 mV/SSCE, $C_{RB5,0}$ = 20 mg L^{-1}, I of KNO_3 = 0.1 M, $C_{Fe^{3+},0}$= 20 mg L^{-1}, T = 298 K. Other notations are the same as specified in Fig. 3.

As E_{WE} > -500 mV, $C_{RB5}/C_{RB5,0}$ increased or η_{RB5} (= 1 - $C_{RB5}/C_{RB5,0}$) decreased quickly with increasing voltage, interpreting that the potential was not sufficient to reduce Fe^{3+} and DO resulting in decreasing the production of Fe^{2+} and H_2O_2. When E_{WE} < -600 mV, η_{RB5} also dropped as E_{WE} decreased. It may be due to the reason that the excessively strong reduction potential caused the transformation of H^+ and H_2O_2 into H_2 [19] and H_2O by the reactions of Eqs. 4 and 5, respectively, as follows.

$$2H^+ + 2e^- \rightarrow H_2$$

$$E^0 = -197 \text{ mV/SSCE} \quad (4)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

$$E^0 = 1566 \text{ mV/SSCE} \quad (5)$$

The competitive reactions lessened the net production quantities of H_2O_2 and Fe^{2+}. As a result, the suitable η_{RB5} was obtained at E_{WE} of -600 to -500 mV. The value of E_{WE} was fixed at -550 mV for further experiments.

2. pH Effect

The value of pH of the solution is an important parameter affecting the Fenton reaction efficiency. The values of solubility product constants K_{sp} of $Fe(OH)_{2(s)}$ and $Fe(OH)_{3(s)}$ are 5×10^{-15} M^3 and 6×10^{-38} M^4, respectively. The small values of K_{sp} indicate that OH^- can easily combine with Fe^{2+} and Fe^{3+}. Hence, at a high pH value of the solution, Fe^{2+} forms metal hydroxide complex and loses its capacity to catalyze H_2O_2, which is not favorable for a traditional Fenton reaction. Therefore, the electro-Fenton reaction may also be inhibited at high solution pH values. The time variation of $C_{RB5}/C_{RB5,0}$ at various pH values is shown in Fig. 4. The results indicated that η_{RB5} decreased as value of pH increased with η_{RB5} < 0.1% at pH > 4. On the other hand, the reduction reaction of Eq. 4 is favorable for working electrode at high H^+ concentration (low pH), resulting in the decrease of η_{RB5} as pH < 3. As a result, the optimal pH value of η_{RB5} was at pH = 3. The value of pH of solution was kept at 3 for the following experiments.

3. Effect of I

Supporting electrolyte plays an important role of current conduction in the electrochemical reaction. Its ability of conduction is reflected by the I. Therefore, unless the solution possesses sufficient I to overcome the resistance of the electrochemical cell, redox reactions can not occur in the system. In addition, the efficiency of electro-Fenton reaction is also affected by the amount of ions in the solution. Figure 5 illustrates the time variation of $C_{RB5}/C_{RB5,0}$ at various initial I of KNO_3. The ionic strength I is defined as $I = 1/2\sum C_i Z_i^2$, where C_i is the molar concentration of the *i*th ion and Z_i is its charge. The results showed that if I was less than 0.075 M, η_{RB5} rapidly decreased with decreasing I. The deficiency of the supporting electrolyte caused the increase of the resistance of chemical reaction cell, subsequently hindering the electrochemical reaction. On the other hand, as I ≥ 0.075 M, values of η_{RB5} for various I values were about the same. As a result, at I = 0.1 M, the I was sufficient to achieve a successful electrochemical reaction. Therefore, the following experiments were performed with I = 0.1 M.

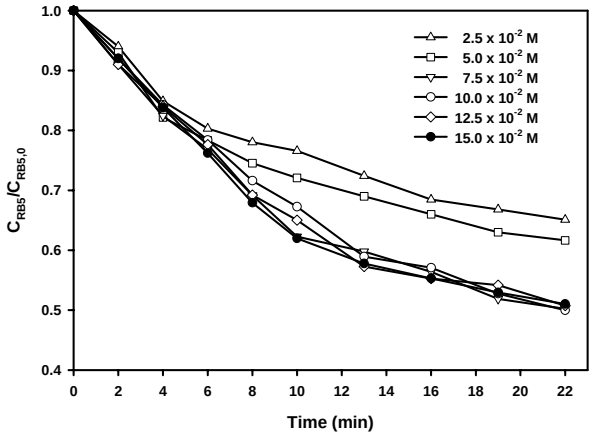

Fig. 5. Time variation of $C_{RB5}/C_{RB5,0}$ of RB5 at various ionic strengths of KNO_3 (I). Experimental conditions: E_{WE} = -550 mV/SSCE, $C_{RB5,0}$ = 20 mg L^{-1}, $C_{Fe^{3+},0}$= 20 mg L^{-1}, initial pH = 3, T = 298 K. Other notations are the same as specified in Fig. 3.

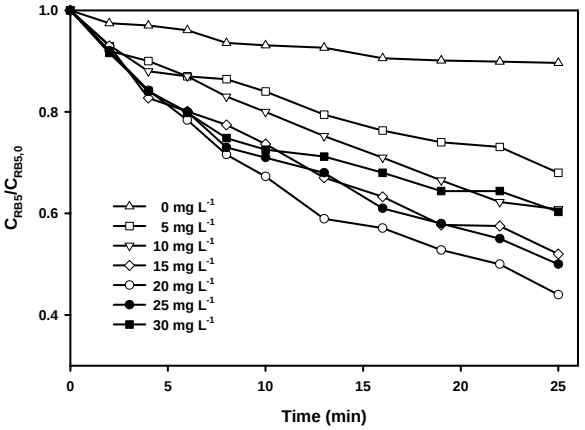

Fig. 6. Time variation of $C_{RB5}/C_{RB5,0}$ of RB5 at various initial concentrations of Fe^{3+}. Experimental conditions: E_{WE} = -550 mV/SSCE, $C_{RB5,0}$ = 20 mg L^{-1}, I of KNO_3 = 0.1 M, initial pH = 3, T = 298 K. Other notations are the same as specified in Fig. 3.

4. Concentration Effect of Fe^{3+}

Comparing the reduction potentials of Fe^{3+} and O_2 as shown in Eqs. 2 and 3, we note that it is easier to reduce Fe^{3+} to Fe^{2+} than O_2 to H_2O_2. The effect of $C_{Fe^{3+},0}$ on the time variation of $C_{RB5}/C_{RB5,0}$ is shown in Fig. 6. As the reaction was carried out without addition of Fe^{3+} (with $C_{Fe^{3+},0}$ = 0), η_{RB5} at 25 min was around 0.16, indicating low decoloration efficiency obtained by means of the direct electrode reaction. As $C_{Fe^{3+},0}$ increased up to 20 mg L^{-1}, the produced Fe^{2+} can consequently react with H_2O_2 to form hydroxyl radical to decompose RB5, resulting in an increase of η_{RB5} with the increase of $C_{Fe^{3+},0}$. However, as $C_{Fe^{3+},0}$ was greater than 20 mg L^{-1}, η_{RB5} tended to decrease, indicating that a significant competition arose between the reduction reactions of Fe^{3+}/Fe^{2+} of Eq. 2 with excessive Fe^{3+} and of DO/H_2O_2 of Eq. 3 causing the less production of H_2O_2. This thus decreased the formation of hydroxyl radicals, resulting in the decrease of η_{RB5}. As a result, the optimal range of $C_{Fe^{3+},0}$ in this investigation was 15-20 mg L^{-1} for the electro-Fenton reaction with RB5.

5. Kinetics of Decoloration of RB5

The reaction kinetic expression of the decoloration of RB5 by electro-Fenton process is as follows.

$$\frac{dC}{dt} = -kC^m \tag{6}$$

where C, m, t, and k represent the concentration of RB5, order of the reaction, time, and reaction rate constant, respectively. For a first-order reaction (m = 1), Eq. 6 can be integrated and expressed as Eq. 7.

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{7}$$

where C_0 is the initial concentration of RB5 (mg L^{-1}). The experimental data of Fig. 6 with $C_{Fe^{3+},0}$ ranging from 5 to 20 mg L^{-1} were followed by the first-order reaction kinetics. The results indicated that the values of R^2 of regression analysis were all larger than 0.93. Furthermore, the values of k obtained from the slope of the linear regression curve were varied with $C_{Fe^{3+},0}$. Therefore, the relationship of k and $C_{Fe^{3+},0}$ can be further examined and was assumed to be in the form of Eq. 8 as follows.

$$k = k_0 (C_{Fe^{3+},0})^n \tag{8}$$

In Eq. 8, n is the order of reaction with respect to $C_{Fe^{3+},0}$ ($C_{Fe^{3+},0}$: already defined). The value of n of 0.55 can be calculated from the slope of linear regression curve by plotting ln k against $C_{Fe^{3+},0}$. The value of k_0 can also be obtained by plotting k versus $(C_{Fe^{3+},0})^{0.55}$, giving k_0 of 165.5 min^{-1} (mg L^{-1})$^{-0.55}$ at T = 298 K. Therefore, Eq. 6 can be expressed as k = 165.5 $(C_{Fe^{3+},0})^{0.55}$, which is applicable for the conditions with $C_{Fe^{3+},0}$ in the ranges of 5-20 mg L^{-1}, E_{WE} = -550 mV/SSCE, initial I = 0.1 M KNO_3, pH = 3, and T = 298 K.

6. Electro-Fenton Reaction with Cu^{2+}

H_2O_2 reacts with transitional metal ions of low-valent except iron ions, generating strong oxidizing radical ($\cdot OH$). The reaction is commonly called as Fenton-like reaction [18]. Fe^{3+} or other transition-metal ions can be continually reduced to lower oxidation state throughout the electrochemical treatment.

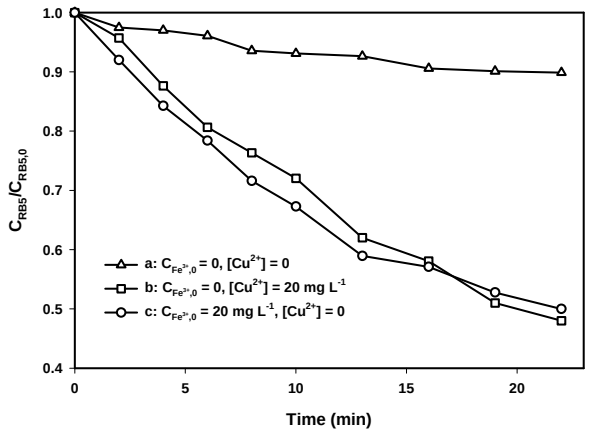

Fig. 7. Time variation of $C_{RB5}/C_{RB5,0}$ of RB5 at various conditions. Expérimental conditions: a (△): $C_{Fe^{3+},0}$= 0, $[Cu^{2+}]_0$ = 0; b (□): $[Cu^{2+}]_0$ = 20 mg L^{-1}, $C_{Fe^{3+},0}$= 0; c (○): $C_{Fe^{3+},0}$= 20 mg L^{-1}, $[Cu^{2+}]_0$ = 0. [ ]: concentration. Other experimental conditions are as specified in Fig. 6.

The reduced metal ions thus generated can act as catalysts in the electro-Fenton system. The standard reduction potential to reduce Cu^{2+} versus SSCE is 39 mV as shown in Eq. 9 [19].

$$Cu^{2+} + e^{-} \rightarrow Cu^{+}$$

$$E^0 = 39 \text{ mV/SSCE} \qquad (9)$$

In this work, η_{RB5} of the system employing Cu^{2+} instead of Fe^{3+} during electro-Fenton type treatment was obtained as shown in Fig. 7. The case a [$[Cu^{2+}]_0$ = 0 and $C_{Fe^{3+},0}$ = 0] exhibited a low η_{RB5} (0.16 at 25 min), where the symbol [ ] denotes the concentration. The results signified that η_{RB5} contributed by the direct reaction of working electrode was inefficient. The cases b ($[Cu^{2+}]_0$ = 20 mg L^{-1}, $C_{Fe^{3+},0}$= 0) and c ($[Cu^{2+}]_0$ = 0, $C_{Fe^{3+},0}$= 20 mg L^{-1}) were used to investigate the reaction kinetics as described in Eq. 7. The values of k of lines b and c were 29.1 and 28.3 min^{-1}, respectively. Further, the k value for case b with $C_{Cu^{2+},0}$ = 20 mg L^{-1} was close to that of case c with $C_{Fe^{3+},0}$ = 20 mg L^{-1}. According to the standard reduction potential, the reduction of Cu^{2+} to Cu^{+} is more difficult than that of Fe^{3+} to Fe^{2+}. However, the reaction rate of Cu^{+} with H_2O_2 to produce hydroxyl radical is higher than that of Fe^{3+} with H_2O_2 [18]. These two reasons cause opposite effects, resulting in similar values of η_{RB5} via Cu^{2+} and Fe^{3+} in the electrochemical system. This result revealed that, in the aqueous electrochemical system, Cu^{2+} can act as a catalyst in the presence of H_2O_2, expanding the application of copper ion.

CONCLUSIONS

The electro-Fenton reaction can be used to decompose RB5. From the obtained results, the following conclusions were drawn.

1. The η_{RB5} with electro-Fenton reaction was optimal under the conditions: E_{WE} = -550 mV, initial I = 0.1 M KNO_3, pH = 3, and $C_{Fe^{3+},0}$ = 20 mg L^{-1}.
2. The values of η_{RB5} with Cu^{2+} were about the same as those with Fe^{3+} in this electrochemical system.
3. The observed experimental data showed a reasonably good agreement with the first-order kinetic model with respect to the concentration of RB5 in terms of UV/Vis absorbance intensity. The reaction rate constant k can be expressed as the following equation: k=165.5$(C_{Fe^{3+},0})^{0.55}$, where the units of k, $C_{Fe^{3+},0}$, and 165.5 are min^{-1}, mg L^{-1}, and $min^{-1}(mg\ L^{-1})^{-0.55}$, respectively. The obtained k is applicable for the conditions: $C_{Fe^{3+},0}$= 5-20 mg L^{-1}, E_{WE} = -550 mV/SSCE, I = 0.1 M KNO_3, pH = 3, and T = 298 K.

NOMENCLATURE

$C_{Fe^{3+},0}$	initial loading concentration of Fe^{3+} in aqueous solution, mg L^{-1}
C_{RB5}	present concentration of RB5 in aqueous solution, mg L^{-1}
$C_{RB5,0}$	initial concentration of RB5 in aqueous solution, mg L^{-1}
E^0	standard reduction potential, mV
E_{WE}	working electrode potential, mV
I	ionic strength in aqueous solution in terms of KNO_3, M
k	reaction rate constant, min^{-1}
m	order of reaction with respect to C_{RB5}, -
n	order of reaction with respect to $C_{Fe^{3+},0}$
R^2	correlation coefficient
t	reaction time, min

Greek symbols

η_{RB5}	decoloration efficiency of RB5, 1- ($C_{RB5}/C_{RB5,0}$)

Acronyms

AOPs	advanced oxidation processes
BOD_5	five days' biological oxygen demand
CE	counter electrode
COD	chemical oxygen demand
DO	dissolved oxygen
NHE	normal hydrogen electrode
RB5	reactive black 5 dye
RE	reference electrode
SSCE	saturated Ag/AgCl electrode
WE	working electrode

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