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## Plasma degradation of dyes in water with contact glow discharge electrolysis

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### Abstract

Contact glow discharge electrolysis (CGDE) of two dyes, weak acid brilliant red B and weak acid flavine G, was investigated under different concentrations, temperature and mediums. From the variation of their concentration with the reaction time, it was demonstrated that the oxidation would be a first-order reaction. On the base line of UV spectra of solution in the degradation process, we deduced that two dyes underwent the oxidative degradation in CGDE. The rate constants, relevant coefficients and the decolorization degree were displayed under different conditions.

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*Keywords:* Plasma; Contact glow discharge electrolysis; Degradation of dyes

### 1. Introduction

Contact glow discharge electrolysis (CGDE) is a novel kind of electrochemical process in which plasma is sustained by dc glow discharges between an electrode and the surface of the electrolyte. The conventional normal electrolysis is developed into CGDE when the applied voltage is sufficiently high in aqueous media. The principle concerning this technique and the electrochemical process has been introduced in detail in our recent papers [1–4]. A remarkable phenomenon is the strong deviation of the chemical yields at the glow discharge electrode from that expected on the basis of Faraday's law [5–8]. That is, there are a lot of free-radical reactions in the dc glow discharges in both gas phase and aqueous solution. The yields obtained at the glow discharge electrode (anode) are several times the faradic value and the products obtained include novel species that are impossible to be found for conventional electrolysis. In a full glow discharge, the novel chemical

yields of anodic CGDE originate from the primary reaction zones, which consist of the plasma around the anode and the liquid phase near the plasma–anolyte interface. In some ways the primary reaction zone may be likened to a spur in radiation chemistry [9]. When the active species diffuse away from the initial positions to enter into the solution, the reaction zone may be considered as a single spur that is located in a fixed position and constantly renewed. In the reaction zone within the plasma around the anode, vapor H<sub>2</sub>O molecules were ionized or activated, and then bombarded each other to be broken up by charge transfer, with a resultant of the production of free OH radicals and sometimes of H atoms. On the other hand, in the liquid-phase reaction zone near the plasma–anolyte interface, several liquid H<sub>2</sub>O molecules are broken up into H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> plus O<sub>2</sub> by being bombarded by each H<sub>2</sub>O<sub>gas</sub><sup>+</sup> from the anodic plasma. As a mixture of the active species OH<sup>•</sup>, H<sup>•</sup> and H<sub>2</sub>O<sub>gas</sub><sup>+</sup> [10] diffuses across the primary zone (to be called plasma layer) into the bulk electrolyte, they could interact among themselves and with any active substrate in the solution. Consequently, CGDE could be used to induce some unusual chemical changes in the solution.

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In our country, dyes are one of the major pollutants of water. Much attention has been paid to the water treatment. We have reported some plasma degradation of dyes such as acridine orange (OA) [1],  $\alpha$ -naphthol [2], and methyl blue [4]. As part of an effort to understand the plasma degradation, in this paper, we further studied the oxidative degradation of red B (RB) and flavine G (FG) by means of CGDE at the site of treatment of wastewater.

## 2. Experimental

The apparatus is shown in Fig. 1. The anode was a platinum wire (0.5 mm) held in the brass support sealed into a glass tube. The cathode was a stainless steel plate placed in another glass tube of 5 cm diameter, which was covered at the bottom by a sintered glass disk of medium porosity. RB and FG were dissolved in different mediums from which dissolved oxygen was removed. The platinum wire anode was immersed into the solution to a depth of approximately 2.5 mm. In addition, the reaction cell was placed in a temperature-controlled water bath. The supplied voltage was 500 V and the range of electrolytic current was 40–80 mA. In the course of the reaction, the solution was gently stirred with a magnet bar. A model 722 spectrophotometer (Shanghai, China) was used to determine the concentration of the reactant in the solution. The ultraviolet (UV) absorption spectra of reaction solutions were obtained by the model UV-3400 Spectrometer (Hitachi, Japan) at intervals.

The decolorization rate was calculated based on the following equation:

$$\text{Decolorization rate} = (\sum A_0 - \sum A_t) / \sum A_0,$$

where  $\sum A_0$  stands for the sum of the absorbance of the initial solution at various wavelengths;  $\sum A_t$  denotes the

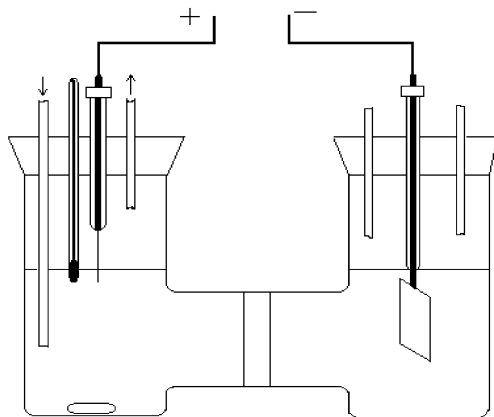


Fig. 1. Scheme of experimental apparatus of CGDE.

sum of the absorbance of the degraded solution at various wavelengths.

## 3. Results and discussion

Fig. 2 shows the UV absorption spectra of RB and FG samples. The medium was sodium sulfate solution and the initial concentration of RB and FG were 12 and 10 mg/L. The structures of RB and FG are listed in Fig. 3. Before the reaction, the absorption curve had absorption maximum at 524 and 440 nm. One hour later, it became weaker. Meanwhile, the curve had absorption at about 335 nm. So it can be inferred that the cleavage of the conjugate system of RB and FG led to the formation of some carboxylic acids. In other

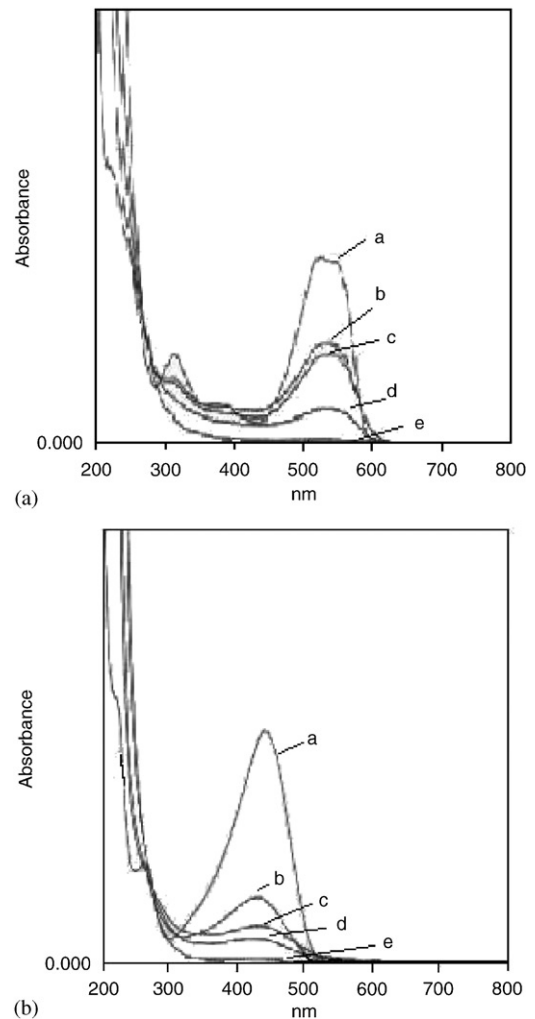


Fig. 2. (a, RB; b, FG) Absorption spectra of samples during CGDE (pH = 7): (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 120 min.

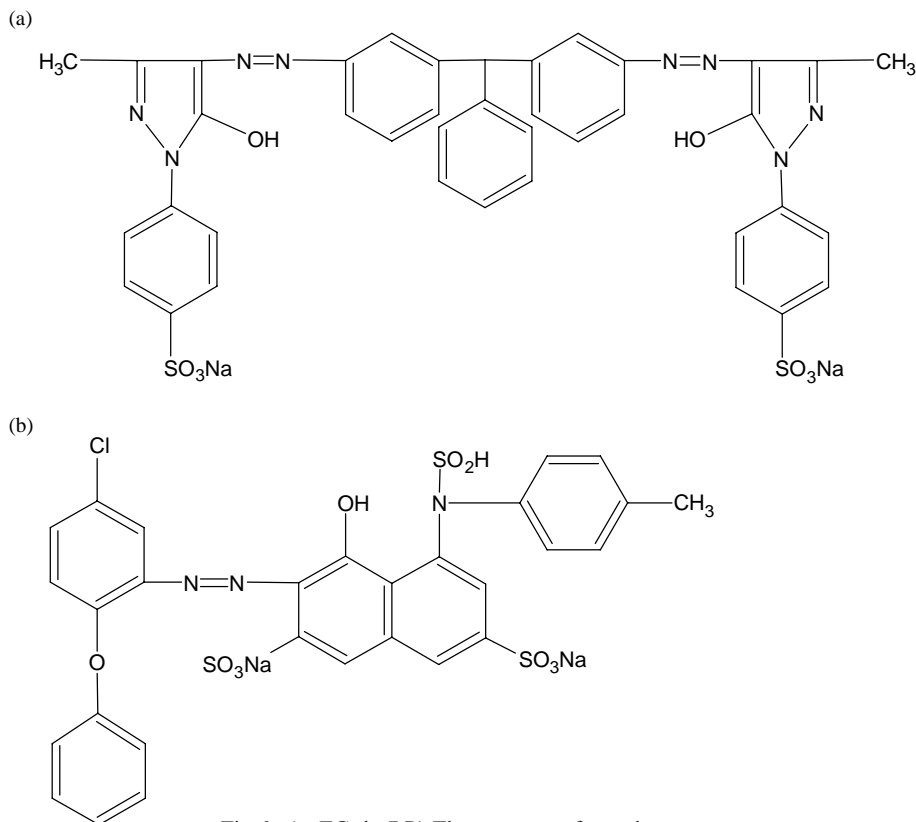


Fig. 3. (a, FG; b, RB) The structure of two dyes.

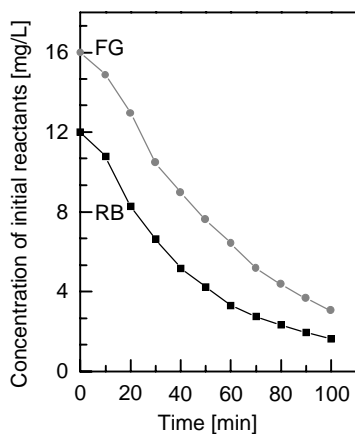


Fig. 4. Curve of concentration versus time in the sodium sulfate.

words, the two dyes underwent oxidative degradation in CGDE.

### 3.1. Kinetic characteristic

In Fig. 4, the variation of concentration of RB and FG is displayed. If their degradation was in accordance

with the first-order reaction, the data could be applied to the integral rate equation

$$\ln(C_0/C_t) = kt, \quad (1)$$

where  $C_t$ ,  $C_0$ ,  $k$  and  $t$  denote their concentration at the given reaction time, the initial concentration, the rate constant and reaction time, respectively. As shown in Fig. 5, the disappearance of RB could completely be considered as the first-order reaction, while the degradation process of FG could approximately obey the first-order law because the straight line did not pass the origin exactly. The values of  $k$ , which were obtained from the slope of the straight line, are listed in Table 1. The values of  $k$  under other conditions are displayed in Table 2, and the relevant coefficients indicated the linearity in regression analysis.

### 3.2. Effect of concentration

To see the influence of the concentration of RB and FG on the rate of reaction during CGDE, a series of experiments were carried out. The higher the initial concentration, the faster the velocity of degradation of acridine orange (AO) will be. But the apparent rate constants of RB and FG were in reverse of those that are

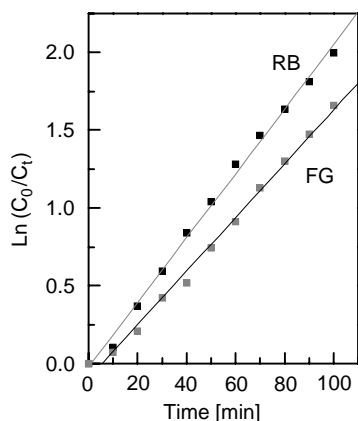


Fig. 5. Plot of regression analysis for the first-order reaction in sodium sulfate

Table 1  
Apparent rate constants

(a) RB			
Temperature (K)	Concentration of RB (mg/L)	Apparent rate constant ( $\text{min}^{-1}$ ) ( $\times 10^2$ )	Relevant coefficient
303	20	1.606	0.999
303	16	1.831	0.999
303	12	2.071	0.998
303	8	2.407	0.997
313	16	1.580	0.999
293	16	2.303	0.999
(b) FG			
Temperature (K)	Concentration of FG (mg/L)	Apparent rate constant ( $\text{min}^{-1}$ ) ( $\times 10^2$ )	Relevant coefficient
303	20	1.642	0.999
303	16	1.782	0.997
303	10	1.934	0.999
303	6	2.375	0.999
313	16	1.687	0.999
293	16	1.910	0.997

The medium was sodium sulfate 2 g/L.

listed in Table 1. The reason was deduced as follows: In full glow discharge, the high energetic species produced by plasma sustained at the specific level. It is reasonably considered that the radical reactions caused by them are non-chain reactions, which is different from those in the gas phase. In these radical reactions, every step uses up one radical, but it did not produce new radicals that can cause chain reaction. Once the initial reactant was oxidized into intermediate products, they participate in

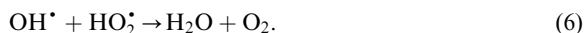
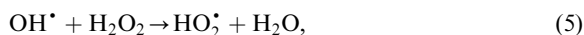
the reaction like initial reactants. The higher the concentration, the stronger the competition between the initial reactant and the intermediate products with active species. So the apparent rate constant decreased with the increase of the initial concentration. But the velocity was determined by the rate constant and the concentration.

### 3.3. Effect of temperature

In the experiments, the temperature of the bulk solution was maintained, respectively, at 293, 303, 313 K by a cooling bath. The apparent rate constants at different temperatures are given in Table 1. For degradation reactions of RB and FG with CGDE, the apparent rate constants decrease somewhat with the rise of temperature. This phenomenon was different from that of normal reactions. It implies that the activation energy of the reactions could be very low. In this case, the main factor influencing reaction rate constants was not temperature but were the concentration and the life of radicals. In general, rise of temperature could help vanish the active radicals. The negative effect of temperature on active species led to a decreasing of apparent rate constants.

### 3.4. Effect of mediums

In CGDE, high energetic  $\text{H}_2\text{O}_{\text{gas}}^+$  bombard with liquid  $\text{H}_2\text{O}$  molecules into  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  radicals that interact each other to form  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  [7,8]:



OH radical was one of the strongest oxidants that can oxidize many organic substances. The degradation of RB and FG was probably induced by the attack of OH radical in solution near the plasma-anolyte interface. Generally, the life of OH radical is very short. The chance of direct interaction between OH<sup>•</sup> and dye molecules is low. So it is easy to interact each other to form H<sub>2</sub>O<sub>2</sub>. It is well known that under the existence of many metals such as Mn<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup> and Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub> in solution easily decomposes into OH<sup>•</sup>. So their addition into reaction systems will bring about the catalysis of the degradation of the dye in CGDE. As shown in Table 2, the catalysis of inorganic salts such as MnSO<sub>4</sub>, CuSO<sub>4</sub>, CoSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and FeSO<sub>4</sub> on hydrogen peroxide decomposition resulted in increasing the velocity of degradation of these two dyes. According

Table 2  
The apparent rate constants under different conditions

Medium	pH	Apparent rate constant ( $\text{min}^{-1}$ ) ( $\times 10^2$ )	Relevant coefficiency	Discharge time (min)	Decolorization rate (%)
(a) <i>RB</i>					
Sodium sulfate + $\text{H}_2\text{SO}_4$	2.14	1.585	0.999	120	87.25
Sodium sulfate + $\text{Co}^{2+}$	2.14	2.601	0.999	110	93.56
Sodium sulfate + $\text{Fe}^{3+}$	2.14	10.073	0.988	30	94.50
Sodium sulfate + $\text{Cu}^{2+}$	2.14	2.730	0.997	90	89.21
Sodium sulfate + $\text{Mn}^{2+}$	2.14	2.093	0.999	120	92.09
Sodium sulfate + $\text{Fe}^{2+}$	2.14	—	—	2	94.99
(b) <i>FG</i>					
Sodium sulfate + $\text{H}_2\text{SO}_4$	2.14	2.061	0.998	120	87.56
Sodium sulfate + $\text{Co}^{2+}$	2.14	2.803	0.999	100	93.85
Sodium sulfate + $\text{Fe}^{3+}$	2.14	8.453	0.984	30	90.89
Sodium sulfate + $\text{Cu}^{2+}$	2.14	2.790	0.997	90	88.65
Sodium sulfate + $\text{Mn}^{2+}$	2.14	2.477	0.996	100	88.83
Sodium sulfate + $\text{Fe}^{2+}$	2.14	—	—	2	95.55

The concentration of RB was 16 mg/L. The amount of inorganic salts used was 8.76 mg/L.  
The concentration of FG was 16 mg/L.

to our previous report [3], the amount of inorganic salts used is 8.76 mg/L. Among them,  $\text{FeSO}_4$  had the most evident catalytic effect. The degradation of these two dyes under the presence of  $\text{Fe}^{2+}$  was so fast that the apparent rate constant under this condition could not be obtained with the same method.

The oxidation of aqueous ferrous sulfate by glow discharge had been reported in the previous paper [11,12]. Now we studied the effect of  $\text{Fe}^{2+}$  on the degradation of these two dyes. The concentration applied was 16 mg/L and the value of pH of the solution was 2.14. When the initial concentration of  $\text{Fe}^{2+}$  was  $1 \times 10^{-3}$  M, 175 ml solution underwent CGDE. Under these conditions, we studied the CGDE of RB solution of different concentration as seen in Fig. 6. The absorbance was measured at its maximum 524 nm. Five minutes later, the variation of absorbance of the solution was slow. It had been demonstrated that the velocity of degradation under this condition was even faster than that without adding  $\text{Fe}^{2+}$ . The reasons for it were presumed as follows:

The formation of  $\text{H}_2\text{O}_2$  took place in two different reaction zones: the plasma around the anode and the liquid phase near the plasma near the plasma-anolyte interface. When  $\text{H}_2\text{O}_2$ , formed in the liquid anolyte during CGDE, accumulated to a sufficient concentration, it underwent decomposition to  $\text{O}_2$  owing to its further reaction with  $\text{OH}^\bullet$  [6]. If  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  was added into the solutions, they can react with  $\text{H}_2\text{O}_2$  to yield  $\text{OH}^\bullet$ ,  $\text{HO}_2^\bullet$  and other ions.

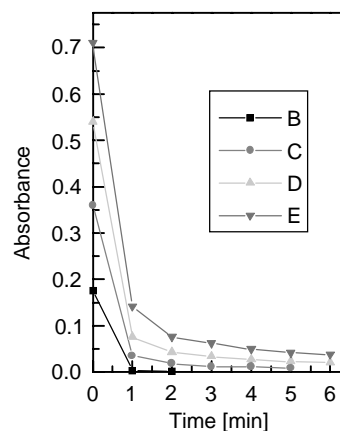
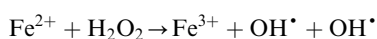
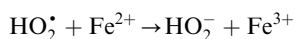
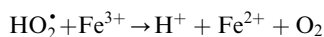
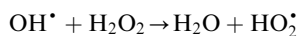
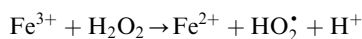


Fig. 6. The catalytic effect of  $\text{Fe}^{2+}$  on the different concentrations of RB: (B) 8 mg/L; (C) 16 mg/L; (D) 24 mg/L; (E) 32 mg/L.



During this redox radical chain,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  could capture  $\text{H}_2\text{O}_2$  and produce powerful oxidizing agents  $\text{OH}^\bullet$ ,  $\text{HO}_2^\bullet$ . This process might be dominant during the first 5 min, and the ultimate product  $\text{Fe}^{3+}$  is collected in the cathodic glass tube due to the electrical transference.

Table 3  
The decolorization degree of different samples in the presence of  $\text{Fe}^{2+}$  in CGDE

Dye	Conc. (mg/L)	Samples	420 nm	440 nm	460 nm	480 nm	500 nm	520 nm	540 nm	560 nm	580 nm	600 nm	620 nm	Reaction time (min)	Decolorization rate (%)
RB	8	Initial	0.025	0.024	0.045	0.087	0.135	0.174	0.172	0.147	0.051	0.003	0.000	3	98.03
		Degraded	0.009	0.004	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000		
	16	Initial	0.050	0.045	0.088	0.167	0.261	0.352	0.344	0.317	0.113	0.009	0.000	5	98.51
		Degraded	0.012	0.006	0.004	0.002	0.001	0.000	0.000	0.001	0.000	0.001	0.000		
	24	Initial	0.074	0.067	0.126	0.248	0.387	0.532	0.516	0.480	0.168	0.016	0.001	10	98.78
		Degraded	0.016	0.008	0.004	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.000		
32	Initial	0.099	0.089	0.172	0.332	0.523	0.705	0.683	0.645	0.227	0.020	0.002	10	98.80	
	Degraded	0.020	0.010	0.006	0.003	0.002	0.001	0.000	0.000	0.000	0.000	0.000			
FG	8	Initial	0.206	0.220	0.185	0.107	0.036	0.007	0.003	0.002	0.001	0.002	0.002	5	98.31
		Degraded	0.008	0.004	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
	16	Initial	0.388	0.427	0.344	0.198	0.070	0.011	0.004	0.001	0.001	0.001	0.001	5	97.86
		degraded	0.016	0.008	0.005	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
	24	Initial	0.565	0.601	0.490	0.290	0.104	0.016	0.002	0.001	0.000	0.000	0.000	10	96.81
		Degraded	0.021	0.013	0.009	0.006	0.004	0.003	0.003	0.002	0.001	0.001	0.001		
32	Initial	0.729	0.768	0.631	0.381	0.134	0.024	0.007	0.004	0.002	0.001	0.002	10	95.23	
	Degraded	0.041	0.032	0.022	0.014	0.008	0.004	0.003	0.003	0.001	0.000	0.000			

The experiment demonstrated that  $\text{Fe}^{2+}$  had catalytic effect on the degradation of these two dyes.

#### 4. Decolorization of samples

The study has shown that the velocity of degradation of RB and FG was even faster in the presence of  $\text{Fe}^{2+}$ . At the same time, it was found that the absorbance of degraded samples became very slow in a very short time in the visible zone from 420 to 620. The decolorization rate of different concentrations of these two dyes has been studied as shown in Table 3. When the initial concentrations of RB and FG were 32 mg/L, the decolorization rate can reach 98.80% and 95.23% in ten minutes. It had been demonstrated that the addition of  $\text{Fe}^{2+}$  could lead to complete decolorization in a few minutes. Hence, this method can be applied to treat the wastewater polluted by dyes.

#### 5. Conclusion

The degradation reaction of RB and FG by CGDE obeys the first-order law. The rise of concentration and temperature causes the decrease of the apparent rate constant. The addition of catalysts for hydrogen peroxide decomposition such as  $\text{MnSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{FeSO}_4$  in sodium sulfate was found to increase the velocity of degradation of two dyes. Among them,  $\text{FeSO}_4$  had the most evident catalytic effect on it. We can apply this method to treat

the wastewater polluted by dyes. Moreover, it can be expected to treat toxic compounds in solution using this technique.

#### Acknowledgements

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