

Plasma degradation of Cationic Blue dye with contact glow discharge electrolysis

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ABSTRACT

Contact glow discharge electrolysis (CGDE) of Cationic Blue SD-GTL (CB) was investigated by determining degradation rates and rate constants under different voltages, pH, temperature and initial concentrations. The results indicated that 500V was the optimum voltage for CGDE of CB under experimental conditions. The effect of pH was not appreciable. Fe^{2+} and Fe^{3+} had a remarkable catalytic effect on the degradation of CB. The degradation rate was up to 99.7% after 3 minutes CGDE treatment when the concentration of Fe^{2+} was 20.0 mg/L. And when the concentration of Fe^{3+} was 5.0 mg/L, the degradation rate was only 68.6% after 10 minutes CGDE treatment. The reaction mechanisms were also well illustrated by relative reactions and their rate constants. It had been demonstrated that CB underwent oxidative degradation in CGDE.

Key words | cationic blue SD-GTL (CB), contact glow discharge electrolysis, degradation, dye, plasma

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INTRODUCTION

Contact glow discharge electrolysis (CGDE) is an unconventional electrochemical process where plasma is sustained by DC glow discharge between the electrode and the surrounding electrolyte (Sengupta & Singh 1991; Sengupta *et al.* 1997). Using a thin platinum anode in contact with electrolytic solution, normal electrolysis develops spontaneously to CGDE if the applied voltage is sufficiently high. A remarkable feature of CGDE is that the chemical yield is several times higher than that calculated from Faraday's law, and the products are always different from the conventional electrolysis (Sengupta & Singh 1994; Sengupta *et al.* 1998). During CGDE, many species such as $\cdot\text{OH}$, $\text{H}\cdot$, $\text{O}\cdot$, H_2O_2 are produced besides H_2 and O_2 . These reactive species in plasma are accelerated due to the steep potential gradient. Subsequently, they enter the solution with a considerable magnitude of kinetic energy to bring about chemical changes in the solution. Among these species, hydroxyl radicals ($\cdot\text{OH}$), with higher oxidation potential (2.8V), are particularly reactive to the organic pollutants present in water. Many organic pollutants could be

mineralized by means of CGDE (Tezuka & Iwaski 1998; Tezuka & Iwaski 1999; Tezuka & Iwaski 2001; Amano & Tezuka 2006; Gong & Cai 2007).

Dyes are one of the major pollutants in wastewater. Much attention has been paid to dyeing wastewater treatment with CGDE (Gao *et al.* 2001, 2003, 2006; Gong *et al.* 2008; Wang 2009). In this study, Cationic Blue SD-GTL (CB) was employed as model pollutant to monitor its degradation process in order to further probe the degradation ability of plasma.

MATERIALS AND METHODS

The apparatus is shown in Figure 1. The anode was a platinum wire (0.3 mm) held in the brass support sealed into a glass tube. The cathode was a stainless steel stick placed in another glass tube of 1.2 cm internal diameter, which was covered at the bottom by a sinter glass disk of medium porosity. CB was dissolved in 2.0 g/L sodium sulfate without

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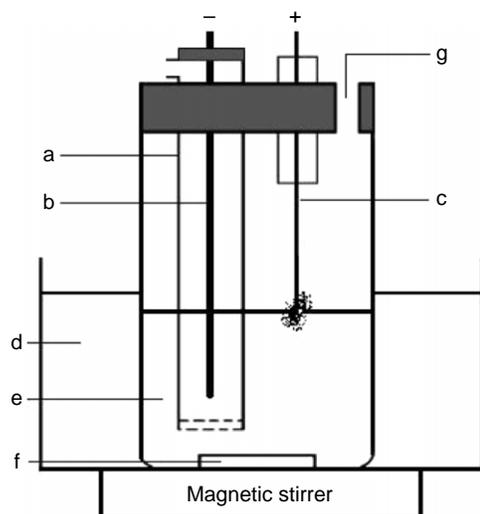


Figure 1 | Schematic diagram of the CGDE reactor. (a) glass tube; (b) cathode; (c) anode; (d) water bath; (e) electrolytic solution; (f) magnetic bar; (g) gas outlet and sampling port.

adjusting electrolytic acidity if no clear indication was given. The platinum wire was immersed into the solution to a depth of approximately 1.0 mm. In addition, the reaction cell was placed in a temperature-controlled water bath. In the course of the reaction, the solution was gently stirred with a magnetic bar. All experiments were carried out at 303 K for 90 minutes without special explanation.

The measurements of pH were carried out using a combined glass electrode standardized with pH buffer solutions (DELTA 320). In addition, the chemical oxygen demand (COD) was determined by a COD analyzer (TR 320, Merck). A Cary 50 UV-vis spectrometer (Varian, America) was used to determine the concentration of reactant and its absorption spectra in the process of CGDE. The degradation rate was calculated based on the following equation:

$$\text{Degradation rate} = 100\% \times (C_0 - C_t)/C_0$$

where C_0 stands for the initial concentration of CB; C_t denotes the concentration of CB in the degraded solution at different time.

RESULTS AND DISCUSSION

Absorption spectra

Figure 2 shows the UV-vis absorption spectra of different CB samples in the process of CGDE. The initial concentration

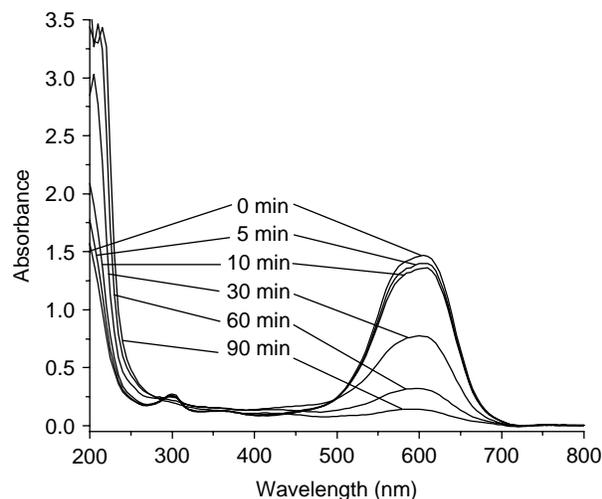


Figure 2 | UV-vis spectra of CB during CGDE.

of CB was 25.0 mg/L. The applied voltage was 500 V. Before the reaction, the initial absorption curve had absorption between 450–700 nm and its maximum absorption at 610 nm. 90 minutes later, it became much weaker. It can be inferred that the chromophore had been damaged in CGDE. Meanwhile, the absorptions at 200–240 nm were improved very strong after 30 minutes CGDE treatment. At this time, the cleavage of the conjugate system of CB could lead to the formation of some carboxylic acids.

The changes of pH and conductivity of CB solution during CGDE are shown in **Figure 3**. It can be found that the pH value of the solution dropped rapidly and the conductivity increased rapidly. The decrease of pH resulted from the increasing concentration of H^+ , which led to

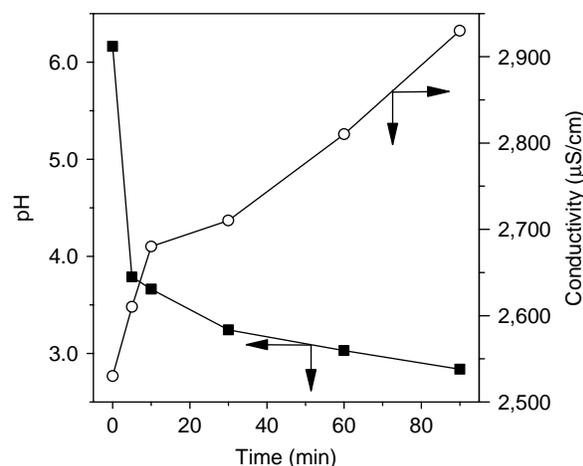
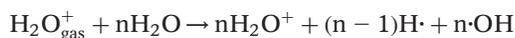


Figure 3 | Changes of pH and conductivity of CB solution during CGDE.

the increase of the conductivity of solution at the same time. The changes of pH and conductivity were the same as the previous study without substrate (Jin *et al.* 2010). The pH of solution dropped rapidly in 5 minutes due to the dissociation of water molecules in CGDE:



With the increasing treatment time, some of producing organic acids also contributed to the decrease of pH.

Dynamic behavior

The dynamic behavior was also investigated. The data was applied to the integral rate equation:

$$\ln(C_0/C_t) = kt$$

where C_t , C_0 , k and t denote its concentration at the given reaction time, the initial concentration, the rate constant and reaction time, respectively. The data of each experiment could be consolidated on a single straight line with a fairly good-correlation ($R^2 \geq 0.995$). This indicated that the degradation process obeyed the first-order law. That also demonstrated that the degradation of CB might be initiated by the attack of hydroxyl radical in the surface layer of electrolyte, exposed to the plasma, and that the rate could be limited by the diffusion of CB toward the reaction region (Tezuka & Iwaski 1999).

Effect of applied voltage on the degradation of CB

In this experiment, the applied voltages, 450 V, 500 V and 530 V were investigated. The initial concentration of CB was 25.0 mg/L and the initial pH value was 3.0. Figure 4 shows the degradation rates and rate constants of CB degradation under different applied voltages. It can be seen that the applied voltage imposed an apparent effect on the degradation rate of CB. At 450 V, the degradation rate was just 41.1%, whereas at 500 V and 530 V, the degradation rate of CB was up to 96.4%, 95.4% with the same treatment time, respectively. And the rate constants were 0.006, 0.038 and 0.035 min^{-1} , respectively. The results could be explained as follows. When the concentration of Na_2SO_4 solution was 2.0 g/L, the critical voltage for the onset of

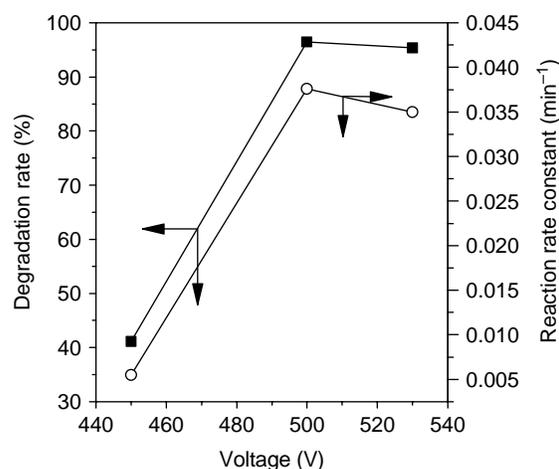


Figure 4 | Degradation of CB under different applied voltages.

CGDE was 495 V. It was found that H_2O_2 started to form near 450 V and underwent a sharp rise after 495 V (Jin *et al.* 2010). When the voltage was 450 V, plasma was not fully formed and the amount of reactive species produced was small, so the degradation rate was low. When the applied voltage increased to 500 V and 530 V, plasma was fully formed and sustained between the anode and electrolyte, and the amount of reactive species increased steadily for degradation of CB. However, the ability of CB's capturing active species was small and the rate constant of oxidative degradation of CB was in the order of 10^{-2}min^{-1} which was far lower than the active species' combination rate constants ($10^9-10^{10} \text{M}^{-1} \text{s}^{-1}$) (Sengupta *et al.* 1998). Most of active species combined mutually, which considerably raised the yield of O_2^{E} , but does not affect that of H_2O_2 to any significant extent (Sengupta *et al.* 1998). Since the oxygen gas did not contribute to the CB degradation, the increased applied voltage just provided excess energy to melt the anode. Therefore, the higher applied voltage 530 V and more did not contribute to improve the degradation rate of CB. In the following experiments, 500 V was employed as the applied voltage for CGDE of CB.

Effect of pH on the degradation of CB

The degradation of CB with CGDE was investigated under initial pH 3.0, 5.0, 6.0, 7.0, 9.0. As shown in Figure 5, the degradation rates of CB under these five conditions were all over 95% and all rate constants were more than

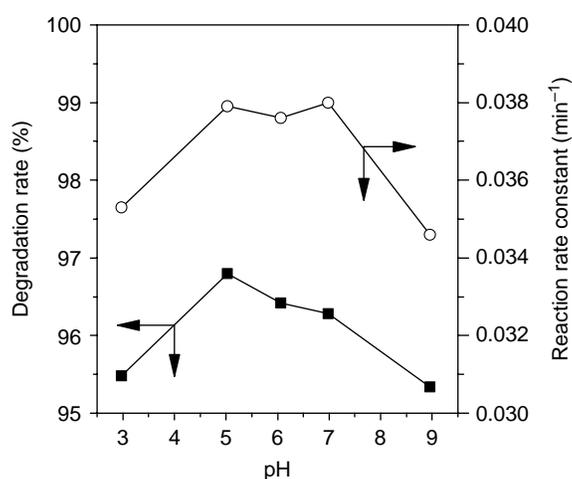


Figure 5 | Degradation of CB under different pH.

0.035 min⁻¹. That is to say, the pH of the electrolyte has less effect on the degradation of CB in CGDE. In addition, for the initial pH value, it was just a temporary value. From Figure 2, we can see that pH decreased rapidly when glow discharge started due to the dissociation of water molecules. The initial pH value of CB solution was 6.0–6.2, so we did not change the acidity of the solution.

Effect of initial concentration on the degradation of CB

In this study, a series of experiments were carried out. The concentrations of four solutions were 10.0, 25.0, 30.0, 40.0 mg/L respectively. The results are shown in Figure 6. Although the degradation rates of these four solutions were

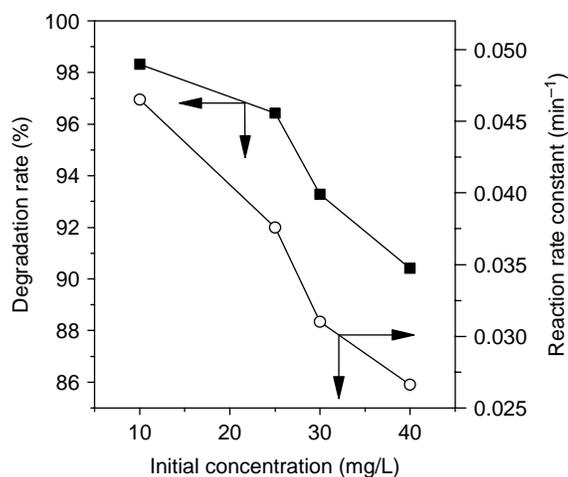


Figure 6 | Degradation of CB under different initial concentration.

over 90%, the degradation rate decreased with the increasing initial concentration of CB. And the rate constant also decreased from 0.046 to 0.027 min⁻¹. It seemed that lower concentration benefits a higher degradation rate. Under the same given condition, the concentration of reactive species kept stable, lower concentration of CB could be completely degraded by hydroxyl radical. Considering the concentration of dye wastewater was not very low, 25.0 mg/L was chosen in the following experiments.

Effect of electrolyte on the degradation of CB

In order to investigate the effect of the electrolyte on the degradation rate, CGDE of CB was studied in 1.0, 1.5 and 2.0 g/L sodium sulfate. As shown in Figure 7, the degradation rates of CB under these three conditions were more than 95.2%, and the rate constants were more than 0.036 min⁻¹. The increasing concentration of sodium sulfate led to a relatively higher degradation rate and rate constant. The result was in accordance with the previous study (Jin et al. 2010). When the concentration of sodium sulfate was 1.0, 1.5 and 2.0 g/L, the critical voltage (V_D) for the onset of CGDE was 555 V, 510 V and 495 V, respectively. Although $|V - V_D|$ were different, the effect of electrolyte was not appreciable. It was because the conductivity of solution could be increased rapidly in CGDE as shown in Figure 3. The initial conductivity of solution was just a temporary value. Although the applied voltage (500 V) was lower than the critical voltage in 1.0

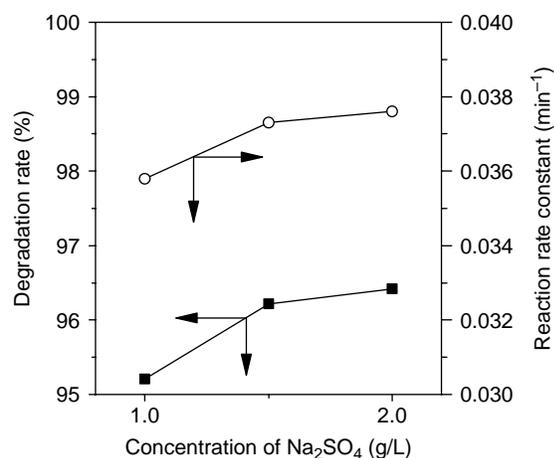


Figure 7 | Degradation of CB under different concentration electrolyte.

and 1.5 g/L Na₂SO₄. The plasma was not fully formed when CGDE started. With the increasing treatment time of CGDE, the plasma became full and the amount of reactive species increased rapidly. Therefore, the effect of electrolyte was not appreciable. In this study, 2.0 g/L Na₂SO₄ was chosen in following experiments.

Effect of temperature on the degradation of CB

We carried out the similar experiments under different temperatures (298 K, 303 K, and 308 K) and the results are shown in Figure 8. When the temperature was raised from 298 K to 308 K, the degradation rate decreased from 97.6% to 94.3%, and the rate constant decreased from 0.042 min⁻¹ to 0.033 min⁻¹. This phenomenon could be explained by the lifetime of reactive species. Under higher temperature, reactive species was easy to decompose to H₂O and O₂, which resulted in the decrease of the number of effective reactive species. As a result, the degradation rate decreased when the temperature was raised. Considering Joule heating produced in CGDE, 303 K was chosen as the experimental parameter.

The catalytical effect of Fe²⁺ and Fe³⁺ on the degradation rate of CB

The effect of Fe²⁺ on the degradation of CB was investigated under the selected conditions. The results were shown in Figure 9. It can be observed that CB

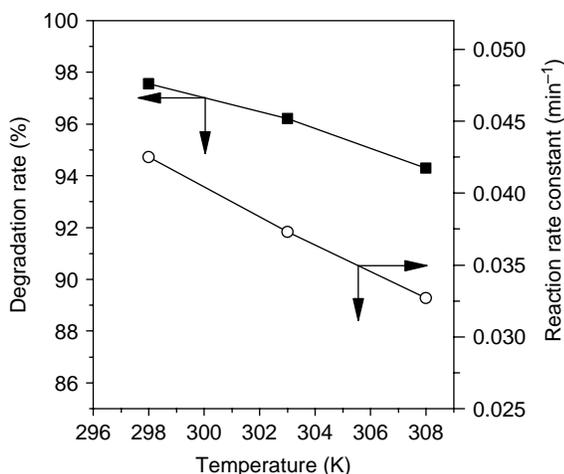


Figure 8 | Degradation of CB under different temperature.

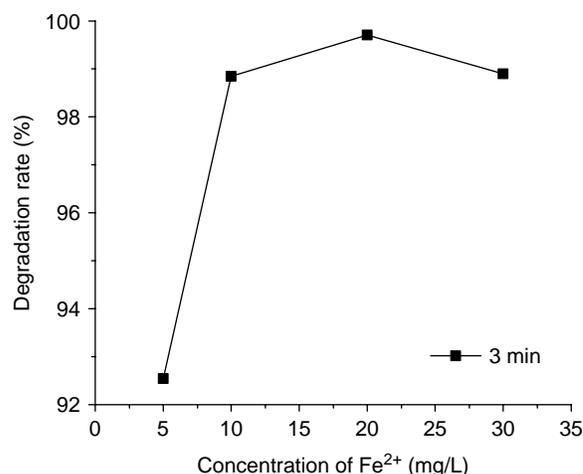


Figure 9 | The effect of Fe²⁺ on the degradation rate of CB.

underwent efficient degradation and the degradation rate was 99.7% after 3 minutes with CGDE treatment when the concentration of Fe²⁺ was 20 mg/L. The removal of COD reached up to 58.7% after 10 minutes CGDE treatment, which was prior to 55.7% after 90 minutes treatment without Fe²⁺. This was because the additional hydroxyl radicals were produced by the following reaction:



Fe²⁺ could capture H₂O₂ and produce powerful oxidizing agents ·OH. However, when the concentration of Fe²⁺ was over 20 mg/L, the degradation rate decreased.

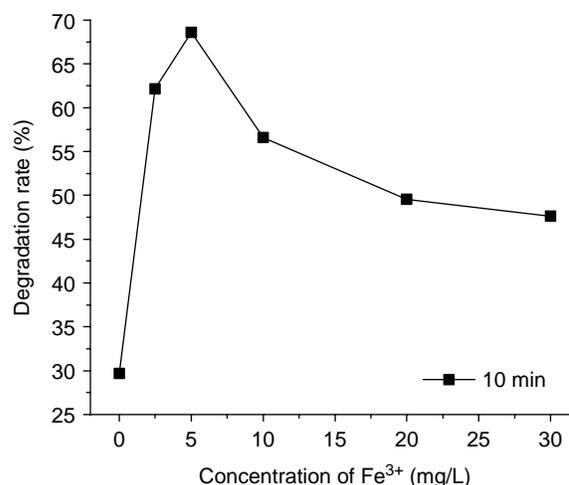


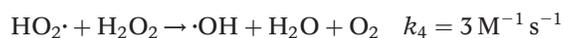
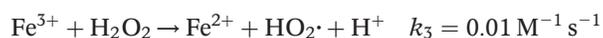
Figure 10 | The effect of Fe³⁺ on the degradation rate of CB.

That was perhaps due to the following reaction:

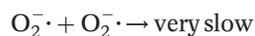
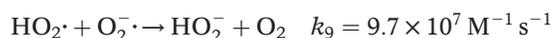
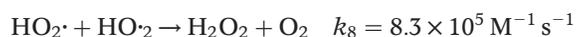
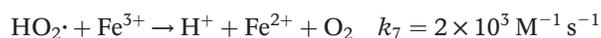
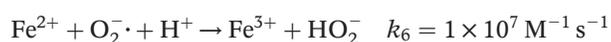


As $k_2 \gg k_1$, excess Fe^{2+} consumed $\cdot\text{OH}$ instead. Therefore, the amount of Fe^{2+} could not be added excessively.

The ferric ion also showed apparent catalytic effect on the degradation rate of CB. As shown in Figure 10, when the concentration of Fe^{3+} was 5 mg/L, the degradation rate was 68.6% after 10 minutes with CGDE treatment. The following reaction may explain the above phenomenon (Pignatello et al. 2006).



However, the catalytic effect was weaker than Fe^{2+} , since the rate constant of Fe^{3+} ion with H_2O_2 ($0.01 \text{ M}^{-1} \text{ s}^{-1}$) was almost four orders of magnitude smaller than that of Fe^{2+} ion with H_2O_2 ($76 \text{ M}^{-1} \text{ s}^{-1}$). In addition, in aqueous solution $\text{HO}_2\cdot$ and its conjugate base $\text{O}_2^{\cdot-}$ radicals were quite unreactive compared to $\cdot\text{OH}$ toward most organic substrates (Pignatello et al. 2006). With the increasing concentration of Fe^{3+} , the curve did not rise, but declined. It was because the following reactions existed.



As $k_5, k_6, k_7, k_8, k_9 \gg k_3, k_4$, hydroperoxyl radical $\text{HO}_2\cdot$ was easy to terminate. Therefore, excess Fe^{3+} could not produce more reactive radicals, which resulted in the decrease of the degradation rate of CB.

CONCLUSION

The following conclusions can be drawn from the present study: CB can be efficiently degraded by CGDE and the

reaction obeyed the first-order law. The applied voltage was the main factor for the degradation of CB. 500 V was optimum applied voltage. The pH of initial solution had no appreciable effect on the degradation of CB. The higher the initial concentration of CB was, the lower degradation rate and rate constant would be obtained. Ferrous and ferric ion greatly enhanced the degradation process. The ferrous ion showed the better catalytic effect.

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REFERENCES

- Amano, R. & Tezuka, M. 2006 Mineralization of alkylbenzenesulfonates in water by means of contact glow discharge electrolysis. *Water Res.* **40**, 1857–1863.
- Gao, J. Z., Hu, Z. A., Wang, X. Y., Hou, J. G., Lu, X. Q. & Kang, J. W. 2001 Oxidative degradation of acridine orange induced by plasma with contact glow discharge electrolysis. *Thin Solid Films* **390**, 154–158.
- Gao, J. Z., Wang, X. Y., Hu, Z. A., Deng, H. L., Hou, J. G., Lu, X. Q. & Kang, J. W. 2003 Plasma degradation of dyes in water with contact glow discharge electrolysis. *Water Res.* **37**, 267–272.
- Gao, J. Z., Yu, J., Li, Y., He, X. Y., Bo, L. L., Pu, L. M., Yang, W., Lu, Q. F. & Yang, Z. M. 2006 Decoloration of aqueous brilliant green by using glow discharge electrolysis. *J. Hazard. Mater.* **137**, 431–436.
- Gong, J. Y. & Cai, W. M. 2007 Degradation of Methyl Orange in water by contact glow discharge electrolysis. *Plasma Sci. Technol.* **9**(2), 190–194.
- Gong, J. Y., Wang, J., Xie, W. J. & Cai, W. M. 2008 Enhanced degradation of aqueous methyl orange by contact glow discharge electrolysis using Fe^{2+} as catalyst. *J. Appl. Electrochem.* **38**, 1749–1755.
- Jin, X. L., Wang, X. Y., Zhang, H. M., Xia, Q., Wei, D. B. & Yue, J. J. 2010 Influence of solution conductivity on contact glow discharge electrolysis. *Plasma Chem. Plasma Process* **30**, 429–436.

- Pignatello, J. J., Oliveros, E. & MacKay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **36**, 1–84.
- Sengupta, S. K. & Singh, O. P. 1991 Contact glow discharge electrolysis: a study of its onset and location. *J. Electroanal. Chem.* **30**, 189–197.
- Sengupta, S. K. & Singh, O. P. 1994 Contact glow discharge electrolysis: a study of its chemical yields in aqueous inert-type electrolytes. *J. Electroanal. Chem.* **369**, 113–120.
- Sengupta, S. K., Srivastava, A. K. & Singh, R. 1997 Contact glow discharge electrolysis: a study on its origin in the light of the theory of hydrodynamic instabilities in local solvent vaporization by Joule heating during electrolysis. *J. Electroanal. Chem.* **42**, 23–27.
- Sengupta, S. K., Singh, R. & Srivastava, A. K. 1998 A study on the origin of nonfaradaic behavior of anodic contact glow discharge electrolysis. *J. Electrochem. Soc.* **145**, 2209–2213.
- Tezuka, M. & Iwasaki, M. 1998 Plasma induced degradation of chlorophenols in an aqueous solution. *Thin Solid Films* **316**, 123–127.
- Tezuka, M. & Iwasaki, M. 1999 Liquid-phase reactions induced by gaseous plasma. Decomposition of benzoic acids in aqueous solution. *Plasmas Ions* **1**(12), 23–26.
- Tezuka, M. & Iwasaki, M. 2001 Plasma-induced degradation of aniline in aqueous solution. *Thin Solid Films* **386**, 204–207.
- Wang, L. 2009 Aqueous organic dye discoloration induced by contact glow discharge electrolysis. *J. Hazard. Mater.* **171**(1–3), 577–581.